A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY

VOLUME I

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A COMPREHENSIVE TREATISE
ON
INORGANIC AND THEORETICAL CHEMISTRY

BY

J. W. MELLOR, D.Sc.

VOLUME I

WITH 274 DIAGRAMS

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Dedicated

TO THE

PRIVATES IN THE GREAT ARMY
OF WORKERS IN CHEMISTRY

THEIR NAMES HAVE BEEN FORGOTTEN
THEIR WORK REMAINS

PREFACE

WITH due regard to the law *humanum errare est*, this work aims at giving a complete description of all the compounds known in Inorganic Chemistry, and, where possible, these are discussed in the light of the so-called Physical Chemistry. The separation of Organic from Inorganic Chemistry is nothing more than a conventional convenience; it is probable that the sharper the line of demarcation, the greater the loss which each of these divisions of chemistry will suffer. In the analysis of inorganic compounds, for example, some extraordinarily sensitive tests are available, and some extraordinarily clean separations can be effected by utilizing the properties of certain organic compounds of the metals.

In the past, several complete records have been made. Starting from W. Nicholson's *A Dictionary of Chemistry* (London, 1795–1808), there have appeared in **England**: A. Ure's *A Dictionary of Chemistry* (London, 1821–35), and H. Watts' *A Dictionary of Chemistry* (London, 1866–68), which was later edited by H. F. Morley and M. M. P. Muir. There is also Sir Edward Thorpe's *A Dictionary of Applied Chemistry* (London, 1890–92), a new and revised edition of which is now in the press (1921). The English translation of L. Gmelin's *Handbook of Chemistry* (London) appeared in nineteen volumes between 1848 and 1872. This work covered both organic and inorganic chemistry. The sixth German edition appeared as the *Handbuch der anorganischen Chemie* (Heidelberg) in 1871–86, while the seventh edition, commenced in 1905, is not yet complete. A number of other related books have appeared in **Germany**. The more important of these are A. Ladenburg's *Handwörterbuch der Chemie* (Breslau, 1882–89); H. von Fehling's *Neues Handwörterbuch der Chemie* (Braunschweig), which commenced in 1874 and is not yet completed. It was founded on J. von Liebig, J. C. Poggendorff, and F. Wöhler's *Handwörterbuch der reinen und angewandten Chemie* (Braunschweig, 1837–64). There is O. Dammer's *Handbuch der anorganischen Chemie* (Stuttgart, 1892–1903), and his *Handbuch der chemischen Technologie* (Stuttgart, 1895–98). R. Abegg's *Handbuch der anorganischen Chemie* (Leipzig), commenced in 1905, is not yet completed. In **France** there are E. Frémy's *Encyclopédie chimique* (Paris, 1882–1905); C. A. Wurtz's *Dictionnaire de chimie* (Paris, 1868–1908); and H. Moissan's *Traite de chimie minérale* (Paris, 1904–6). In **Italy**, L. Guareschi's *Nuovo enciclopedia di chimica* (Torino), commenced in 1900, is still in progress. I have been more or less indebted for hints and ideas to all the above-named works, as well as to H. Kopp's *Geschichte der Chemie* (Braunschweig, 1843–47).

Much of the material of this work was compiled in card-index form long before my *Modern Inorganic Chemistry* appeared; and that work was really an abridgement of this one. The references which were not included in the scheme of that work will be found here. It was not originally intended to make the larger work assume the exhaustive character which this book has now acquired. Rightly or wrongly, I came to the conclusion that it is a mistake to load up a student with facts as if he were going to be a specialist in all branches of inorganic chemistry. In addition to the general principles, the salient features of certain type-compounds should be taught, and anything further should be left for works of reference, where full information may be obtained—to be absorbed or forgotten as may be expedient. Consequently, in the ideal case, a work of reference should not only give the authorities for statements of fact, but it should also indicate what knowledge has been gleaned on the particular subject in question. To do this in a practicable manner, attention must be directed to the original publications on the subject. This naturally makes the work of compilation extremely laborious ; in some cases, indeed, it happens that scores of independent references are involved in the statement of one particular fact. Fortunately I have rather a unique collection of dissertations and theses ; in a few cases, these have not appeared in the regular channels of publications. Where the original references are not in the libraries of this country, I have had to depend on an assistant in Berlin, who has generally been successful in tracking them where our libraries have failed. This has made some references very costly. A large proportion of the references will be found in the Abstracts of the London and American Chemical Societies, and of the Society of Chemical Industry.

In the references, the usual abbreviation for the title of a periodical is given, then follow in clarendon type the volume number, the page or pages, and, last of all, the year of publication. In cases where a volume is made up from a number of bulletins with independent pagination, the number of the bulletin is employed instead of the page. In the cross-references, the first number in clarendon type refers to the volume, the second to the chapter, and the third to the § (section). It will be observed that the diagrams of the chapters have an independent numeration.

In former times little more than a mere qualitative knowledge of the so-called physical and mechanical properties of elements and compounds was considered ample, but with the tremendous ramifications of the various industries increasing demands for precise data have been made from the workers in pure science. In reviewing the data I have been impressed with the prevailing lack of perspective in the measurements of physical properties, for, in some cases, these have been carefully measured with elaborate apparatus involving an experimental error hundreds of times smaller than the magnitude of the disturbing effects produced by impurities. It is not always enough to say that the materials were Herren X.Y.Z.'schen " chemically pure " preparations. For instance, in pre-war days I have had to make very serious complaints about the quantities of glass contained in their highest grade " chemically pure " potassium pyrosulphate. This would not have been suspected had its use not been attended by an epidemic of bad analyses. Of course, the best representative values of the physical constants of pure elements and compounds are very important, but in commercial work, materials of an extremely high degree of purity are regarded more as chemical curiosities, and larger errors may be introduced by using data—atomic weights, etc.—derived from pure materials, than by using data obtained with material of " commercial " purity.

I think it was P. J. Macquer who apologized for the alphabetic form of the subject-matter of his *Dictionnaire de chymie* (Paris, 1766), by stating that chemistry was little more than a collection of facts scarcely entitled to the name of science, or capable either of synthetic or analytic explanation ; and hence he concluded that the dictionary form was the best mode of arranging the facts. The dictionary thus belongs to a primitive stage in the development of a science in that it is but a collection of facts to be employed in building up the science.

We now flatter ourselves that the periodic law has given inorganic chemistry a scheme of classification which enables the facts to be arranged and grouped in a scientific manner. The appearance of order imparted by that guide is superficial and illusory. Allowing for certain lacunæ in the knowledge of the scarcer elements prior to the appearance of that law, the arrangements employed by the earlier chemists were just as satisfactory, and in some cases, indeed, more satisfactory than those based on the periodic law.

The arrangement of the subject-matter of inorganic chemistry according to the periodic scheme is justified solely by expediency and convention. It has a tendency to make teachers over-emphasize unimportant and remote analogies, and to underestimate important and crucial differences. I imagine that when we have found a truer basis of classification, such differences as are displayed between, say, *ferrosum* and *ferricum* compounds will be exhibited as if two different elements are involved, and that iron alone appears as the stable form when separated from these compounds. Similar remarks apply to other multi-valent elements. The difference between the higher and lower valent forms of an element with a given acid are often greater than between the compounds of two totally different elements with the same acid.

The first volume of this work is mainly introductory, and in it the atom is considered to be the chemist's unit, or the unit of chemical exchange. The newer work on the structure of atoms, and the so-called elements with variable atomic weights will be introduced in the third volume, as a sequel to the radio-active elements. The collection in the first volume of most of the generalizations required for application to special cases in subsequent volumes has simplified many explanations. This applies, for example, to thermal diagrams, equilibrium diagrams for ternary systems, etc. The general historical sketches in this volume facilitate the reviews of the histories of the elements and their compounds which appear in subsequent volumes.

Hydrogen and oxygen, and the compounds of these two elements, have been worked in with the introductory volume. The second volume includes the halogens and the alkali metals. The ammonium compounds are included with the compounds of the alkalies. The other elements will appear mainly in the order of the periodic law. The metal hydrides, oxides, halides, sulphides, sulphates, carbonates, nitrates, and phosphates are included with the metals; the other compounds are described with the acids, or the acidic elements. With the complex salts and intermetallic compounds of an element are included analogous compounds of ammonium, hydrazine, and hydroxylamine, as well as of all those elements which have been previously discussed. It should therefore be possible to locate a desired compound from an inspection of the backs of the volumes, which are lettered to show what elements are discussed inside. The indexes and cross-references are also available.

In the 1778 edition of his *Dictionnaire*, P. J. Macquer referred to *la nomenclature très complète* which was available. We are not so well provided to-day. Our nomenclature is inadequate and insufficient; nor has it sufficient elasticity to adapt itself to increasing knowledge. Unfortunately, we have grown so accustomed to the system inaugurated near the beginning of the last century that we are afraid to make a drastic change.

The systematic names of many compounds naturally depend on what view is taken of their constitution. Many names are thus determined by the prevailing fashion as to the nature of the compounds. For example, the mercury ammonia-compounds; the complex salts involving two metals and an acid radicle—sodium sulphato-aluminate, or sodium aluminium sulphate, etc.; the character of the contained-water as water of crystallization or aquo-water: ammonia of crystallization or ammino-ammonia; hydrogen-peroxide of crystallization, or hydrated peroxide, etc.

The application of the methods of physical chemistry is rendering it necessary to revise the list of compounds of a given element; as a result, descriptive chemistry is in state of flux. There is no doubt that many compounds of the older chemists are not chemical individuals, but rather mixtures. The laws of constant composition and multiple proportions have proved inadequate; analysis alone is not a test of chemical individuality. It is, however, necessary to use care because compounds may be prematurely rejected when they do not appear on, say, a thermal diagram, and yet they may be quite stable under another set of conditions. Similar remarks apply to the application of the phase rule to binary or ternary systems at a given temperature. Compounds may be rejected because they do not appear on an equilibrium diagram, and yet they may be quite stable at other temperatures; or in the presence of some other compounds—stabilizers.

There are a couple of minor difficulties in connection with the spelling of names in Slavonic countries with alphabets different from those of the Romance languages. The spelling of the name may appear different according as the paper has been published in England, France, or Germany. The result is that work may seem to have been done by a totally different savant. Thus, Менделѣевъ becomes Mendeléeff, Mendelejeff, Mendelejew, etc.; Жемчужнао may be rendered Zemczuzny, Schemtschuschny, or some other way. I have then taken the liberty of trying to keep to one uniform interpretation. In some cases, therefore, where a Slavonic name appears misspelt, it is probable that one of a number of possible spellings has been selected. Where possible I have included most of the initials with each name. This elaboration might appear redundant; but there are cases where four different workers on the same subject have the same surname. The initials do not always appear with the original publications. Some have been found in J. C. Poggendorff's *Biographisch-literarisches Handwörterbuch zur Geschichte der exakten Wissenschaften* (Leipzig, 1863–1904) or elsewhere. It will be observed that by collecting the references at the end of each section, instead of placing them as footnotes, the appearance of the page is considerably improved, and space economized.

I desire to thank many helpers. My colleagues, Dr. A. Scott and Mr. H. V. Thompson, M.A., have kindly read the proofs and made good suggestions; Messrs. A. T. Green and A. Rigby have given valuable help in proof-reading; Mr. F. Clifford, Librarian of the Chemical Society, has kindly helped in locating many awkward references; and Mr. P. Roche has checked innumerable references. The typewriting and indexing have been in charge of Miss M. Lycett. Many specific obligations are indicated in the references.

J. W. MELLOR.

STOKE-ON-TRENT,
January, 1922.

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Page 318, *Line* 17 *from bottom, and page* 324, *note* [14], *for* Lynman *read* Lyman.

CHAPTER I

THE EVOLUTION AND METHODOLOGY OF CHEMISTRY

§ 1. The Evolution of Chemical Science

> The progress of science is as orderly and determinate as the movement of the planets, the solar systems, and the celestial firmaments. It is regulated by laws as exact and irresistible as those of astronomy, optics, and chemistry.—S. Brown (1843).

As a result of fiery controversies waged about the philosophy of Aristotle, we are told that the citizens of Geneva, towards the end of the sixteenth century, decreed: "For once and for ever, in no branch of learning shall anyone stray from the philosophy of Aristotle." The modern student cannot obey this dictum in blind faith. Knowledge grows. There is a universal law of progressive development whereby error gradually diminishes and truth expands. Consequently, the opinions of Aristotle were founded upon a less developed and a cruder knowledge of facts and phenomena than is the case with the present generation, which has a wonderful heritage of accumulated experience and ideas which have been stored, selected, and sifted by centuries of toil and labour.

There is no evidence that "all knowledge was revealed to the primitive races of mankind, and subsequently obscured by civilization," although this belief is said to be deep-rooted in many religions; for example, in the ancient Indian doctrine of Crishna, we are told:

> Truth was originally implanted in mankind, but having been suffered gradually to slumber, it was finally forgotten. Since that period, knowledge returns to us as a recollection.

In 1554, in his *Cena di cenere*, G. Bruno combatted the saying that "in antiquity there is wisdom," for he showed that what is called the ancient or golden age really represents an early or youthful stage of growth in contrast with recent or modern times which must, in turn, represent older and more mature knowledge. Hence, also, Francis Bacon could wittily say that "we are more ancient than those who went before us."

Auguste Comte's celebrated *Cours de philosophie positive* (Paris, 1839)[1] teaches that it is characteristic of the progressing human mind to employ three different methods of explaining natural phenomena, and that man's opinions *de rerum natura* can usually be traced through three epochs which he called—*l'état théologique ou fictif; l'état métaphysique ou abstrait; l'état scientifique ou positif*—the theological or fictitious, the metaphysical or abstract, and the positive or scientific stages. Otherwise expressed, in the first stages of his learning, man attempted to explain natural phenomena by supernatural agencies; in the second, by metaphysical abstractions; and in the third stage, by ascertaining the laws of succession and similitude by a study of accurately observed facts. This famous hypothesis, first announced by A. Comte in 1822, is sometimes called **la loi des trois états,** and it appears to have been derived from A. R. J. Turgot (1750), or possibly T. Bergmann, who, in his essay *De primordiis chemiæ* (Upsala, 1779), said: "The history of chemistry is properly divided into the mythological, the obscure, and the certain." True, the three epochs may overlap and blend with one another so that no sharp boundaries can be made with respect to time or place, and, owing to special circumstances, there may be a retrograde movement by the advent of an age of intellectual darkness; yet, in the main, these three periods characterize the growth of science as surely as the child, the boy, and the man characterize the development of an individual's mind. Chemistry is a particularly happy illustration of Comte's idea.

I. The first, the mythological, anthropomorphical, or superstitious stage.—This represents the childhood of chemistry, for, as man emerged from the mists of prehistoric antiquity, everything must have appeared to be full of wonder and mystery. He was overawed by the wind and the rain; by the lightning and the thunder; by the eclipse and the comet; and by the rainbow and the clouds. The student of nature lived in a bewildering dreamland of mixed magic and myth which led him to ascribe supernatural explanations to inaccurately known facts, and consequently, he seemed to be surrounded on all sides by *un monde invisible des esprits et des démons*. Just as man's own actions seemed to be the result of his own efforts and volitions, so did natural phenomena appear to be the work of benignant or malignant spirits in air, earth, or sea; and man accordingly made oblations to their residing deities to secure their kindly offices. Chemical phenomena were produced by spirits—the salamander or the sylph, the naiad or the nymph, the undine or the gnome—indwelling in different bodies, whose aid was invoked by incantation or charm to produce successful experiments.

Accordingly, men who studied nature in those days were often suspected of tampering with the spirits of evil, and chemistry came to be known as one of the seven devilish arts. So too arose a childish fear and hatred of science, and the belief—widespread in the Middle Ages—that science is dangerous, and its votaries ought to be suppressed. In illustration, in 1287, the Order of Dominicans proposed to suppress chemical studies as had been attempted with physics in 1243; again, the *Accademia dei Segreti*—Academy of Nature's Secrets—founded by J. B. Porta in 1602 for the discussion of scientific subjects, was dissolved by Pius III, after *une existence courte mais glorieuse*, apparently because it was believed that magic and the black arts were practised at its meetings. In the thirteenth century, Roger Bacon was arraigned at Oxford on an indictment for practising sorcery and magic; and in order to disprove these accusations, he wrote his celebrated *Epistola de secretis operibus artis et naturæ et de nullitate magiæ* to show that phenomena and appearances, then attributed to supernatural agencies, were simply due to the operation of natural laws. Again, in his *Magiæ naturalis* (Naples, 1558), J. B. Porta tried to show that the magic of nature is quite as wonderful as that of wizards and witches.

T. Thomson opens his work, *The History of Chemistry* (London, 1830), by pointing out that chemistry sprang originally from delusion and superstition, and was at its commencement exactly on a level with magic and astrology. Superstition can flourish only where knowledge is imperfect and fragmentary. Day, adds C. J. Keyser (1914), is just as mysterious as night, and the mystery of knowledge and understanding is more wonderful and awesome than the darkness of the unknown. Mysterious phenomena, explained in one generation as the vagarious work of invisible demons or deities, appear to succeeding generations as the ordered workings of natural laws. The mists of superstition are always dissipated as positive knowledge extends into wider and wider fields.

The cuneiform inscriptions and the records of antiquity which have been transmitted to us, show that the early chemists were dominated by the gratuitous assumption that "the interior agencies which keep the world in motion were personal forces essentially out of and above nature." The magician and the sorcerer, the necromancer and the wizard were the founders and keepers of the first rudimentary knowledge of nature. Accordingly, knowledge and superstition were interwoven with wondrous ingenuity and subtilty. The alchemists, following the mysticism introduced by the Alexandrian and Arabian schools, had virtually reverted to this stage of development when they spoke of red bridegrooms (gold) and lily brides (silver); of green dragons (mercury) and red lions (gold); of black crows (lead), and yellow scorpions (sulphur); and of flying eagles, fugitive stags, and inflated toads. One of the older chemists described the result of triturating mercuric chloride with mercury, resulting in the formation of mercurous chloride, in these pompous words :

> The fierce serpent is tamed and the dragon so reduced to subjection as to oblige him to devour his own tail.

The anonymous work, *Artis auriferæ quam chemiam vocant* (Basil, 1572), represents the dissolution of gold in aqua regia by a lion devouring the sun, as depicted in Fig. 1. This language persisted even as late as the eighteenth century. In W. Clarke's *The Natural History of Nitre* (London, 1670), for example, the red vapours formed when nitre is heated in a retort are called " the flying dragon."

The seven metals—gold, silver, an alloy, copper, tin, iron and lead—known to the early Chaldeans, were also designated by the names and symbols of the seven greater heavenly bodies—the Sun, Moon, Mercury, Venus, Jupiter, Mars, and Saturn. A close relation was supposed to subsist between the metals and their respective planets so that nothing could happen to the one which was not shared by the other ; and it was further supposed that experiments with any particular metal were more likely to succeed when the governing planet was in the ascendant, and near its zenith. Thus, in Paracelsus' directions for preparing an amalgam of lead and mercury, the two fluid metals are to be mixed " at the very moment of the conjunction of Saturn and Mercury." In some cases it is possible to see a fanciful reason why a particular metal was assigned to a particular heavenly body, but in other cases the connection is too remote to hazard even a guess. *En passant,* it may be pointed out that an ingenious hypothesis to explain how the metals are affected by the planets was in circulation long after the original fancies had been forgotten. As N. Lemery expressed it in his *Cours de chimie* (Paris, 1675) :

FIG. 1.—Copied from an old Symbol representing the Dissolution of Gold in Aqua Regia.

> An infinite number of minute corpuscles pass to and from the metals and the planets, these corpuscles can easily pass through the pores of the metals and the planets they represent, but they cannot pass into other bodies whose pores are not figured properly to receive them, or if they do get into other bodies, they cannot stay there to contribute any nourishment. The metals are thus perfected and nourished by the influence which comes from the planets and conversely.

II. The second or philosophical stage.—At last man roused himself from his stupor of helpless wonder and childish guessing. He dimly realized some method in nature's inscrutable complexity. Unfortunately, his vision was soon bedimmed and his mind intoxicated. Accordingly, we now find him arrogantly proclaiming the supremacy and omnipotence of the human reason. The majority of educated people of that age believed it to be undignified for a self-respecting man to make experiments, and they did not consider knowledge obtained by observing nature to be a serious subject worthy of mental occupation. Indeed, men were so proud of their intellectual supremacy that they persuaded themselves that their fancies about nature were finer, nobler, and more worthy of belief than nature herself ; and Plato apparently considered that the secret laws of nature could be invented by abstract thinking ; for, in his *Republic,* he said that " real knowledge is obtained by a simple process of reasoning independently of all information furnished by the senses." In his *Phædo,* Plato expresses his delight with Anaxagoras' saying that "the mind is the cause and orderer of all things." The numerous absurdities obtained by the application of this principle are well exemplified in the pages of Plato's *Timæus*, where there are many illustrations of the vanity of the attempt to explain incomprehensible facts by nebulous words; for example, Plato there states:

> The universe is a unique, perfect, and spherical production, because the sphere is the most perfect of figures; and it is animated and endowed with reason, because that which is animated and endowed with reason is better than that which is not.

Even Aristotle, the father of logic, reasoned that a vessel containing ashes would hold as much water as when the vessel contained no ashes. The conclusion is not true, showing that Aristotle did not always recognize the need for the discipline of the imagination by relentlessly checking reason against inexorable fact.

Thus, man did not always see with Cicero that nature is a better teacher than the most ingenious philosopher. Prompted by a sublime imagination, R. Descartes, in his *Principia philosophiæ* (Amsterdam, 1644), built a hypothetical universe which had no substance, and is now regarded as little more than an idle dream. Well might T. Bergmann's essay *De indagando vero* (1779) claim:

> The philosophical method, by pretending to unlock the secrets of nature with ease and expedition, soothes a natural impulse to explain all things; and by assuming everything to be accessible to the human intelligence, administers pleasing flattery to vanity and arrogance.

The methods of thinking, the much vaunted philosophy of Plato and Socrates, in its attempt to proclaim the laws of nature from the throne of human reason, actually obscured the path of progress for many centuries, for it became the fashion to look with lofty scorn on knowledge gleaned by observing nature. Accordingly, the leading philosophers worshipped what Francis Bacon might have called *idola cogitationis*—idols of the imagination; they devoted themselves to fantastic and chimerical hypotheses about material things; and made no earnest attempt to discriminate between the unreal and the real. As a result, their minds became so prejudiced that the facts were either denied, or else explained by extravagant ideas and fancies uncontrolled by truth and reality as we understand these terms to-day.

III. The third, the scientific, or the positive era.—The marvellous Greeks gave promise of inaugurating this era before the advent of Christianity, but the feeble light kindled by Aristotle flickered and almost expired in the atmosphere of mysticism which prevailed in the Middle Ages. During this period, man almost reverted to the pandemonium of miracle and magic of his childhood days. The light re-appeared about the thirteenth century, and gained brilliancy during the succeeding centuries; man then learned to see that nature is as she is, and is not subjected to the capricious will of deity or demon; man recognized that nature is always conformable with herself without contradictions and without inconsistencies.

The growth of chemistry as a science was nourished in the seventeenth century by the establishment of academies and societies for the cultivation of science. The famous *Society of Rosicrucians*,[2] which flourished mightily towards the end of the sixteenth or beginning of the seventeenth century, was perhaps an exception, for, judging from the many books which were poured from its presses between 1600 and 1630, it rather fostered mysticism and obscurity, and was not favourable to the true scientific spirit. Long before the advent of the scientific societies, there were associations which fostered human knowledge, for example, the priests of Egypt had their temple laboratories; and the same spirit led to the formation of the various schools of philosophy in Greece; but the special feature of the later associations was their energetic protest against the worship of antiquity, where the authority of an ancient master was placed above experience.

The *Accademia del Cimento*, founded at Florence, in 1657, under the presidency of Prince Leopold de Medici, was the first scientific society of any importance ; its main object was " the repudiation of any favourite system or sect of philosophy, and the obligation to investigate nature by the pure light of experiment." Although it lived but ten years, it enriched the world by leaving a volume of important records of experiments, chiefly in pneumatics—*Saggi di naturali esperienze fatti nell' Accademia del Cimento* (Firenz, 1666). This work has been reprinted a number of times in several languages. *The Royal Society* of London was founded in 1660 ; *l'Académie des Sciences* of Paris in 1666 ; the *Academia naturæ curiosorum* of Germany in 1652 ; and many others were founded in the eighteenth century. In some exceptional cases, these associations degenerated into " fastnesses from which prejudice and error were latest in being expelled ; and they joined in persecuting the reformers of science." The attitude of the University of Paris towards Galilei, and of the University of Oxford towards Roger Bacon have been cited as examples. In general, however, the policy of these associations was to encourage the investigation of nature by observation and experiment ; *Arrière les théories, vivent les faits !* was their watchword ; and, instead of clothing their results in the enigmatical and allegorical language of the Rosicrucians, they sought to give a candid and straightforward account of their investigations and thoughts. In this way, the obscure mysticism of the Middle Ages was gradually dispelled. Man thus rediscovered that he does not bring any knowledge into the world with him ; that " the subtilties of nature far transcend the subtilties of the human reason " (F. Bacon) ; and that " knowledge cannot be invented, it must be discovered." Progress was then assured, and the manifold achievements of the observational and positive sciences during the past century are in striking contrast with the paucity of the results of philosophical thinking applied in vain for thousands of years.

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[2] A. E. Waite, *The Real History of the Rosicrucians*, London, 1887 ; H. Jennings, *The Rosicrucians, their Rites and Mysteries*, London, 1887.

§ 2. The Observation and Record of Facts. Collecting Data

The mind is like a blank tablet upon which experience writes that which is perceived by the senses.—ARISTOTLE (B.C. 320).

To what can we refer for knowledge ? What can be a more certain criterion than the senses themselves ? If we cannot trust the senses, how is it possible to distinguish what is true from what is false ?—LUCRETIUS (B.C. 60).

I know only that truth is in the things and not in my mind which judges them, and that the less I put my mind in my judgments about them, the more sure am I to come near to the truth.—J. J. ROUSSEAU (1770).

H. Poincaré, in his *La science et l'hypothèse* (Paris, 1904), emphasized in a very telling manner that true knowledge about material things can be acquired only through the senses—*experientia docet* ; there is no other way. Experience is the well-spring of true knowledge ; experience alone can teach something new ; it alone is irrefutable ; it alone can give certainty. The same idea was suggested by Aristotle and the peripatetical philosophers : *nihil est in intellectu, quod non prius in sensu*—nothing is in the intellect which was not first in the senses ; and by Roger Bacon in his *Opus majus* about 1266, when he said : *Sine experientia nihil sufficienter sciri potest*. Experience comprises all the impressions we observe and perceive through the various organs of sense. These impressions are recorded in our notebooks, dictionaries of chemistry, etc., as empirical realities or facts. Although knowledge cannot transcend the human faculties, much of the data of science is not *directly* furnished by the senses, for the senses are quite unable to discriminate the subtilties of nature. For instance, the speed of light and the size of atoms are magnitudes either too great or too small to be accessible to sense perceptions. Yet much data derived indirectly from the insensible physical world are assumed to be realities or facts, when actually they are known only by inference from data furnished by the senses. Without facts, science can do nothing; they are the foundation and building stones of the whole superstructure. The edifice can be stable only in so far as it is founded upon the immutability of facts. The facts must be accurate, or the edifice will be unstable.

Not very many years ago, an apt quotation from one of the classical writers—say Aristotle—was considered ample proof of the truth of any statement, and this in spite of repeated warnings; even in the thirteenth century, Albertus Magnus could say:

> I pored over the books of all the sages from Morienus, Aristotle, and Plato downward, but yet I went wrong, until, by trial and mistakes, I at length discovered the truth.

Science does not accept P. Bonus' dictum, in his *Margarita novella* (Basil, 1572): "The mere fact that a great body of learned men believe a statement supersedes the necessity for proof." To-day, science looks askance on records of mere opinions, and focuses its attention on records of facts. It is not always easy to record facts faithfully without unconscious distortion or bias. What we wish, said Demosthenes, that we believe; what we expect, said Aristotle, that we find.[1] Things are not always what they seem. Seeing is not always believing. It is often difficult to distinguish appearances from realities for we are easily deceived by the mockery of sensations. The senses cannot be divorced from the mind; neither is always to be trusted alone. The sun appears to rise and set; in reality it does neither. So, although experience is the source of truth, it may also be a source of error. Superficial appearances may obscure hidden realities. Plato of old was unduly oppressed with the illusions and deceptions of sensory impressions, and he was accordingly led to deny the validity of knowledge derived from the sensations; but Aristotle rightly showed that difficulties arise only when the mind wrongly interprets the testimony of the senses.

In 1689, John Locke[2] emphasized the view that the senses are the tentacula of the mind because the mind primarily derives its knowledge of the external world through the senses. All our knowledge, said he, consists of a stock of ideas which were primarily produced in the mind by sensation, and which have remained after the sensation had ended. Our knowledge of chemistry, physics, etc., depends on the ability of the senses (i) to receive accurate impressions of the external world; and (ii) to convey these impressions to the mind or brain. When the mind receives a sensation, it immediately begins to interpret the meaning, and it usually *infers* the existence of something outside itself which gave rise to the sensation. It may seem as if the mind directly perceives the external object which gives rise to the sensations; but this is an illusion. The mind apprehends the sensation alone; and it *assumes* that there exists a cause of the sensation external to itself. There is no doubt about the sensation, but there is less certainty about the inference; the sensation must be accepted as a fact, but the inferential knowledge will be true or false according as the interpretation of the external cause of the sensation was correct or otherwise. The sensation does not err, it is the mind which fails when it misinterprets the material furnished by the senses. Hence, Plato could say that we do not see with the eyes but with our reason; J. W. Goethe, that we see only what we know; and E. Mach (1883), that the adaptation of thoughts to facts is the aim of all scientific research.

It is therefore sometimes necessary to receive with caution the testimony of evidence derived from sensations. The mind interprets a sensation by comparing it with some former sensation, the source of which has been previously determined. Consequently, the faithfulness of the interpretation is dependent upon the memory of past sensations, or upon the sensitiveness of the mind to detect resemblances and differences. Otherwise expressed, the accuracy of an inference as to the nature of the *objective* source of a *subjective* sensation varies from a mere guess to virtual certainty.[3] The idea has been aptly illustrated this wise : just as a number of bits of glass irregularly arranged always form symmetrical patterns when viewed through the kaleidoscope, so does the understanding of each man impose a pattern of its own upon the various sensations which it perceives. Consequently, as Robert Hooke [4] once said : It is necessary to be on guard against deep-rooted errors which may have been grafted upon science by the slipperiness of the memory, the narrowness of the senses, and the rashness of the understanding. The greatest caution must be exercised in accepting, on secondhand evidence, facts which cannot be verified. No reliance can be placed on vague impressions. Evidence must be clear and precise.

Few persons can estimate and register facts impartially and fairly. As W. S. Jevons [5] puts it: "Among uncultured observers, the tendency to remark favourable, and forget unfavourable events is so great that no reliance can be placed on their supposed observations." T. Bergmann long ago drew attention to this very trait. He said :

> One observer will relate an event with the most extravagant encomiums ; another will detract from its real merit ; a third, by some oblique insinuation, will cast suspicion on the motive ; and a fourth will represent it as a crime of the blackest dye. These different descriptions represent the character of the respective observers.

Untutored minds are very prone to mistake inferences for observations, and prepossessions for facts ; their observations and their judgments are alike vitiated by dogma and prejudice ; they do not seek to investigate, they seek to prove. The old proverb is inverted, believing is seeing. The student of science must pledge himself to do his best to eliminate prepossession and dogma from his judgments, and he must spare no pains to acquire the habit of recording phenomena as they are observed ; and to distinguish sharply between what is or has been actually seen, and what is mentally supplied. It requires a mind disciplined like a soldier to avoid the natural inclination to look away from unwelcome facts.

The purity of truth is almost certain to be corrupted when the observer is ruled by preconceived opinions, for, as O. W. Holmes puts it : When we have found one fact, we are very apt to supply the next out of the imagination ; or as T. Bergmann said in his essay *De indagando vero* (1779) :

> An observer swayed by preconceived opinions, may be considered as one who views objects through coloured glasses, so that each object assumes a tinge similar to that of the glasses employed. He who seeks the truth must learn to observe with equal candour those facts which controvert his opinions, and those which favour them.

It is only in a pseudo-science, said O. W. Holmes, that positive evidence, or such as tells in favour of its doctrines, is admitted ; and all negative evidence, or such as tells against it, is excluded. C. Darwin, in his *Autobiography* (London, 1887), states that one of his golden rules was to make a memorandum of any fact or thought which he found to oppose his general results, because he noticed by experience that such facts or thoughts were far more apt to escape the memory than favourable ones. Above all, said Robert Hooke (1665), a good observer needs a sincere hand and a faithful eye, to examine and record things themselves as they really appear. "The mind and the reason of the trustworthy observer must be trained to rebel against all desire, and to disobey all inclinations."

The belief that bodies contained a definite quantity of heat substance or caloric prevented Black's successors from regarding the fact, known to every savage, that heat is produced by friction ; the theory of phlogiston prevented some of the early chemists from recognizing the increase in weight which occurs when metals are calcined—*oculos habent et non videbunt* (Psalm **115.** 5) ; the assumption that air is absorbed when lead is roasted prevented Stephen Hales recognizing oxygen as the gas evolved when red lead is heated ; and, as E. Mach (1892) has pointed out in his *Populäre Vorlesungen* (Leipzig, 1903), the undulatory theory of light prevented C. Huygens marking the fact of polarization which Isaac Newton, undisturbed by theories, perceived at once.

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§ 3. The Collating, Sifting, and Clarifying of Observations. Classifying Data

> History teaches that the commencement of every branch of science is nothing more than a series of observations and experiments which had no obvious connection with one another.—J. VON LIEBIG (1846).
>
> In order that the facts obtained by observation and experiment may be capable of being used in furtherance of our exact and solid knowledge, they must be apprehended and analysed according to some conceptions which, applied for this purpose, give distinct and definite results, such as can be steadily taken hold of, and reasoned from.—W. WHEWELL.

The record of facts obtained by observation and experiment, *per se*, is empirical knowledge. *Empirical* is derived from the Greek word ἐμπειρικος, meaning experienced. It has just been emphasized that all knowledge is derived from experience, and hence empiricism would appear to be the right method of acquiring knowledge. The term, however, has slightly changed in meaning, for it is now usually applied to chance experiences which occur irregularly without any orderly plan of investigation.

All true science, said T. Huxley, must begin with empirical knowledge. Nature, however, presents to our senses a panorama of phenomena co-mingled in endless variety so that we are sometimes overwhelmed and dazed by the apparent complexity of empirical knowledge. It is work for the intellect to educe the elements of sameness amidst apparent diversity, and to see differences amidst apparent identity. It is work for the judgment to reject accidental and transient attributes, and to consolidate essential and abiding qualities. Consequently, while the primary aim of science is to collect facts, the higher purpose of science is to show that, amidst wild and terrible disorder, order and law reign supreme. The man of science seeks a refuge from this bewildering complexity in unifying principles by which the facts can be grouped and classified into systems. As he gazes into nature, the man of science must be quick to discern hidden resemblances amidst a thousand differences; he must be quick to disentangle natural relations from a medley of detail; and quick to detect dissemblances amidst alluring similarities.

Empirical knowledge describes facts; science begins by comparing facts. Empirical facts, in consequence, can form a science only when they have been arranged, rearranged, grouped, or classified so as to emphasize the elements of similarity and identity in different phenomena. Accordingly Thomas Hobbes expressed the opinion that the main purpose of science is the tying of facts into bundles. This bundle-tying, indeed, forms no small or insignificant part in the development of science; otherwise expressed, a significant advance has been made in the development of a science when the observed facts have been codified into a system so that a medley of empirical facts is systematically summarized under a small number of heads. This means that the facts must be arranged in a methodical and systematic manner until finally all the relevant facts taken together may form one system. The process of classification and correlation is one of the methods of scientific investigation. Knowledge so systematized is scientific knowledge. T. Bergmann (1779) illustrated the idea in his essay previously cited:

> A vast number of observations without order or regularity is not unlike a confused heap of stones, lime, beams, and rafters requisite for constructing an edifice, but which being combined with no skill fail in producing the proposed effect.

The material framework of the world appears in a myriad different guises and combinations, but the chemist can resolve each combination into a few definite elementary forms of matter; similarly, a multitude of forces can be resolved into comparatively a few primitive forms of energy. About 150 A.D., the Egyptian astronomer Claudius Ptolemy measured the angles of incidence and refraction of a beam of light passing from air into water, but more than fourteen hundred years elapsed before W. Snell (1621) detected the law of refraction hidden in Ptolemy's data. By tabulating his measurements of the volumes of air confined under different pressures, Robert Boyle discovered the law known by his name. Each of these laws summarizes in one simple rule myriads of possible measurements.

Scientific knowledge is not necessarily more accurate than empirical knowledge. Empirical uncoordinated facts are no less true, definite, and real than scientific facts, for all facts are equally true *per se*. A collection of empirical facts always requires some theory to serve as framework in order that the facts may be arranged, grouped, and pigeon-holed. According to F. Hoefer (1843):

> Il n'y a rien de plus stupide qu'un fait, quand il ne se rattache à aucune cause connue, à aucune loi dominante. Il faut donc concilier l'individualisation des faits avec leur généralisation. C'est là que réside le vrai critérium, l'avenir de la science.

If a group of facts—scientific facts—has been organized on an erroneous system, the facts are no less true though the system be false. Chemistry presents a curious mixture of empirical facts with isolated fragments of scientific knowledge.

§ 4. The Generalization of Observations

> Facts are the body of science, and the idea of those facts is its spirit.—S. BROWN.
>
> It is the intuition of unity amid diversity which impels the mind to form science.—F. S. HOFFMAN.

The correlation of empirical facts requires qualities of the mind different from those employed in observation and experiment. Both qualities are not always located in the same individual. Some excel in the one, not in the other. J. Priestley, C. W. Scheele, and H. Davy, for instance, were admirable observers, but they were not brilliant in the work of correlation; J. Dalton and A. L. Lavoisier were not particularly distinguished as experimenters, but they excelled in correlating observed data. W. Hamilton[1] did not rate the fact-collecting faculty very highly. He said:

> In physical science the discovery of new facts is open to every blockhead with patience, manual dexterity, and acute senses; it is less effectively promoted by genius than by co-operation, and more frequently the result of accident than of design.

J. Priestley (1783) recognized his own limitations when he said: "I have a tolerably good habit of circumspection with respect to facts, but as to conclusions from them, I am not apt to be very confident." Skill in the critical analysis of observational data, and in collating, sifting, and clarifying records, is not a sufficient recommendation to the adytum—the *sanctorum sanctissimum*—of science. There is still a higher type of work for but a few seekers after knowledge. It is

> To search thro' all
> And reach the law within the law.—TENNYSON.

It is the sprite imagination which usually reveals the deeper meaning of facts which have been diligently garnered, and laboriously sifted.

It cannot be doubted that science in its higher work, requires a supple and well-developed imagination [2] which T. Gomperz says is the instrument of genius, no less for scientific discovery than for artistic creation. The secret charm of scientific discovery is not in the facts *per se*, but rather in the extrication of natural relations among the facts one with another. Particular groups of facts must be unified or generalized into a system—the so-called **law.** Science begins with facts and ends with laws. Law is the essence of facts. As pointed out elsewhere, Newton's celebrated law epitomizes in one simple statement how bodies have always been observed to fall in the past. Immortal Newton did not discover the cause or the why of the falling of the apple, but he did show that it was due to the operation of the same forces which hold the earth, the planets, and their satellites in their appropriate orbits. Newton's simple and comprehensive law epitomizes in one single principle the many and varied phenomena associated with falling bodies, planetary motions, etc., and generally, the scientific generalization explains the operations of nature by showing the elements of sameness in what at first sight appears to be a confused jumble of phenomena. Generalization is the golden thread which binds many facts into one simple description. That peculiar type of genius, that rare quality of mind required for the work of generalization, is found only in a Newton or a Darwin. Plato said that if ever he found a man who could detect the *one in many* he would follow him as a god.

Unification is the supreme goal of modern science, or, as Heracleitus (*c.* 450 B.C.) proclaimed, the highest goal of knowledge is the one law regulating all events. However, with A. Comte,[3] the majority will have *la profonde conviction personelle*, that the attempt to explain all phenomena by *une loi unique* is chimerical. Several natural phenomena belong to different categories, and are irreducible one to another. At best, man has to apply a very weak intellect to a very complicated world ; and the resources of the human intellect are too narrow, and the universe is too complex to leave any hope that it will ever be within man's power to carry scientific perfection to Tennyson's last degree of simplicity :

> . . . one law, one element.

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§ 5. The Aim of Science in General, and of Chemistry in Particular

> Let us remember, please, that the search for the constitution of the world is one of the greatest and noblest problems presented by nature.—G. GALILEI.
>
> The ordered beauty of the world of nature suggests an infinite intelligence with powers of action such as no man possesses.—BENJAMIN MOORE.

Science embraces the sum-total of human knowledge, and it ranges over the whole realm of nature. Science is not a mass of empirical knowledge gained by observation and experiment, but it is an organized body of facts which have been co-ordinated and generalized into a system. Science tacitly assumes that nature is a harmonious unity, and that rational order pervades the universe. Science seeks a complete knowledge of the multitude of inter-related parts of the universe which act and react on one another producing endless variety. In fine, science aims at omniscience. The target, however, appears to recede with increasing knowledge. As man grows in wisdom and knowledge, he begins dimly to realize that the unknown multiplies into boundless proportions.

The sciences are too complex and too vast to be comprehended by one man's mind.

> One science only will one genius fit,
> So vast is art, so narrow human wit.—POPE.

Our feeble wit has rendered it necessary to rear a tree of scientific knowledge with many branches: astronomy, physics, chemistry, mineralogy, geology, biology, sociology, etc. "The divisions of the sciences," said Francis Bacon, "are like the branches of a tree that join in one trunk," and they are therefore more or less closely related with one another. The astronomer, the physicist, the chemist, each usually keeps to his own particular branch. This separation of the sciences is mere convention. Even in the middle of the thirteenth century Roger Bacon saw that there are no real lines of demarcation between the different sciences, for he pointed out in his *Opus tertium* (1267):

> All the sciences are connected; they lend each other material aid as parts of one great whole. Each does its own work, not for itself alone, but for the other parts. . . . No part can attain its proper result separately; since all are parts of one and the same complete wisdom.

The science of chemistry is man's attempt to classify his knowledge of all the different kinds of matter in the universe; of the ultimate constitution of matter; and of the phenomena which occur when the different kinds of matter react one with another. The science of chemistry is itself so vast, that many branchlets are necessary for useful work, and thus we have: inorganic chemistry, organic chemistry, physical chemistry, mineralogical chemistry, bio-chemistry, agricultural chemistry, pharmaceutical chemistry, etc. The chemist also frequently aims at applying his knowledge to useful purposes in the arts and industries; and thus arises applied, industrial, or technical chemistry.

Applied chemistry.—About the middle of the thirteenth century, Roger Bacon distinguished between knowledge sought for the sake of truth, and knowledge utilized in the practice of the various arts; or, as I. R. Averroës expressed it a century earlier: In pure science, *scimus ut sciamus*; and in applied science, *scimus ut operemur*. The distinction, however, was recognized in the fourth century B.C., for it was explicitly expounded in Aristotle's *Metaphysics*, and it was also intimated still earlier in Plato's *Republic*.[1] The purpose of pure science is to observe phenomena and to trace their laws; the purpose of art is to produce, modify, or destroy. Strictly speaking there is no such thing as applied science, for, the moment the attempt is made to apply, science passes into the realm of art. It has been well said that "science is indebted to art for the means of experimenting, but she instructs art concerning the properties and laws of the materials upon which the latter operates." In an essay on *The usefulness of experimental philosophy*, Robert Boyle (1663) emphasized the mutual benefits which would obtain when science, or, as he called it, when natural philosophy is applied to the various arts and crafts; and he claimed that it is prejudice, no less pernicious than general, which has kept science so long a stranger in the industries. Boyle's ideas have been still further emphasized by Lord Kelvin (W. Thomson), who said in 1883:

> There cannot be a greater mistake than looking superciliously upon practical applications of science. The life and soul of science is its practical application, and just as the great advances in mathematics have been made through the desire of discovering the solutions of problems which were of a highly practical kind in mathematical science, so in physical science many of the greatest advances that have been made from the beginning of the world to the present time have been in the earnest desire to turn the knowledge of the properties of matter to some purpose useful to mankind.

The so-called applications of science to the industrial arts—say, applied chemistry—may be (i) An attempt to extend the methods of scientific investigation to the industrial arts; or (ii) To adapt known operations and laws to useful purposes. When the chemist is occupied in the systematic observation of phenomena, and in tracing their laws, he is engaged in scientific investigation, no matter if the work be conducted in academy, in counting house, or in factory.

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§ 6. Experiment

Experiment is the interpreter of nature. Experiments never deceive. It is our judgment which sometimes deceives itself because it expects results which experiment refuses. We must consult experiment, varying the circumstances, until we have deduced general rules, for experiment alone can furnish reliable rules.—LEONARDO DA VINCI.

Nature speaks to us in a peculiar language, the language of phenomena. She answers all the questions we ask her, and these questions are our experiments.—J. VON LIEBIG.

Chemistry is largely an experimental science. Experiment is really a method of observation, which is employed when the facts are so masked by other conditions that they cannot be accurately observed unless the obscuring conditions are suppressed. The chemist would not make much progress if it were only possible to observe phenomena just as they occur in nature, and not possible to make observations under determinate conditions. By experiment, it is possible to make combinations of different forces, and different forms of matter which are not known to occur in nature; to eliminate complex disturbing conditions; and to observe phenomena under simplified conditions. An experiment has been well defined as *une observation provoquée*. Experiment, said G. A. Reid, is useful only when there are conditions which obscure direct observations. The most successful experiment does no more than make a fact which was previously obscure as patent as one that was open to direct observation from the first. Chemical phenomena, *per se*, are usually too complex for our minds to grapple, and they must be simplified by simple experiments. Consequently, chemistry is an experimental science because its facts can rarely be observed in any other way. If data could be obtained by direct observation, there would be no need for experiment.

It requires much acumen to determine the precise conditions under which an experiment shall give a successful result. Every experiment has the character of a specific question. The skilled questioner—the experimenter—knows what he is asking, and he tries his best to interpret nature's reply, be it affirmative, negative, or evasive. If the answer be negative or evasive, the question has not been properly asked, and it must be plied again and again until

A sharphooked question baited with such skill
It needs must catch the answer.

Paradoxically enough, the investigator can usually say with "Dr. Moreau": "I asked a question, devised some method of getting an answer, and got—a fresh question." Some such ideas were in Robert Hooke's mind when he said:

> The footsteps of nature are to be traced, not only in her ordinary course, but when she seems to be put to her shifts, to make doublings, and turnings, and to use some kind of art in endeavouring to avoid our discovery.

The more intricate the experiment, the greater the probability of an obscure and ambiguous result. As A. L. Lavoisier has pointed out, "it is a necessary principle in experimental work to eliminate every complication, and to make experiments as simple as possible." The *quality* of an experiment, not the *quantity*, is best adapted to throw light upon a phenomenon. Experiments carelessly performed may be sources of error and obscurity. Many of the results obtained by the alchemists in the Middle Ages show how ineffective or abortive are the results of experiments in incompetent hands—here, the experiments wandered into eccentric by-paths, and furnished preposterous conclusions. Experiment is an art, said G. A. Lewes (1864) and demands an artist.

Joseph Priestley believed in making a large number of haphazard experiments, and said that he discovered oxygen by trying the effect of heat on many substances, apparently selected at random by John Warltire of Birmingham. Thomas A. Edison, also, appears to have discovered the phosphorescence of calcium tungstate when exposed to Röntgen's rays by deliberately trying the effects of these rays on a large collection of different substances. This old prosaic method of experimenting by trying everything is necessary in some cases, and, though usually dubbed empirical or rule-of-thumb, the process is fundamentally scientific, but it is not generally economical in time and labour. Discoveries are then due, as J. Priestley once argued, more to "chance than to any proper design or preconceived theory." More frequently, the track of the experimenter is blazed by means of working hypotheses.

§ 7. Hypothesis, Theory, and Law

We are gifted with the power of imagination, and by this power we can enlighten the darkness which surrounds the world of senses. Bounded and conditioned by co-operant reason, imagination becomes the mightiest instrument of the physical discoverer.—J. TYNDALL.

The nearer to the practical men keep, the mightier their power. The theorist who dreams a rainbow dream, and calls his hypothesis true science, at best is but a paper financier who palms his specious promises for gold.—T. L. HARRIS.

Hypotheses are cradle songs by which the teacher lulls his pupils to sleep.—L. W. GOETHE.

It is a popular belief that the aim of science is to explain things ; as a matter of fact, the so-called explanations of science do not usually get much beyond describing the observed facts in the simplest possible terms so as to make their relations with one another clear and intelligible.[1] The description may emphasize the history of a phenomenon, or the conditions under which the phenomenon occurs : In other words, science may explain a phenomenon by describing how one event is determined by an antecedent action—sometimes called a **cause;** and how one particular set of conditions—the cause—can give rise to another set of conditions—the **effect.** Science explains a phenomenon (the effect) by showing that it is a necessary or rather a probable consequence of another phenomenon (the cause).

Classical scholars tell us that Aristotle has forty-eight, and Plato sixty-four meanings for the word cause. The later metaphysicians have also played a game of shuttle-cock with the term. The word cause is usually applied to an event, action, or process which "produces" an effect ; or, with R. Shute, cause may be regarded as that which the mind selects as a sign of the coming of that other phenomenon which it calls the effect ; or conversely, an effect is regarded as something which the mind selects as a sign of the past existence of a cause. There can therefore be no cause without an effect, and no effect without a cause. The one presupposes and completes the other. Hence, as P. Carus has observed, the law of causation describes a transformation in which form alone is changed ; and consequently, the law of causation is nothing more nor less than another aspect of the famous law of the conservation of matter and energy. The search for the cause of an event is a search for the determining factors which would produce that event. When the cause of an event has been discovered, the event is said to be explained by the cause.

There are certain circumstances or conditions which may exercise, directly or indirectly, a determinative influence on the effect produced by the activity of a cause ; and very often certain *conditions* must obtain before an event can occur, thus the temperature of hydrogen must be raised above its ignition point before combustion can ensue. The effect obtained by burning hydrogen is more vigorous if the flame be in oxygen gas than if it be in air. Hence, an atmosphere of oxygen gas is a favourable condition for the combustion of hydrogen ; a reduced pressure is a retarding condition because it hinders the speed of combustion and reduces the vigour of the flame. The term cause is frequently employed when *reason* is intended. The difference is marked in different countries by the use of different terms—Greek : *αἰτία* (cause), *αἐχή* (principle, reason) ; Latin : causa, ratio ; French : cause, raison d'être ; German : Ursache, Grund ; Italian : causa, ragióne ; etc. Gravitation is said to be the cause of the falling of a vase from the mantelpiece, whereas the cause of the fall may have really been a push from the elbow. In the former case, the reason why the vase fell downwards is the very same reason why all masses gravitate, and a push was the real cause of the catastrophe. Here the reason of the fall is referred to an inherent quality of bodies, just as the reason why bodies react chemically is explained by investing matter with an inherent quality or *vis occulta*—chemical affinity. If these distinctions be borne in mind, there is no need for confusing cause, reason, and condition, even if one term be used for all three concepts.

The **law of continuity**—emphasized by G. W. von Leibniz (1687)—assumes that no interruption between cause and event is possible, and that there is a connected chain in the order of natural phenomena so that when several of the links are known, the intermediate links can be inferred. Consequently, men of science assume that each phenomenon is an effect of a previous event, and is itself the cause of a succeeding effect, and that under like conditions, the same causes produce the same effects. Apart altogether from the question whether or not nature can do precisely the same thing again under precisely similar circumstances as she has done before, the principle of continuity or uniformity assumes that any phenomenon will be repeated if all the preceding phenomena be precisely repeated; otherwise expressed: the same antecedents are invariably accompanied by the same consequents. Hence, it has been said that science does not now seek for the reason or the why of events, but rather for invariable relations between phenomena. The law of causation is taken to *describe* a sequence of changes starting with the cause and ending with the effect. G. Kirchhoff introduced the term *description* as a synonym for *cause* at the very beginning of his *Vorlesungen über mathematische Physik* (Berlin, 1876), where he said: " The object of mechanics is to give a complete *description* in the simplest possible manner of such motions as occur in nature."

Although every effect may be traced to a previous event as its cause, in the physical world, phenomena follow one another as links in an unbroken chain of cause and effect. It is soon recognized that the cause of a phenomenon is an effect which itself needs explaining by some ulterior cause, so that causes can be traced backwards in a never-ending chain of events. Owing to the limited range of man's understanding in a world of infinite complexity, we are far, very far, from comprehending the true conditions, the true causes, or the true reasons for natural phenomena.

The mind cannot receive a long series of details without encircling and connecting them by a common bond which is a kind of *mental nexus*; similarly, in the attempt to find the causes of many phenomena, man is compelled to build an imaginary model showing how a given set of conditions—the hypothesis or theory—is always followed by particular effects. A phenomenon is then explained by showing that it is bound to occur by the operation of the set of conditions postulated by the hypothesis. Consequently, hypotheses are essentially guesses at truth. The rational observer does not trust to random guesses, but he is guided by a more or less vague intuitive conjecture (hypothesis) as to the meaning of the phenomena under investigation, and experiments are devised accordingly, for

Man's work must ever end in failure,
Unless it bear the stamp of mind.
The head must plan with care and thought,
Before the hand can execute.—SCHILLER.

The Spanish philosopher J. L. Balmés emphasized this same idea in his *Filosofia fondamental* (Barcelona, 1846), when he said:

> Although one accepts as a *real* truth the most uncontested and the most certain fact, it remains sterile if ideal truths do not fecundate it. . . . To acquire scientific value, the facts must become objective, or, being submitted to reflection, must be impregnated by the mind with the light it lends to necessary truths.

Hypotheses precede observation and prompt experiments, for they indicate the conditions under which the search for new facts is likely to be successful. Hence, when Leonardo da Vinci (*c.* 1500)[2] said that "hypothesis is the general, and experiments are the soldiers," he probably meant that hypotheses direct or indicate what experiments should be made. Accordingly, hypotheses are indispensable aids in the systematic quest after the secret meaning in nature's deeds. Those who refuse to go beyond fact, said T. H. Huxley (1887), rarely get as far as fact. It is difficult to believe that so astute an investigator as Joseph Priestley really overlooked this mode of investigation, as might be supposed from some preceding remarks—nor did he. On the contrary, he said:

> It is by no means necessary to have just views, and a true hypothesis, *a priori*, in order to make real discoveries. Very lame and imperfect theories are sufficient to suggest useful experiments which serve to connect those theories, and give birth to others more perfect. These then occasion further experiments, which bring us still nearer to the truth, and in this method of approximation, we must be content to proceed, and we ought to think ourselves happy if, in this slow method, we make any real progress.

The many gaps in our knowledge are temporarily bridged by the assumptions called hypotheses. Hypotheses thus help to render intelligible the interrelations between different facts, and they are employed by men of science to extend and deepen their experience by predicting and disclosing new facts; to correct and purify their knowledge of natural phenomena by eliminating errors and contradictions; and to systematize their description of facts so as to obtain the greatest control over them with the least possible effort.

An hypothesis contains a speculative term, an assumption which goes beyond the observed facts; while a law is a generalization which does not extend beyond the observed facts. A law is thus limited by the facts it describes. When an hypothesis has been so extended that it has a wide and comprehensive scope, the hypothesis becomes a theory. Like the hypothesis, a theory usually contains an unproved assumption—*e.g.* the kinetic theory, the electron theory, etc. Some writers—*e.g.* W. Ostwald—apply the term theory to a generalization which does not extend beyond the observed facts, and in that case, theory becomes law when the generalization has a wide and comprehensive scope. There are several other uses of the term theory. For historical reasons the term may appear to be confused because the passage from hypothesis to theory, or from theory to law, has not always been attended by a change in the corresponding terms—*e.g.* Avogadro's hypothesis, by the definitions here given, might be called a theory.

The verification of hypotheses. An hypothesis may seem to be the logical consequence of known facts, or it may be a random flash of the imagination. However probable an hypothesis might appear, both the hypothesis and the logical consequences of the hypothesis must be tested by comparison with facts. Aristotle (*c.* 320 B.C.) certainly recognized the need for basing reasoning on observed facts, but, as G. H. Lewes (1864) has emphasized, Aristotle did not realize the very vital importance of verifying his logic by comparing its conclusions with facts, nor did he recognize that the true purpose of experiment is to verify the accuracy of data and of theoretical conclusions. We are indebted to Roger Bacon (*c.* 1280), perhaps more than to any other, for first insisting on verification as the essential pre-requisite for every trustworthy conclusion. He said:

> Experimental science is the mistress of speculative science. She tests and verifies the conclusions of other sciences. . . . In reasoning we commonly distinguish a sophism from a demonstration by verifying the conclusion through experiment.

Experiments have a way of giving results which differ from those which rigorous logic concluded must occur; and when the prediction fails, it is necessary to find what has been overlooked. This does not mean that constant verification is needed to establish the validity of the *process* of reasoning, for that may be irreproachable and yet the conclusion may be false because the facts or premises upon which the reasoning was founded may have been interpreted to mean something very different from what actually obtains in nature, or because some unrecognized or undiscovered factor was involved. It is not wise to dogmatize when direct trial is possible: "Do not think," said J. Hunter, "try."

It has been aptly said that the remarkable discoveries of modern science have been made by invariably sifting the truth through a fine mesh of logical experiment. One of C. Darwin's favourite methods of applying this method was to reason : " If my hypothesis be true, then certain consequences must also be true. Now let us find if they are true ; " and H. St. C. Deville used to say that there is no need to argue if an experiment can be made. In fine, it is necessary to submit all conjectures to the incorruptible test of fact in order to avoid being seduced by immaterial creations of the imagination. Faith without facts availeth nothing. The *ad experimentum* test must be made with unremitting diligence, rigorously and impartially, without conscious bias. Trial by a combat of wits in disputations has no attraction for the seeker after truth ; to him, the appeal to experiment is the last and only test of the merit of an opinion, conjecture, or hypothesis.

If one hypothesis does not fit the facts, it is discarded, and a modification of the old, or totally new hypothesis is tried. Thus, J. Kepler, in his *De motibus stellæ martis* (1608), is said to have made nineteen hypotheses respecting the form of planetary orbits, and to have rejected them one by one until he arrived at that which assumed their orbits to be elliptical. " To try wrong guesses," said W. Whewell, " is apparently the only way to hit the right ones." This method of trial and failure is continued until the golden guess crowns the investigation ; but one single real conflict between fact and hypothesis will destroy the most plausible hypothesis. Of fifty hypotheses, only one may prove fruitful ; the unsatisfactory ones are weeded out, until that particular one remains which has established its right to live by proving itself useful or by satisfying some need. Quoting M. Faraday :

> The world little knows how many of the thoughts and theories which have passed through the mind of a scientific investigator have been crushed in silence and secrecy by his own severe criticism and adverse examination ; that in the most successful instances not a tenth of the suggestions, the hopes, the wishes, and the preliminary conclusions have been realized.

This quotation may give a wrong impression,[3] for Michael Faraday displayed consummate skill, not only in framing hypotheses *per se*, but in deducing hypotheses that were worth testing. Without hypotheses, the experimental method may degenerate into empiricism ; without experiments, hypotheses may degenerate into speculation.

The promulgation of immature or premature hypotheses without a substantial basis of fact is discouraged by most scientific societies. The celebrated nebular hypothesis was ushered in by P. S. de Laplace (1796) with those misgivings and doubts which must of necessity becripple all hypotheses which are not based upon observation or calculation. An hypothesis may be invaluable when it can be verified or refuted by a definite appeal to observation. If this check be not possible, the imagination riots in the wildest speculations. If the evidence of an alleged phenomenon cannot be tested by verification, it is outside the range of science. A. W. Hofmann is reported to have said that he would readily listen to any suggested hypothesis, but on one condition—that he be also shown a method by which it might be tested. Accordingly, scientific inquiry is limited to such objects and phenomena as admit of direct or indirect observational or experimental verification. On the other hand, science cannot enter into the dark territory beyond the scope of man's faculties, and where verification, direct or indirect, is not possible. A vivid imagination can people this region with phantasms and be deluded with the hallucination that these creatures of the imagination are real, substantial, objective facts. It is now generally recognized that imagination, uncontrolled by facts, has produced all the palsying superstitions which have blinded and cursed the human race—past and present.

Rival hypotheses.—Two or more contradictory hypotheses may be consistent with the facts ; both cannot be right. There is then need for an *experimentum crucis,* an experiment which will decide in favour of the one and exclude the other. An hypothesis is supposed to be established when it, and it alone, is in harmony with known facts. The hypothesis then ranks as a theory or law. In the majority of cases, the so-called laws of nature can be regarded as prophecies which, because they have always been fulfilled in the past, are expected to be also fulfilled in innumerable cases in the future. Laws, theories, and hypotheses are all on probation. However successful a theory or law may have been in the past, directly it fails to interpret new discoveries its work is finished, and it must be discarded or modified. However plausible the hypothesis, it must be ever ready for sacrifice on the altar of observation. On account of the unproved assumption embodied in all hypotheses, they are of necessity transient, fleeting, and less stable than theories ; and theories, in turn, are less stable than laws. A theory believed to-day may be abandoned to-morrow. New facts need new laws. An hypothesis is invalid when it fails to unite and coordinate facts. All our hypotheses and theories are to be superscribed "subject to revision," for they are continually changing. "Science in making is a battlefield of competing theories," the path of progress is strewn with dying and dead hypotheses. For example, W. Ostwald (1893) claims that the theory of chemical combination is a strange and contradictory conglomerate of the fossil constituents of earlier hypotheses. Science is not a *state*, but is rather a *stage* of progress. Even Isaac Newton's law of gravitation is included in this category ; and the astronomer R. Ball[4] could say :

> When the law of gravitation is spoken of as being universal, we are using language infinitely more general than the facts warrant. At the present moment we know only that gravitation exists to a very small extent in a certain indefinitely small portion of space.

Ever since T. Bergmann's time (1779), science has been compared with a building in the course of erection, and scientific hypotheses have been compared with the scaffolds and ladders required by the builder in order to place the stones of experience where they belong. The scaffolding must be rejected when it hinders further developments, and when the purpose for which it was erected has been fulfilled. Accordingly, an hypothesis is not the end, but rather the means of attaining that end. To think otherwise would be to suppose that the builder erects a mansion for the sake of showing off the ladders and scaffolds used in its construction. The imperfect notions and hypotheses of men of science must not be mistaken for descriptions of observed facts. In the *chemica docens* of our schools, the term science usually includes both the growing building and the auxiliary scaffolding ; otherwise expressed, the term includes the immutable facts, the ephemeral hypotheses, the transient theories. and the more or less incomplete generalizations from observations. The facts alone are certain to endure throughout all time. When S. Brown (1849) inquired : Is it necessary to the nature of a science that it be all true, and that it contains no admixture of error ? and answered : By no means ! Otherwise chemistry was no science during the reign of phlogiston, and the Lavoisierian chemistry no science so long as oxygen was taken for the principle of acidity—he included in the term science those transient theories which are necessarily employed in the erection of the temple of truth.

Deductive and inductive induction.—The term *induction* is applied by the logician to the quest of science for generalizations, that is, for the *canones* or *universales regulæ* of Roger Bacon. In *deduction*, the attempt is made to widen the bounds of knowledge without stepping outside known facts—the Euclidean method is a good illustration ; in *induction*, a leap is taken from the known into the illimitable beyond. Two important methods of induction will be recognized—one may be called the deductive method, the other the inductive method. The former was favoured by Francis Bacon, the latter by Isaac Newton.

1. *Bacon's deductive method*, by what he called the *interpretatio naturæ*. Here the facts are exhaustively classified until the generalization becomes clear. a is either M or N, or O, or P, or . . . ; but a is not N, nor O, nor P, nor . . . ; and consequently, a is M. Thus, in the 105th aphorism of his *Novum Organum* (London, 1620), F. Bacon said :

> The induction which is to be available for discovery and demonstration . . . must analyse nature by proper rejections and exclusions; and then, after a sufficient number of negatives, come to a conclusion on the affirmative instances.

The method appears to proceed from known facts to general conclusions, *a particulari ad universale*. It is based on facts already known, and has therefore been called *a priori* reasoning. The method by which Boyle's and Charles' laws were discovered might be cited in illustration of one form of the method of deductive induction.

2. *Newton's inductive method*, by what F. Bacon called the *anticipatio naturæ*. Here the attempt is made to infer the hidden generalization from the consequences of the assumption (hypothesis) what that generalization is. The process is sometimes called *a posteriori* reasoning. This method of investigation was extensively employed with glorious results by Isaac Newton, although it had been advocated by Aristotle two thousand years earlier. Francis Bacon, indeed, before Newton's time, protested against anticipating nature by hypotheses, but the greatest triumphs of modern science have been won by the application of the Newtonian method while the Baconian method has been singularly unfruitful. Francis Bacon's failure in the practice of his own method was complete.

The particular form which the Newtonian method takes in science is to devise provisional generalizations called hypotheses or *working hypotheses* to explain facts and phenomena. The appeal is then made to observation and experiment in order to test the validity of the proposed generalization. Examples: The cause of the increase in the weight of metals calcined in air; A. L. Lavoisier's theory of combustion, and his experiments on the transformation of water into earth; J. Mayow's work on combustion; etc. The application of this method of inquiry involves (*a*) The accumulation of facts by observation and experiment; (*b*) The employment of the imagination in framing hypotheses to explain the facts; and (*c*) The appeal to facts to prove or disprove the hypotheses. By this procedure, said W. Whewell, the hypothesis becomes the guide of its former teacher—observation. There is a kind of cycle from facts to hypothesis, and from hypothesis to facts.

Induction, said Aristotle, does not prove. I. Newton's phrase: *Hypotheses non fingo*—I do not frame hypotheses—is often quoted to show that he discountenanced the inductive method of scientific investigation. This is based upon a misunderstanding, for Newton here referred to hypotheses not suggested by observation. On the contrary, Newton's own procedure was to use hypotheses deduced from phenomena similar to the way science uses them to-day. Accordingly he asserted that "no great discovery was ever made without a bold guess," and his immortal *Philosophiæ naturalis principia mathematica* (London, 1687) is a wonderful record of discoveries made possible only by the exercise of the greatest freedom in the elaboration of hypotheses. Indeed, from the first of his communications on light to the Royal Society to the last revision of his *Principia*, Isaac Newton seems to have been steadily and persistently guessing.

The method of investigation employed in scientific, positive, or modern chemistry thus involves four operations: (i) observation and experiment; (ii) classification and comparison; (iii) deduction, or speculation and hypothesis; (iv) testing and verification. Francis Bacon did not grasp the prime importance of testing his induction by comparison with facts. A. de Morgan (1872)[5] puts this rather cleverly: According to Francis Bacon, facts are used to make theories *from*, and according to Isaac Newton, to try ready-made theories *by*. Chemistry could progress as a science only when this method of investigation was discovered, so that, as S. Brown stated in 1843, before discovering chemistry it was necessary to discover the art of discovering chemistry.

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§ 8. The History of Chemistry in China, India, and Chaldea

> It is vain and ridiculous to attempt to trace the origin of chemistry to the first men who worked in the metals, cut and polished stones, fluxed sand, or dissolved and crystallized the salts. This would be analogous to an attempt to trace the elements of geometry in the efforts of the savage to trim irregular fragments of rock to a more regular form in order to adapt them to his first needs.—A. F. DE FOURCROY (1782).

There can be no doubt that the chemical arts had their origin in the darkness before the dawn of history; the very etymology of the word chemistry is lost in obscurity. Many have been the attempts to fix a date at which chemistry began, and as often have these attempts proved abortive. The names of mythological, classical, and scriptural writers have been enrolled among the adepts, and as often have these names been expunged from the list. What L. Blanc (1847) said of the beginning of the French Revolution applies also to chemistry. Its history begins and ends nowhere. The origins are so confused and the many facts known to the ancients are so obscurely connected that there is no event which can be regarded with certainty as a first cause.

The historians and antiquarians in chemistry now recognize how futile must be the attempt to fix time or place for the birth of chemistry. They see that inquiries can be profitably directed only in the attempt to find what particular form chemistry took, or what particular ideas concerning chemical phenomena prevailed during any given epoch. Thus, in his work *Les origines de l'alchimie* (Paris, 1885), M. Berthelot[1] says:

> Chemistry is not a primitive science like geometry or astronomy, because it is constructed from the *débris* of a previous scientific formation which, half chimerical and half positive, is itself founded on the treasure slowly accumulated by practical discoveries in metallurgy, medicine, industry, and domestic economy.

Evidence of an old prehistoric civilization, long prior to that indicated at the beginning of the biblical record, has been laid bare during excavations in Egypt and elsewhere. The antiquities which have been unearthed are arranged by archæologists in three successive periods—the stone age, the bronze age, and the iron age. It is assumed that stone would be used by a rude savage people before metal, and that copper, being oftenest found native, and readily hammered into shape, would come into use before iron. This view was taken by Lucretius in his *De rerum natura* (**5**. 1282) written about 60 B.C. He said:

> The first weapons used by man were the hands, the nails, and teeth, also stones and the branches of trees; and then was discovered the power of iron and copper. The use of copper was known earlier than that of iron, since copper is more abundant and easier to work than iron.

Long before Lucretius, Hesiod (*c.* 700 B.C.) stated that the earth was first tilled with copper instruments because iron had not been discovered.

The three periods do not altogether represent divisions of time, but rather stages of human culture, and they were not uniform in all parts of the world; rather did they merge more or less one into the other so that stone weapons were used throughout the age of bronze, while bronze and iron were known in the stone age; and similarly, stone and bronze were used in the iron age. Hence, this classification is not altogether reliable historically, but it is so convenient that it has been adopted by the leading museums in the world for the classification of antiquities or ancient relics.

The Aryans.—Comparative philologists [2] who have studied the languages of the different countries of Europe and Asia, have brought forward evidence in favour of the theory that most of the European languages were derived from a family of people speaking one language—now called the *Aryan language*—and that this primitive language is also the source of much of the Indian, Iranian, and Armenian languages. The common parentage is suggested by striking similarities in the roots of many words in the languages of these different peoples. The evidence further indicates that the primitive Aryan tongue was spoken by nomad herdsmen wandering over the plains of Europe during the neolithic age, that is, when man had learned to polish his flint weapons—very roughly about 6000 B.C. There is no satisfactory evidence to prove that the Aryans were a civilized people which invaded Europe from the East—as was once supposed. In time, the geographical continuity of the primitive Aryans was disturbed and local variations in speech—dialects—began to arise which ultimately were fractionally crystallized, producing the different languages which now separate the different families derived from the original Aryans.

Owing to the absence of any common root for words connected with the smith's craft, we are told that the arts of extracting and working the metals were developed after the linguistic separation; and for similar reasons, the philologists suppose that the Aryans were not acquainted generally with iron, tin, or gold. Their common knowledge of copper is supposed to be shown by the relation of the different words—Sanscrit, *ayas ;* Gothic, *aiz ;* Latin, *æs ;* German, *erz ;* English, *ore*—for the metal or its ore. The probability is increased by the fact that copper occurs native in the metallic state. Some of the oldest metal implements, imitating the older stone implements, found in old tombs and in the remains of pile-dwellings in various parts of Europe, are of copper, not bronze. The knowledge of the metals seems to have spread in Europe from the Mediterranean northwards, and is supposed to have been introduced by Phœnician traders. The different stages of development of the people, after the differentiation of the language, were not synchronous, since, when one nation was in the stone age, another was in the bronze age, and a third in the iron age.

Chaldea.—In Chaldea the remains of ancient cities and temples have been ransacked, and the existence of another civilization before that of Egypt has been revealed. The early Chaldeans must have been skilful workers in the metals over sixty centuries ago—4000 B.C.—and, since there were no mines and very little fuel in the country, it is thought that the Chaldeans must have got some of their knowledge from another people more favoured in this respect. There is no written record of early Chaldean chemistry, nor of any historical names in connection with their chemical arts. Zoroaster (*c.* 1500 B.C.) is reputed to have been the founder of the philosophy of the early Chaldeans and Persians. This subject, however, is very obscure. Zoroaster is said to have made a very special study of the movements of the planets. The cuneiform inscriptions show that the Chaldean wise men or priests were practised in the arts of astrology, incantation, divination, and conjuring. The number 7 appears to have been considered very important in their philosophy and religion ; and the Chaldeans recognized this number of gods, devils, planets, colours, metals, etc. The Babylonians established the divisions of time which are employed to-day ; the seven days in a week thus originated from religious and astrological considerations before 2300 B.C. The same number is sacred in the Zarathustrian faith, the Mithras religion, and among the Buddhists, Jews, and early Christians. A. Origen in his *Contra Celsum* (*c.* 22), says that the Persians represented the revolutions of the heavenly bodies by seven stairs which led to the same number of gates each of a different metal—lead, tin, copper, iron, a mixed metal, silver, gold. He added :

> The leaden gate had the slow tedious motion of Saturn ; the tin gate the lustre and gentleness of Venus ; the third gate of copper was dedicated to Jupiter ; the fourth, iron,

was dedicated to Mercury on account of its strength and fitness for trade; the fifth, mixed metal, to Mars; the sixth, silver, to the moon; and the last, gold, to the sun.

The astrological nomination of the metals has thus been traced to the Chaldeans, and it appears to have been used by the Hindus, for F. Philostratus said in his *Vita Apollonii* (**3.** 41), that the Brahmin Iarchas gave Apollonius seven rings named after the seven planets; one ring to be worn daily—each one on the day of the week which bore its name.

The characters employed by the early writers to represent the planets were also used for the corresponding metal,[3] but they were not agreed in the dedication of particular metals to particular planets, and the characters themselves were subjected to certain changes of form. Thus, G. F. Rodwell says that in a manuscript written by Antonio Neri before 1613, mercury is designated by no less than thirty-five different names and twenty-two symbols; lead by sixteen names and fourteen symbols; and sulphur by two names, and sixteen symbols. The mythological symbols used largely by the alchemists of the Middle Ages were:

☉	♀	♂	♃	♄	☾	☿
Gold	Copper	Iron	Tin	Lead	Silver	Mercury
Sun	Venus	Mars	Jupiter	Saturn	Moon	Mercury

J. Beckmann has suggested that these symbols are the remains of Egyptian hieroglyphics, or else corrupted forms of the initial letters of the names of the deities which were supposed to reside in particular planets; and he claims that the symbol for copper ♀, said to symbolize the looking-glass of Venus, may really be a distorted form of the initial letter of the Greek term Φωσφόρος for that goddess; the so-called scythe of Saturn, a corruption of the first two letters of his Greek name Κρόνος; the imaginary caduceus of Mercury, a modified form of the initial letter of his Greek name Στίβωι which in the oldest manuscript was written C or ◡ with the next letter added below; the lance and shield of Mars, an abbreviation of the Greek name of the deity Θοῦρος, obtained by placing the last letter above the first; and the symbol for the thunderbolts of Jupiter was similarly derived from the initial letter of the Greek equivalent Ζεῦς for Jupiter with the last letter added below, as is actually done in some of the older writings. The circle, the symbol for the sun, was also the symbols of divinity and perfection. The semicircle for the moon is appropriate since it is the only one of the heavenly bodies which appears in that form to the naked eye. The following excerpt from K. Digby's *Chemical Secrets* (London, 1683) illustrates the way the alchemists employed the symbols:

> Take good mineral ♀, mortifie it with radicated vinegar; then separate its quintessence with pure S.V.; with that quintessence, dissolve ☿ duplicatum of ♀, that both become an oyl, which unite with a subtle calx of ☉, and bring them to an incombustible oyl, which will transmute ☿ into ☉.

Hence, astrology, and the emphasis which the alchemists later sometimes laid on the number 7, are relics of Chaldean thought. The Chaldeans supposed that the planets influenced the properties of the metals, the organs of the body, and the destiny of man.

The Chaldeans seem to have had some knowledge of metallurgy, dyeing, weaving, the manufacture of colours, glass, and the imitation of gem stones. The chemical arts practised by the early Chaldeans were probably adaptations of chance observations to useful purposes; these arts gradually drifted to the early Egyptians. For instance, it is related that Abraham came from Ur in Chaldea (*Gen.*, **11.** 31),[4] and he probably brought a higher civilization into Canaan, and also to Egypt. The Egyptians developed and improved the Chaldean arts in the laboratories and workshops attached to their temples. When the Babylonian empire ceased to exist, the Chaldean nation was dispersed, and the priests were scattered over the neighbouring lands, so that the term *Chaldean* became a by-word synonymous with "a wise man from the East." The scholars also tell us that the Assyrian *rab-mag* or the Semitic *mag*—meaning a priest—has furnished the Latin and European language with the terms *magus*, *magic*, and *magician*.

India.—India played no direct part in the development of Western science. It is a tradition that Hermes the Egyptian predicted that naught of the history of Egypt, but the letters engraved on stone, would survive. Whether this be true or not, scholars are now mainly dependent upon the inscriptions on tombs and monuments for their knowledge of the early Chaldeans and Egyptians. On the other hand, what remains of Indian thought is recorded in their books—the *Vedas*, the *Charaka*, and the *Susruta*—for the Indians were a literary people. According to Max Müller, there are many points in common between the early Greek and Indian philosophers, and there is a historical possibility that the Greeks were influenced by Indian thought travelling through Persia. From this point of view, it was only when commerce had opened up the country that it became possible to recognize the debt which European science owes to India, and to find that a great deal formerly attributed to the Arabians was of Indian origin. The learning of Greece, Persia, and India is said to have been taxed to help the sterility of the Arabian mind.

In his *History of Hindu Chemistry* (London, 1902), P. C. Rây has shown that Indian chemistry developed largely on independent lines—medicine, not the metals, was mainly emphasized. The contact between the Hindus and Persians is thought to have given the latter a bias towards medicine which later showed itself in the polypharmacy of the Arabians. Very fair accounts of the philosophical views of the Hindus are available. H. T. Colebrooke,[5] for instance, has shown that an early philosopher Kanaka developed an atomic theory rivalling that of Lucretius (60 B.C.). The Hindus also developed a five-element theory of the constitution of the world, but the elements of the Hindus were not the same as the quintet—air, earth, fire, wood, metal—of the early Chinese. The Hindu quintet embodied: *Water*, the first thing created; the sacred *fire;* the unbounded *æther*; the foster-mother *earth;* and the *air* which animates all living beings. The idea that water is the most primitive element of all is found in many of the classical books of India.

The Vedic hymns, over 1000 B.C., personify the elements and natural phenomena—for instance, they raise the active principles of plants to the dignity of gods. The medical work *Charaka*, and the more recent *Susruta*, seem to be repositories of information—chemical and therapeutical—which had accumulated between the Vedic period and approximately the eighth century. Gold, silver, copper, iron, tin, lead, as well as some varieties of brass were known. The writers also mention a number of salts of the metals—*e.g.* alum, copperas, sodium and potassium carbonates, and a few products of the mineral kingdom. The Hindus developed some alchemical notions, but they directed their attention mainly to medicine. According to P. C. Rây, the practice of chemistry between the twelfth and thirteenth centuries was distinctly in advance of that of the same period in Europe. The Hindus learned about zinc and mercury; but, as L. Hoefer has pointed out, real progress in chemistry in India and China was not possible so long as the preparation of the mineral acids was unknown. These acids are incidentally described in works dating from the sixteenth century.

The arts and sciences were largely cultivated by the higher classes, but, according to P. C. Rây, when the caste system was established, the opinion that industrial work tends to lower the standard of thought, which at one time threatened Europe, seems to have likewise developed in India with disastrous results. The arts and sciences were relegated to the lower castes, the spirit of inquiry gradually died, and the artisan classes, guided solely by their mother wit and common sense, alone kept up the old traditions. The withdrawal of the intellectual community from active participation in the arts rendered India "unfit for the birth of a Boyle, a Descartes, or a Newton, and her very name was all but expunged from the map of the scientific world."

China.—So far as we can gather, the Chinese were civilized, and cultivated the arts and crafts at a time when the European nations were barbarians. Some scholars claim that there is strong evidence of a Western origin of Chinese civilization, and that the first Chinese settlers came from a country in the far West which was closely connected with the founders of Babylonian culture. The earliest documentary evidence of man's attempts to answer the question: From what are all things made ? occurs in the Chinese work *Shoo King*, which is said [6] to contain a document called *The Great Plan* purporting to have been given by heaven to Yü the Great, about 2200 B.C., and which is considered by the scholars to be older than Solomon's writings. Here reference is made to five elements—water, fire, metal, wood, earth. The Chinese element wood was never recognized as an element in the West. The early Chinese philosophers supposed that two elementary principles—*yang* (male or active) and *yin* (female or passive)—were derived from *t'ai kih*—the Great Origin of the Grand Cause. The two principles *yang* and *yin* gave rise to the five elements. Fire and wood belong to the *yang* element; water and metal to *yin ;* and earth is neutral. The union of the five elements produces *yang* and *yin ;* and the union of these two principles produces the grand cause which is itself without cause. The Chinese Buddhists symbolized the five elements by the square (earth), circle (water), triangle (fire), crescent (air), and the gem (æther)—as indicated in Fig. 2. In the mediæval European symbolism, the two latter figures are treated as one, and serve as the common symbol of air. It is said that all over those parts of Asia dominated by Chinese civilization, *stupas* or monuments built in the general shape of the symbols of the five elements are to be found—*e.g.* the gateway to the Buddhist monastery of Pekin, etc.

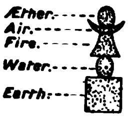

FIG. 2.—Stupa form of the Chinese Symbol for the Five Elements.

The philosopher Lao-tze, founder of the Taou religion in the sixth century B.C., believed that a fine essence or spirit arising from matter may become planets and stars; and these speculations led to the search after the sublimated essence of things. The Taouists sought some flux which would purge man from the dross of animalism and leave the higher part of man's nature to be crystallized out and sublimed into some stable and eternal form. They had no success in finding an elixir of life, or philosopher's stone; but they obtained a number of fairly pure mercurial preparations. According to J. Adkins (1855), the earliest Chinese work on alchemy now extant is the second-century treatise *Chen tung chi*, by Wei Peh Yang; and two centuries later, P'au P'on Tsze wrote many works on alchemy and kindred subjects. Later still, a disciple of Lao-tze—Wei Poh Yang—wrote a book *The Uniting Bond* in which reference is made to a *red elixir* which was probably mercuric sulphide or vermilion, prepared from galena or lead ore—symbolized by a white tiger—and mercury—symbolized by a blue dragon. The red elixir was regarded as an elixir of life even though Wei Poh Yang appears to have been poisoned when he attempted to practise his own philosophy. There seems to have been some contact between eastern and western Asia during the seventh-century invasions of the Mahomedans, and the teachings of the Taouistic alchemists penetrated Arabia, and appear there as the philosopher's stone and the elixir of life.

W. A. P. Martin,[7] in a chapter on *Alchemy in China* (1901), considers that the alchemy of China is not an exotic but a genuine product of the soil of that country; alchemy is indigenous to China, and coeval with the dawn of letters. He understands the words alchemy and chemistry to represent different stages in the progress of the same science, and says that the skill of the Chinese in the chemical arts and their knowledge of many chemical compounds give evidence of lives passed among the fumes of the alembic. Whatever be the true facts, there can be little doubt that the early Chinese practised the chemical arts somewhat extensively, and they knew quite a long list of chemical preparations—nitre, borax, alum, corrosive sublimate, arsenic, mortars, cements, oils, paper, sugar, etc. They appear to have invented printing, the manufacture of paper, and gunpowder—or rather a kind of Greek fire which was placed in vessels, ignited, and projected from a throwing machine. They were acquainted with various precious stones; some of their pottery has never been surpassed. Chinese porcelain seems to have originated about the time of the Han dynasty—206 B.C. to 220 A.D.—and it attained its highest development under the Ming dynasty—1368–1644. Glass was made in China in the Wu Ti dynasty—422–455—and was probably derived by contact with Western nations. They knew about gold, silver, mercury, lead, copper, iron, zinc, nickel, and various alloys. The method for making zinc was probably derived from India. They seem to have had ideas about the transmutation of the base metals into gold; and they are credited with a knowledge of oxygen and the composition of water as early as the eighth century. All this, however, exerted no direct influence on the development of European chemistry, although there is much evidence to show that indirect communication between Europe and China was possible—*e.g.* the Arabian alchemist Avicenna is said to have been born at Bokhara on the borders of the Chinese empire. From the time of Confucius, the Chinese made little progress in the arts and sciences, while Europe rapidly grew in knowledge.

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§ 9. The History of Chemistry in Egypt

> Let us confess at once, without going round the subject, that practical chemistry took its rise in the workshops of the smith, the potter, or the glass-blower, and in the shops of the perfumer; and let us agree that the first elements of scientific chemistry date no further back than yesterday.—J. B. DUMAS.

According to Diodorus Siculus' report[1] of his visit to Egypt—*Bibliotheca historica* (*c.* 30 B.C.)—during the reign of Julius Cæsar, the Egyptians regarded **Hermes Trismegistus** as a man[2] to be esteemed above all others for his penetrating genius in discovering everything that could be useful in life; and it was the favourite opinion of the Arabian and European alchemists in the Middle Ages, that this Hermes laid the foundations of chemistry about the time of Moses. Hermes was accordingly called the father of philosophy and of alchemy by the alchemists of the Middle Ages—*e.g.* by Albertus Magnus (*c.* 1250), Roger Bacon (*c.* 1250), etc. It was also said that before the time of Hermes, the transmission of knowledge from one generation to another depended upon oral tradition, but Hermes invented a system of recording events upon stone pillars in the same way that modern writers employ parchment or paper; consequently, engraved pillars were the standard literature of the day. Some of those who now appear to be the more credulous writers of early history, state that Hermes inscribed upon an emerald the most essential secrets of alchemy, and presented this jewel to Sarah the wife of Abraham; and that after many subsequent adventures the stone was lost; they also state that a copy of the inscription survives. From the translations which have been made of the supposed inscription it appears that even if the inscription itself be not lost, its meaning has gone. The alchemists honoured Hermes when they spoke of the *hermetic* sealing of a vessel.

Attempts have been made to identify Hermes Trismegistus with the Egyptian king Siphoas or Memnon, who had the surname Hermes, and also with various biblical celebrities—Adam, Cain, Enoch, Joseph, Moses, and Abraham. Some writers maintain that Hermes Trismegistus is a fabulous personage, and it is generally supposed that this Hermes was identical with the Egyptian god *Thoth*—literally a pillar. Thoth is represented by the Egyptians as an ibis-headed god with a pen in his hand, the tutelary deity of wisdom and letters, Fig. 3. It is further said that the supposed writings of Hermes really cover three successive epochs—the first Hermes dealt with the period down to the deluge; the second Hermes was concerned with early traditions; and the third Hermes embodied the full-grown science of Egypt. The whole system of Thoths or pillared literature was personified as Hermes Trismegistus—τρις, thrice; μέγιστος, greatest—meaning literally thrice great interpreter. It is therefore easy to understand how Hermes might have been credited with being an extraordinarily prolific author. Thus, in his *De mysteriis Ægypt* (*c.* 360 A.D.), Iamblichus says that Hermes was the author of 36,525 books—T. Bergmann (1779) laconically observes that, if so, the books must have been very concise after the manner of those times, and that each book could have contained but a few sentences. Indeed, in his *Stromata* (*c.* 200), Clement of Alexandria describes imposing celebrations in which the books of Hermes were borne in processions.

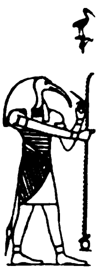

FIG. 3.—The Egyptian God Thoth.

Most of the writings attributed to Hermes appear to have been lost at the destruction of the Alexandrian library; a few passages are quoted from them by Zosimus (*c.* 400); and copies of some dealing with burial rites and the future life have been found buried with the mummies of kings and priests; these have been embodied in what is now called *The Book of the Dead*. In general, it has been said that Egyptian thought was heavily hampered and severely restrained by a powerful priestcraft; that the people were haunted by dread and dismal shadows from the underworld; that they fostered an elaborate cult of the dead; that their houses were temporary abiding places; while their tombs were their eternal homes.

Herodotus (*c.* 440 B.C.) believed that the early Egyptians were the wisest of men. He said that they had three communities of priests—at Heliopolis, Memphis, and Thebes. The priests were responsible for the preservation of such knowledge as was considered worthy of being retained; this knowledge was kept secret and not divulged except to the elect. The sacerdotal secrets were in part described by hieroglyphics on stone pillars, and on manuscript papyri, but the allegorical nature of the symbols prevented them being read or understood by the uninitiated. According to Iamblichus (*c.* 360), every discovery which was approved by the priests was engraved, without the author's name, on stone pillars in the temples. Clement of Alexandria, Plutarch, and others say that the priests possessed still more secret writings. No original record of the early writers is available, and our knowledge of the practice of the Egyptian arts is gleaned from fragments in the writings of Pliny (*c.* 23), Plutarch (*c.* 100), C. Galen (*c.* 190), etc.

About 332 B.C., while Egypt was under Greek rule through conquest by Alexander the Great, the Greeks were received in the Academy of Alexandria; and some of the Egyptian manuscripts were translated into Greek, and later on distributed over Europe—Paris, for instance, among others, has one by Zosimus; the St. Mark manuscript is preserved at Venice; and a number are reported to be at the Vatican in Rome, the Sultan's museum in Constantinople, etc.[3]

The *Rhind mathematical papyrus* in the British Museum is the main source of our knowledge of the early Egyptian mathematics. It is considered to be a copy made about 1600 B.C., by an Egyptian priest, from a document seven hundred years older. Researches near Memphis have given indications of Egyptian medical practices 4500 B.C., and pictures of surgical operations of a date not later than 2500 B.C. have been found. The celebrated *Georg Ebers' papyrus*[4] was found in the winter of 1872–3, near Memphis, in a terra-cotta vessel between the legs of a mummy which was buried about 10 ft. deep. The papyrus is supposed to be a copy of one of the six medical papyri of Hermes (*c.* 1550 B.C.) about the time of Moses, and the text refers back to kings who reigned 3700 B.C. The papyrus is a kind of materia medica and medical treatise; it gives some directions to the medical attendant of a sick person, and describes the necessary incantations and invocations for the co-option of the help of the gods. The papyrus also contains references to a number of metals and some compounds.

A portion of one of the earliest Egyptian manuscripts is preserved in the museum at Leyden, and is known as the *Leyden papyrus*. It was found enclosed in the wrappings of a mummy at Thebes, and is considered to have been written about the third century. It was presented to the Netherlands by I. d'Anastasi, the Swedish consul at Alexandria in 1828. The work contains over a hundred magic formulæ, and recipes for the preparation of alloys used in making various objects of the goldsmith's art. It also has drawings of some chemical apparatus. It has been investigated by C. J. C. Reuvens, M. Berthelot, etc.[5] The grammatical errors and spelling have led to the opinion that the papyrus must have been the memorandum book of an uneducated artisan engaged in attempts to imitate gold and silver for fraudulent purposes—*e.g.* the preparation of *asem*, an alloy of copper and tin, occupies a prominent place among the recipes for imitating gold. The Royal Swedish Academy of Stockholm also acquired a papyrus about the same time and from the same source as the Leyden papyrus; but the existence of the *Stockholm papyrus* seems to have been overlooked until about 1906. It was translated by C. O. Lagercrantz in 1913.[6] It deals with tho diplosis of silver, the imitation of precious stones, and dyes.

These papyri are supposed to represent the class of books on the chemistry of gold and silver which, according to Suidas' *Lexicon* (*c.* 1000), were burned by the order of the Roman emperor, Diocletian, about 290 A.D., as a supposed punishment for an attempted rebellion, and to prevent the Egyptians making gold, and so acquiring wealth sufficient to enable them to oppose the authority of the Romans. These incendiary forays on the books of a prohibited and feared art—alchemy—were not infrequent in the early Christian era—witness *The Acts of the Apostles* (**19.** 19). This helps to explain the paucity of the early records of Egyptian science; yet, in spite of various conquests of Egypt by the Persians, Babylonians, Greeks, and Romans, the arts were cherished by the priests with more or less vigour until the Saracen invasion of the seventh century, when every abode of learning, and every monument of science was destroyed with a ruthless hand. In 642 A.D., the famous Alexandrian Library, with its 700,000 books, was condemned to destruction by Kaliph Omar, who, in refusing a petition to spare at least a part of the library, is reported to have said: "If the books agree with the Koran, they are useless; and if they differ from it they are dangerous." A mania for pillage and destruction with the idea of terrorizing the stricken inhabitants of a conquered territory, has long been characteristic of the temper of invading barbarians in ancient and modern times—witness the invasion of Europe by the Goths, the Vandals, and the Huns early in the Christian era, and the more recent rape of Belgium and North France by Teutonic hordes maddened with the lust of a world's conquest. Egypt never recovered from the severe blows she received, and what was presumably the greatest treasury of knowledge garnered by the ancient world, was used for kindling the fires of the baths of the invaders. Probably a few volumes were surreptitiously preserved; others, said to have been saved from the plunderers, are probably forgeries.

The Egyptians appear to have been acquainted with some six or seven metals and with some alloys.[7] Various metallurgical processes for extracting or melting metals have been depicted in their tombs, etc.—Fig. 4, for instance. The Egyptians were well versed in the arts of glass-making, potting and the manufacturing of precious stones and enamels; they were familiar with the arts of dyeing, painting, tanning, brewing, and baking; they were acquainted with many poisons and their antidotes, and with expressed and distilled oils. They were highly skilled in the use of antiseptics—particularly in the embalming of the dead. Among the operations employed in the arts and crafts of the Egyptians were: calcination, digestion, decoction, distillation. expression, evaporation, fusion, fermentation, levigation, and sublimation. So far as the available records go, there is nothing to show that any results were obtained by experiments directed as deliberate questions to nature. To know that liquids boil and evaporate, or that metals fuse and form calces, may indicate an unconscious sagacity in observation, but it is not scientific observation; the early arts, said W. Whewell,[8] were the parent, not the progeny of science.

So far as we can learn, the disjointed knowledge of technical processes, so jealously guarded by the Egyptian priests, was purely empirical, and it required centuries of effort before man learned to view these processes in a comprehensive rational way. Evidences of the practice of these chemical processes are found in ancient monuments and tombs of high antiquity—see, for example, R. Lepsius' *Die Metalle in den ägyptischen Inschriften* (Berlin, 1872)—and Fig. 4 represents the washing, fusion, and weighing of gold as is reported to have been depicted on an old Egyptian tomb. The records are too imperfect to form a clear idea of Egyptian science, if they really had one such. There is some fragmentary evidence, more or less confused by fictions, and disguised by personifications, that the Hermetic writings assumed that all substances are produced from two elements: *fire*, the spirit of the world; and *mortuum malum*, the inert matter of the earth—that is, energy and matter; although, according to Seneca's *Quæstiones naturales* (**3**. 14, *c.* 63 A.D.), the Egyptians adopted an extended form of the four-element theory in which each element had an active (male) or passive (female) form—*e.g.* active air was the *wind*, and passive air the *atmosphere; flame* was active fire, and *light*, passive fire. According to Diodorus the Sicilian (*c.* 30 B.C.), the Egyptians taught that by some internal changes, all bodies sprang from their seeds or *atoms*, and were changed, perfected, and then destroyed.

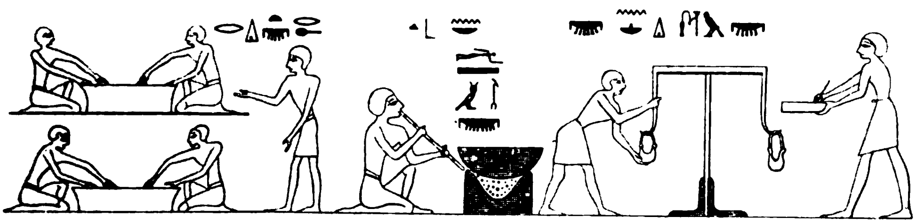

FIG. 4.—Gold Washing, and the Fusion and Weighing of the Metal as depicted in an early Egyptian Tomb.

Consequently, the impression that Egyptian chemistry was mainly practical recipe and unverified speculation, is well founded on pertinent evidence; but others claim that too little inside knowledge is available to justify speaking with any confidence. In any case, it will be clear that before the Christian era, Egypt must have been a kind of focus or centre which collected, assimilated, extended, and developed knowledge derived from various Eastern sources; otherwise expressed, the rise of chemistry in Egypt can be compared with a river which drains a large tract of territory, there is not one source, but many sources, each feeding a tributary of the river.

Phœnicia.—It is fairly clear that the indefatigable merchant Phœnicians had acquired some knowledge of the so-called chemical arts during their contact with the Egyptians. The Phœnicians were famous for the manufacture of a purple dye —*Tyrian purple*—the special boast of Tyre ; for the manufacture of glass—*Sidonian glass*—particularly at Sidon ; for the weaving of fabrics of various kinds ; for working in metals; and for the engraving of gems (*II Chronicles*, **2**. 14). The Phœnicians were great navigators, and it is supposed that they circumnavigated Africa. Strabo says that they made a special study of astronomy and arithmetic. Posidonius, a Greek writer of the first or second century B.C., made a special study of Phœnician mining, and gathered his data from the remains of the Phœnician mines in Spain.[9]

The biblical record.—The biblical records of the unfortunate Israelites show evidence of the chemical arts and crafts employed by their Egyptian masters. The Israelites must have carried much of this knowledge into Asia during their exodus from Egypt under the leadership of Moses. Even from the beginning of *Genesis*, we are told that Tubalcain (3870 B.C.), the eighth man from Adam, was a worker in metals (*Gen.*, **4**. 22) ; good gold is said to have been obtained at Havilah (*Gen.*, **2**. 11), and silver coins were in use at the time of Abraham (*Gen.*, **23**. 16) ; in all, about six metals—gold, silver, copper, iron, lead, and tin—were known to the Israelites (*Numb.*, **31**. 22) ; Noah made wine from grapes (*Gen.*, **9**. 21) ; and vinegar was in use (*Numb.*, **6**. 3) ; bricks were burned for the building of the tower of Babel (*Gen.*, **11**. 3) ; weaving and dyeing were known (*Exod.*, **26**. 1) ; and oils, perfumes (*Exod.*, **30**. 23), and butter (*Gen.*, **18**. 8) were manufactured.

The mechanical performance of operations essentially chemical in their nature is not chemistry, otherwise the first man to light a fire, boil a rabbit, or roast a pig was the father of chemistry. It is difficult to see why the mere practice of these arts should be taken to prove that the early artisans were chemists in all but name, unless there is some collateral evidence of scientific procedure in the development of the empirical crafts—roasting and boiling, baking and brewing, or potting and dyeing. Moses' demonstration[10] of the solubility of Aaron's golden calf (*Exod.*, **32**. 20) has been taken to show the profundity of the chemical knowledge he must have acquired during his tuition by the Egyptian priests ; but, before the indignant prophet can be credited with any profound knowledge of chemistry, more details are required. Well might Francis Bacon, in his *Novum Organum* (London, 1620), protest against the vanity of the attempt to found science upon the scriptures.

In *Exodus* (**31**. 3) we are told that Bezaleel, the son of Uri, was endowed with the spirit of the Lord, and with skill to work in metals and precious stones. These hints of the early arts have been expanded by surmise and guess, and deformed by fiction and fable. For instance, it has been said that man received his first knowledge of the arts and sciences by divine or diabolic revelation. In his *Chronicorum canonum* (*c*. 300), P. Eusebius tells us that the apocryphal Enoch was taught by the angels, and transmitted his divine revelations orally, through Methuselah (*c*. 3300 B.C.) and his descendants down to Abraham. From the writings of Zosimus (*c*. 400), it would appear as if there was once a race of amorous genii prone to fall in love with women, for he says that the secrets of nature were revealed by such genii to the daughters of men in return for love. The dowry was called *παρδώσιν θείαν*—the divine tradition ; the first account of these revelations was called *χήμα* (chema) ; and the art itself, *χήμια* (chemia). Chema is thus an early tradition respecting the operations of nature taught to mankind by angels, who appear to have been *damnati a Deo* for their ill-timed loquacity. The credulous and imaginative O. Borrichius, in his *De ortu et progressu chemiæ dissertatio* (Hafniæ, 1668), said that the angels or demons here mentioned were the offspring of Seth and of Tubalcain, who had been instructed by their progenitors in the mysteries of nature, and who profaned their trust by communicating heavenly secrets to the daughters of Cain by whose charms they were seduced (*Gen.*, **6.** 2–4). The gynecial myth of the origin of chemistry recalls the Jewish story of the fall of man, and also the Grecian legend of the Sibyl who demanded both length of years and a knowledge of the divine *arcana* as the price of her favours to Apollo the sun-god. Somewhat similar myths are reported to have been current among the Phœnicians, the Persians, and the Egyptians. They illustrate the extreme credulity of man in the first of Comte's *les trois états*, when everything that is not understood is believed to have a supernatural origin.

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§ 10. The History of Chemistry in Greece and Rome

They had visions. Oh! They were as grand
As ever floated out of fancy land.

From the testimony of Diodorus the Sicilian (*c.* 30 B.C.), Clement of Alexandria (*c.* 200 A.D.), and Iamblichus (*c.* 350 A.D.), it would appear that the Greeks learned the practice of the chemical arts and crafts largely from the Egyptians.[1] Diodorus says in his *Bibliotheca historica* (*c.* 30 B.C.):

> Orpheus, Musæus, Melampus, Dædalus, Homer, Lycurgus, Solon, Plato, Pythagoras, Eudoxus, and Democritus the Abderite all went into Egypt, and they doubtless learned there all those things which rendered them afterwards famous among the Greeks. For thirteen years Plato and Eudoxus associated with those priests in Egypt who most excelled in the knowledge of celestial things. They kept their knowledge in the greatest secrecy for a long period and would not deign to impart it to any one. At length, subdued by time and humble entreaty, they revealed some few things, but the greater part they concealed entirely from the vulgar.

In the opinion of E. Zeller[2] there is little trustworthy evidence to support the assumption that the philosophy of the Greeks was derived from Oriental or Egyptian influences, although it is highly probable that it received some impulses from the East; but whatever the Greeks borrowed from foreign sources was clarified and refined by the fire of their own genius. For example, it has been said that the Phœnicians taught the Greeks the art of writing, but that it was the Greeks who wrote.

The knowledge of the secret arts, and the prevailing opinions of the Egyptian priests, as Herodotus (*c.* 440 B.C.) relates, must have been communicated in part to many vagabond Greeks during their sojourn in Egypt from about 660 B.C. The unrivalled Grecian artists surpassed their teachers in the beauty and elegance of their æsthetic productions, and also in works dependent upon imagination and fancy; but artisans and craftsmen made much slower progress with the philosophical Greeks than with the more practical Egyptians. An Alexandrian Society is reported to have been formed among the Greeks in Alexandria about the third century, but, so far as we can gather, the knowledge which they are supposed to have acquired mainly from the Egyptians, was confused with metaphysical fancies; and its expression was obscured by ambiguous allegories and cabalistic symbols—possibly aping the hieroglyphics of Hermes—so that their writings now appear to us as if the authors tried to conceal their own ignorance in a cloud of words and symbols.

The Greeks did not contribute much to the chemical arts, but they furnished chemistry with a science of method applicable to all the sciences. The Egyptians accumulated facts and invented useful arts; the Greeks discovered the laws of investigation, the principles of discovery, and the laws of thought. The most important result of centuries of Grecian effort was consummated in the mighty *Organon* of Aristotle (*c.* 320 B.C.). This organon of deductive and inductive methodology should have inaugurated the third of Comte's *les trois états*, but it did not. The facts had not been determined with sufficient accuracy. Isaac Newton could not have discovered the gravitational law if accurate data had not been prepared for him by J. Kepler and G. Galilei. Aristotle's organon came too early. In any case, the method of investigation so gloriously established by Aristotle was unproductive; it was degraded, misunderstood, and perverted by his disciples, who, instead of applying the great principles of the organon, worshipped their master's opinions on a host of special subjects as if they were oracles divine. Thus, I. R. Averroës, about the middle of the twelfth century, went so far as to say, "The doctrine of Aristotle is the perfection of truth, for his understanding attained the utmost limit of human ability."

The method of Aristotle was rediscovered and restated by Francis Bacon in his *Novum organum* (London, 1620). The two methodologies are substantially the same. To some, Bacon's organon appears to have inaugurated a kind of Lutherian reformation in science; rather did the Baconian organon grow tardily from seeds planted by Aristotle and his predecessors in the unproductive soil of metaphysical speculation. According to G. H. Lewes' *Aristotle* (London, 1864), the main cause of the sterility of the method of Aristotle and Francis Bacon was their failure to appreciate the need for unremitting verification, so well emphasized by Roger Bacon (*c.* 1280)[8]—Bacon the First—in order to vindicate the principles deduced from the available facts. The same idea was emphasized by Albertus Magnus, about the same time as Roger Bacon:

> A principle which does not agree with *experimentali cognitione* (experimental knowledge acquired by the senses) is no principle, but rather the opposite.

Aristotle himself frequently emphasized the danger of relying on mere guesses as if they were observed facts, but he so often departed from his own precepts that he was frequently inveigled by the perils of his own speculations. The illustrious Francis Bacon likewise completely failed in vigilance when he attempted to apply his own method because he did not practise the very principles he had expounded so well. Bacon the Second even went so far as to say that if his methods were adopted, little would depend upon the acuteness of the intellect, for the varied talents of all men would be reduced to one common level. He said:

> Our method of discovering the sciences is one which leaves not much to the acumen and strength of wit, but nearly levels all wits and intellects.

Although the principles of Francis Bacon's organon have been available for nearly three hundred years, they have proved quite inadequate, and there are no signs of this socialistic levelling, for the interval between mediocrity and talent is as great as ever it was. Francis Bacon himself can scarcely be considered to have been a scientific man, or even to have possessed the scientific instinct. Science may have been *about* him but it certainly was not *in* him.

The Greeks seem to have generally emphasized subtilty in speculation and debate rather than accuracy in observation and experiment. In theoretical work, they had an overweening tendency to extreme abstraction, and they were careless and credulous in observation; otherwise expressed, they founded arguments too confidently on unproved statements. and seem to have regarded logical consistency of greater weight than accuracy in the statement of facts. This characteristic was well summed up by the saying which Plato, in his *Timævs*, ascribes to the Egyptian priest of Sais: "Ye Greeks will be always children . . . for though wisdom falls from your lips, your actions are weak and puerile;" or as S. Brown expressed it: "In the art of experiment, the Greek was as feeble as a child; but in the sphere of ideas and vast conceptions it is not a paradox to say that he was sometimes stronger than a man."

The Ionian doctrine of one primal element.—The *Theogony* of **Hesiod** (*c.* 700 B.C.) assumed that "the **earth** is the unmovable basis of the cosmos," but the poem is rather a record of mythic cosmology, and anthropomorphism, characteristic of the first of Comte's *les trois états*, and it had no influence on the development of philosophical opinions.[4] Similar remarks apply to **Pherecydes** (*c.* 600 B.C.), who followed Hesiod with an improved mythology. Pherecydes made a definite attempt to distinguish between the material constituents of the universe—*e.g.* between the earth and its atmosphere, and also between matter and force. He regarded force as a mysterious power exerted by the god Zeus.

The Ionian philosophers—Thales, Anaximander, and Anaximenes—still further substituted impersonal causes, acting uniformly and continuously, for personal causes acting capriciously and arbitrarily. At this time, therefore, the Greeks were in a transitional stage between the first and second of Comte's *les trois états*. Thus, the early philosophers of Greece soon recognized that a belief in superhuman gods was not sufficient to explain the complex phenomena in the physical world. They then promulgated hypothesis after hypothesis to explain how the universe grew from some simple principle—earth, water, air, fire. The new explanations proved just as unmanageable as those which regarded natural phenomena as the work of supernatural agencies. These early speculations of the Greeks do certainly testify to the vigour and activity of their questioning spirit,[5] but their ardour and confidence were untamed by labour or reverses. It required centuries of chastening discipline for man to learn that "he must acquire, slowly and patiently letter by letter, the alphabet in which nature writes the answers to such inquiries."

The first of the seven wise men of Greece, **Thales** of Miletus (*c.* 600 B.C.)—a contemporary of Solon—made one of the earliest protests against the personification of nature by assuming natural phenomena to be produced by capricious designing agencies—diabolic or divine. Three centuries later, Epicurus likewise protested emphatically against referring natural phenomena to the deliberate interventions of gods. Thales believed that natural phenomena are due to the operation of invariable laws to be discovered by a proper application of the human intellect. According to Thales, all the various forms of matter are different manifestations of one underlying essence or *prima materia*. The universe, to him, was made from **water**, which he regarded as the primal element. The same idea occurs in many of the sacred books of the Hindus—*e.g. The Institutes of Manu*—about the ninth century B.C. There is really nothing to show how Thales was led to make the assumption. It has, however, been noted that it is typical of systematic thinkers to reduce to one general proposition that characteristic which is possessed in common by a number of simple facts; and it is therefore hinted by Aristotle that Thales, meditating on the constitution of the universe, saw that water or moisture is omnipresent; that Thales was impressed by the marvellous transformations of water in the form of rain and dew, snow and hail, river and sea; and that the earth appeared to be floating in an ocean of water. All things also seemed to be nourished by water, and he accordingly assumed that water is the sole primal element which is convertible into all the manifold varieties of matter—mineral, vegetal, and animal—found in the world. W. Whewell, however, emphasizes his belief that the opinions of the philosophers of this period are based on vague suggestions and casual analogies, rather than on reasons which will bear examination. It is very remarkable, said A. Comte (1839), that the most inaccessible problems, such as the origin and cause of phenomena, should be the very ones which first occurred to students of nature, while those which were within their reach were considered to be unworthy of *méditations sérieuses*.

Another Miletian, **Anaximenes** (*c.* 500 B.C.), is considered to have been the pupil of Anaximander, who, in turn, was the disciple of Thales. Anaximenes sought for the first principle of things in the omnipresent yet invisible **air**, which he regarded as the equivalent of life because all living beings were nourished by air. Air embraces the whole world, said Anaximenes, and he regarded air as the one eternal essence, more primitive than Thales' water. He called air τὸ ἄπειρν—the infinite—and considered it to be devoid of any material differentiation. Even as late as the eighteenth century, some chemists accepted Anaximenes' air as the primordial element. Thus S. Hales, in his *Vegetable Staticks* (London, 1727), supposed that atmospheric air deprived of its elasticity entered in a solid form into the composition of most substances, and that air is the universal bond in nature. G. E. Stahl also wrote to the same effect in his *Experimenta, observationes, animadversiones CCC numero chymicæ et physicæ* (Berlin, 1731). We have no record how the Ionians—Thales and Anaximenes—accounted for the formation of the different forms of matter from their primitive elements, since matter by itself can only be matter.

The Ephesian **Heracleitus** (*c.* 450 B.C.) expressed himself in such enigmatical terms that he has been called the Obscure Philosopher.[6] A few fragments of his writings have survived. Heracleitus appears to have maintained that all ideas are derived from sensations, and he was the author of the celebrated doctrine that all things are perpetually in a state of motion or flux, and that there is no rest or quietude. Strife between opposite tendencies is the parent of all things. All life is change, and change is strife. The living and moving element in nature seemed to him to be an ætherial exhalation, or **fire**. All things in nature are formed of the principle of fire, which, in turn, is composed of small indivisible parts, ψιγμάτα or atoms, which are in perpetual motion. If all things are conceived to be in perpetual motion or change, then all things are fire. Never-resting fire rules all. Everything has arisen from fire by condensation or rarefaction, and all things resolve themselves back into fire. This idea is but a modification of the water and air elementals of the Ionian philosophers. Obviously, Heracleitus' elemental fire was not ordinary fire; he probably understood fire to mean that which by constant transmutation causes all the varied changes seen in the universe, and which itself remains unchangeable. This idea of a *primum mobile* comes as near to the modern doctrine of *energy* as was possible with the facts then available.

The Grecian **Hippocrates** (*c.* 400 B.C.) was not exactly a follower of Heracleitus, although there is a strong resemblance between the views of both. Hippocrates specialized in medicine, and he has been called the oracle of medicine; he expressly rejected the use of hypothetical philosophy in medicine; he did not altogether rely on empirical experience, but attempted to formulate general rules and principles derived from experience and knowledge. From the chemist's point of view, a small treatise, *On airs, waters, and sites*, is considered to be the most interesting of the works attributed to him. As might have been anticipated it contains many errors and inexactitudes.

The Ionian doctrine of one primitive element was abandoned by **Anaxagoras** in a work *On nature* (*c.* 450 B.C.).[7] He assumed that every difference in the sensible qualities of bodies is fundamental, original, and inalienable; and that there are so many elements as there are simple substances; no means were known at that time for breaking down the majority of substances, and they were accordingly assumed to be simple or elemental. The number of elements was therefore supposed to be very large, or infinite. By repeated subdivision, Anaxagoras argued that all natural things could be resolved into ultimate particles which were later on termed *homœomeriæ*—ὅμοιος, like; μέρος, a part. The homœomeriæ were supposed to be eternal, unchangeable, infinitely divisible, and capable of continuous extension. Like homœomeriæ act on like, and so form matter. If the qualities of the homœomeriæ are assumed to be developed only when the particles are in combination with others, Anaxagoras' homœomeriæ are not very different from the atoms of Leucippus, Democritus, and Lucretius. Anaxagoras' atoms are the same in kind as the substance itself; Leucippus' or Democritus' atoms are indivisible particles of one kind of matter. Anaxagoras also introduced the idea of a motive principle, which he called νοῦς, as the cause of all changes. Democritus called this principle ἀναγκη; Heracleitus, ἀναθυμιασις or *fire*; and Aristotle, αἰθὴρ, æther.

The four and five element theories.—The four and five element theories are among the oldest attempts to classify the protean and multitudinous forms of matter which make up the world. The five-element theory seems to have been favoured by the Chinese and Hindu philosophers. The Greeks reduced the number of elements to four. Diogenes Laertes (*c.* 250) tells us that the five-element theory was first promulgated by the Pythagoreans, and that **Empedocles** (*c.* 500 B.C.) first advocated the four-element theory as a consistent doctrine. Empedocles cited the burning of wood in favour of his hypothesis. When wood burns, *smoke or air* rises upwards, and this is followed by *flame or fire*; *moisture or water* is deposited upon any cold surface in the vicinity; and *ash or earth* remains behind. Empedocles' simple statement seems to be the first record of a chemical analysis. Wood is resolved into its supposed elementary constituents—fire, earth, water, air. True enough, modern methods can probe much deeper, but Empedocles' analysis is excellent for its time. The doctrine of the four elements thus appears as a methodical deduction from facts observed during the analysis of wood, by burning it in air. This analysis has been claimed as "the starting-point of chemistry in history."

Empedocles also formulated the germinating conception of chemical affinity, for he said that the cause of the various combinations and separations of these four elements is love (φίλια) and hate (νεῖκος), which are exerted as active forces producing the union or decomposition of substances. The four elements of Empedocles soon lost their *material* character, and grew into *abstract principles*. It was then fancied that the whole world was compounded of four distinct principles or entities—the *earth* typified all solids; *water*, liquids; *air*, the winds, clouds, and the breath; and lastly, *fire*, which was symbolized by the sun, and worshipped by many as a god. Hence, in the writing of the alchemists of the Middle Ages, there is usually a chapter devoted to this quartet—earth, water, air, and fire. In J. Lacinius' alchemical treatise *Pretiosa margarita novella de thesauro* (Venice, 1546), fire is symbolized by an angel, air by a bird, water by a dragon, and earth by a bull. Aristotle added a fifth element, αἰθὴρ, æther, more divine than the others, and which pervaded all things, and was in perpetual motion. Later, Aristotle's æther became the *quinta essentia*—a kind of primal matter, a divine subtle extract, the quintessence of the other four. The ancient Hindu philosophers also had a fifth element, which, in their system, was wrongly supposed to be a medium for propagating sound, etc., and which, in consequence, had something in common with the modern concept of an æther pervading all space. The *Institutes of Manu* regarded the subtle æther as being first created; and from this, by transmutation, sprang air, which changed into light or fire, and thence into water, and finally earth.

Aristotle assumed that the one primitive quintessence of matter can act as a vehicle or carrier for four primitive qualities: hot or cold, wet or dry. If these four qualities or elements are united with inert passive matter in pairs, the four primary forms of matter—air, earth, water, fire—are produced; for instance, *fire* has hot and dry; *water*, cold and wet; *air*, hot and wet; and *earth*, cold and dry. The different varieties of matter arise when different degrees of these four elemental qualities are impressed on matter. Aristotle denied that the four elements of

Empedocles are really elements because they are mutually convertible one into another. Empedocles' elements, however, may represent the four primary forms of matter perceived by the senses, and into which the four qualities appear to be resolvable :

> For hot, cold, moist, and dry, four champions fierce,
> Strive here for mast'ry, and to battle bring
> Their embryon atoms.—J. MILTON.

The alchemists of the Middle Ages supposed that the elements were formed when the primal essence was clothed with **three principles**—*tria prima*—which they called respectively salt, sulphur, and mercury. In the quaint words of Paracelsus :

> Eisen, stahel, bley, smaragd, sappir, kieszling, nichts anders seind denn schwefel, salz, und mercurius.

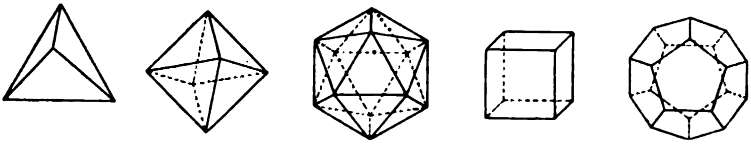
Salt represented the earth or *the principle of fixity and solidity ;* **mercury** represented air and water, or *the principle of liquidity and gaseity ;* and **sulphur** typified fire or *the principle of combustion.* Thus, said Paracelsus, " whatever fumes and evaporates in the fire is *mercury ;* whatever flames and is burnt is sulphur ; and all ash is *salt.*" Albertus Magnus typified the three principles by arsenic, sulphur, and mercury, for he supposed the metals were compounded of these elements.

The three principles of the alchemists were not substances or *corpora*, but rather *principia* or qualities ; they were representative types of qualities or classes. Sometimes the *tria prima* were confused with the four elements of the Greeks, and it is difficult to understand clearly what was gained by the invention of the three principles. The mystic alchemists went even further and imagined that all material things were composed of a trinity : " A body and a soul held together by a spirit which is the cause and the law." They believed the soul of matter to be the transforming principle which they tried to extract in a pure form, and which they expected would enable them to transform the baser forms of matter into the purer forms, of which gold was the best type.

The four-element theory was demolished when water, air, and the earths were decomposed into still simpler bodies ; and when fire was shown to be a manifestation of energy. The term " element " was obviously not intended to be used in the same sense as it is to-day. The four and five elements of the ancients were not considered to have an independent natural existence, but to be derivatives of one another ; the earlier notion of an element rather referred to the genesis of matter than to its ultimate analysis, for the distinction between simple and compound substances does not seem to have entered their minds. Whatever the idea involved in the three, four, or five element theories, it was believed by many different races in different parts of the globe ; it has pervaded the philosophy of all thinking races ; it has been sung by the poets of every land ; and it has had a longer life than any succeeding philosophy. The theory was living three centuries ago ; it is now dead.

The Greek philosophers.—Three gigantic spirits have dominated Grecian thought —Pythagoras, Plato, and Aristotle. Each one in his turn exerted a profound influence on his contemporaries, and on subsequent thinkers. Thomas Carlyle has well said that all history revolves around certain famous personages. The records of **Pythagoras** (*c.* 500 B.C.) and of his school are overgrown with myths and fictions ; and, as with the records of other influential men of old, the older the records, the greater the tendency to associate miraculous and extraordinary events with the men's lives.[8] The Pythagoreans formed primarily a moral, religious, and political association, although the sect early gave a definite trend to philosophical thought. The scholars are now mainly dependent upon more or less untrustworthy reports for their knowledge of the physical tenets of the Pythagoreans. It is generally agreed, however, that the Pythagoreans believed that *number* is the essence of all things. It is difficult to gather what was meant by this high-sounding phrase, for number appears to be merely a relation, or the expression of certain facts. One section of the Pythagoreans—*e.g.* Iamblichus—held number to be the substantial element of corporeal things; otherwise expressed, like Plato's ideas, numbers are the eternal archetypes of things; another section—*e.g.* Hippasus—held that all things are formed, not out of number, but after the pattern of numbers—otherwise expressed, number is the pattern or model from which things are copied, meaning that all things bear the same fixed relation that a series of whole numbers bears to unity; or again, as expressed by Philo, or whoever wrote the *Book of Wisdom*, "God ordained all things in measure, number, and weight." According to E. Zeller's account of the Pythagoreans, the idea must have arisen as man dimly realized the definite and mathematical order in natural phenomena.

From the more or less legendary accounts of the Pythagoreans, it appears that they reduced all things ultimately to one incorporeal *monad*, and assumed that all things are compounded of monads with dissimilar and opposite natures, the uniting bond being harmony. Later writers—*e.g.* Ecphantus—appear to be in error when they state that Pythagoras' monads were corporeal. The Pythagoreans attached special importance to the number 4, the quarternion, which was said to be the source and root of eternal nature; and the later Pythagoreans—*e.g.* Philolaus—were fond of arranging things in series of four. Philolaus considered that the elementary nature of bodies depended upon their form, and it was assumed that the smallest constituent parts of the *earth* had the form of a cube; *air*, an octahedron; *fire*, a tetrahedron; *water*, an icosahedron; and the fifth dodecahedral element represented the *universe*, and embraced all the others. The diagrams, Fig. 5, explain the idea. The historical evidence has not enabled the scholars to decide whether Empodocles adopted four from Pythagoras' five elements, or whether Pythagoras added a fifth element to Empedocles' four. It is thought that the Pythagoreans probably derived the five-element theory from the Hindus. According to Max Müller, the coincidences between the teachings of Pythagoras and Hindu learning are so numerous as to make it highly probable that Pythagoras obtained his leading tenets by contact with the Indians in Persia.



Tetrahedron (Fire)
Octahedron (Air)
Icosahedron (Water)
Cube (Earth)
Dodecahedron (Universe)

FIG. 5.—Primitive Particles of Pythagoras' Elements.

The celebrated Athenian pupil of Socrates, **Plato,** expounded his views on natural phenomena in his *Timæus* (*c.* 360 B.C.). He assumed that all things and all phenomena are transitory and unreal, but the abstract idea of them is alone eternal and real. Hence, the aim of philosophy is to discover the ideas or abiding principles of which the phenomena of the material world are but the image. I. Kant (1790) described Plato's hypothesis by the celebrated metaphor: Just as a flying dove, feeling the resistance of the air, might wrongly suppose it would be able to fly faster in airless space, so did Plato, feeling the limits which the sensuous world opposed to his understanding, assume that by abandoning the sensuous world, he would be more successful in the void space of pure intellect. Plato asserted as an *a priori* truth that the principle of matter was infinite, eternal, and deprived of all qualities; that matter is converted into bodies by being impressed with some occult moving power; and that matter may possess particular qualities—hotness, dryness, coldness, and wetness. He considered that there are four elements—air, water, fire, earth—and assumed that these elements can never be destroyed. The elements can be divided into infinitely small particles incapable of further subdivision; the ultimate particles of the elements have definite forms analogous to those suggested by Philolaus, Fig. 5.

The differences between the various kinds of the same elements are due to differences in the bounding planes of the constituent particles. Fire, air, and water can be transformed into one another by the coalescence of the primitive particles into forms peculiar to these substances. Earth cannot be converted into any of the other three elements because its cubical particles have no mathematical relation with the forms of the other three.[9]

The influence of Plato's pupil, **Aristotle,** on the world of thought has been rivalled only by the founders of the great religions. Aristotle lived between 384 and 322 B.C. Excluding his *Organon,* to which reference has already been made, Aristotle's most interesting contribution to natural science is entitled *Meteorology,* and it deals with astronomical, chemical, and geological subjects ; his views on the constitution of matter are expounded in his *Generation and Corruption.* There is a work on *Physics* containing unfruitful disquisitions on abstract space, motion, infinity, etc., and also a kind of sequence to this work entitled *The Heavens.* Aristotle also wrote some biological works. There has been some discussion as to whether a work on *Mechanical Problems* attributed to him is really the one to which he sometimes refers.[10]

Greek was not a familiar language to the philosophers of the Middle Ages, and Aristotle's writings in the original Greek do not appear to have been known in Western Europe prior to the thirteenth century. Aristotle's works were translated into Syriac, thence into Arabic, and carried to Spain by the Moors. About the fourteenth century Latin translations, made direct from the Greek manuscripts, were read in Europe, and soon got a remarkable hold on European thought. In a general way, it has been said that although Aristotle professed to rely on experience and induction as the sources of true knowledge, he often went astray ; his treatment of natural philosophy displays a capable mind, hampered by unsuspected superstitious prejudices, wrestling with problems beyond its strength. Aristotle rejected Plato's idea-hypothesis and Pythagoras' number-hypothesis. He supposed matter to be capable of infinite division, and he objected to Democritus' idea of atoms, although he admitted that matter may be made up of particles which are actually though not potentially indivisible. Aristotle did not agree with Pythagoras' and Plato's hypotheses that the elemental monads have definite geometrical forms. He said that the attempt to bestow an intrinsic figure on the elements—Fig. 5—is absurd, an element cannot have one. Elementary matter must be formless and amorphous, ready to take on any form according to circumstances, but itself possessing no particular form.

A famous disciple of Aristotle, **Theophrastus** (*c.* 372–287 B.C.) of Lesbos, succeeded his master at the Lyceum.[11] Theophrastus wrote two works on botany which were standard even throughout the Middle Ages ; a history of physics, a work on natural science, and several other fragments—some writings ascribed to him are no doubt spurious. Theophrastus followed the philosophy of Aristotle rather closely in his *Treatise on Fire* (*c.* 315 B.C.)—περὶ πυρός. Theophrastus removed fire from the list of elements ; and he recognized that air plays an important part in the maintenance of a flame, and in the development of plants. In a fragment *On Odours,* he adds that the odour of a substance is due to its volatility. The more important parts of Theophrastus' writings, from the chemists' point of view, dealt with minerals—περὶ λίθων. Here he mentions coal, cinnabar, orpiment and sandarach (arsenic sulphides) for the first time, and he also describes the preparation of white lead, red lead, verdigris, colcothar, chrysocolla, etc.

A number of writings and fragments of **Archimedes** of Syracuse (287–212 B.C.) has been preserved.[12] They deal with some mechanical and hydrostatical problems. The discovery of the celebrated *principle of Archimedes*—if a solid be weighed in air, and then immersed in water, the apparent loss of weight is equal to the weight of a volume of water equal to the volume of the solid—is described in M. P. Vitruvius' *De architectura,* published near the beginning of the Christian era. Al-Khazini's account in the twelfth century lacks the piquancy and interest of that of Vitruvius.

It has been remarked that although Archimedes had fairly entered upon the right path of his department of experimental science, no further advance was made for nearly two thousand years, when Galilei and Stevinus took up the work. The celebrated **Hero** flourished about 117 B.C. In his work on *Pneumatics*, he described the principal physical properties of air known to the ancients, and indicated some ingenious mechanical contrivances operated by means of rarefied or compressed air; he also wrote a treatise on the properties of reflected light; and two treatises on the mechanical powers.[13]

The main contributions of the Greeks to chemical science are the *prima materia* hypothesis; the four-element theory; the atomic theory; the idea of the transmutation of matter from one form to another by some agent or principle; and more or less vague notions of an active principle causing combination or change. There is also Aristotle's work on methodology.[14] The Greeks were not generally guided by observation and experiment either in founding or in verifying their hypotheses. Consequently, their great conceptions were wondrous feats of the imagination; but Lord Macaulay would have none of it, for, in his essay on *Lord Bacon* (London, 1837), he claimed that the Greeks aimed at the stars, and through no want of skill the shot was thrown away. The arrow was indeed followed by a track of dazzling radiance, but it struck nothing. Their philosophy began in words and ended in words.

Rome.—The Romans acquired some knowledge of the chemical arts after they had conquered the Egyptians and the Greeks. The Romans had no philosophy of their own, but they borrowed ideas and learned lessons at the feet of conquered Greece.[15] War was the strength of the Romans, and they favoured the arts and crafts which made good soldiers. The works of art which the Romans acquired as loot from conquered nations attracted much attention, and stimulated some of their artisans to imitate these productions. The Romans, however, displayed but little inventive genius, and it is probable that what successes they obtained were largely due to the work of imported craftsmen. The early Romans developed a code of civil law which has been a pattern for succeeding nations. The doctrine of the supremacy of law inculcated by the Romans probably exerted some influence on man's subsequent attitude towards external nature, and some confusion has resulted from the assumption that a law of nature represents an obligation on the part of natural phenomena analogous to the obligations of a people to its civil law. The modern view of a law of nature is very different from this.

The poem of **Lucretius** (95–52 B.C.), *De rerum natura*, is much admired, and is intimately associated with the history of the atomic theory. It has been considered curious that, with the exception of a few fragments and letters, the works of the three founders of the Grecian atomic theory—Leucippus, Democritus, and Epicurus—should have been lost, and that we have to rely upon the Roman's eloquent poem for a clear and concise account of Epicurus' doctrine. There is nothing to show if Lucretius added anything new to what he found in Epicurus' two works—*Concerning nature*, and *On atoms and voids*—which have been lost.

The principal writings dealing with the physical arts and crafts of the Romans are the works of Vitruvius, Galen, Dioscorides, Varro, Seneca, and Pliny. **M. P. Vitruvius** was an engineer and architect in the service of the Roman state at the time of Augustus—near the beginning of the Christian era. He wrote the cultured work, *De architectura*,[16] in which he gives many indications of the learning of his time, viewed more particularly from the point of view of the practical application of theoretical knowledge. Another celebrity—**Dioscorides**—was born in Asia Minor and flourished in Rome about 75 A.D.[17] contemporaneously with Pliny. His *De materia medica* was a standard work for many years. In this book, Dioscorides describes the art of distillation for the first time, although Aristotle (*c.* 320 B.C.)[18] seems to have had this operation in his mind when he wrote in his *Meteorology* (2. 2):

> Sea water is rendered potable by evaporation; wine and other liquids can be submitted to the same process, for, after having been converted into vapours, they can be condensed back into liquids.

Dioscorides also describes other chemical operations—*e.g.*, the extraction of mercury from cinnabar, by heating a mixture of the latter with carbon. He also mentions lime-water, zinc oxide, blue vitriol, white lead, etc.

Another Greek, **C. Galen** (131–201 A.D.), regarded himself as a disciple of Hippocrates. He practised medicine in Rome about 160 A.D. He was an experimental physiologist, and wrote on human anatomy, physiology, and botany. **M. T. Varro** (116 B.C.–28 A.D.) wrote on agriculture, law, mensuration, etc. **A. Seneca** wrote a work, *Quæstiones naturales* (*c.* 63 A.D.), which appears to have been largely drawn from Aristotle's *Meteorology*.[19] It deals mainly with astronomy, meteorology, and physical geography; and it was the authority on science in the Middle Ages up to the fourteenth century, when it was largely supplanted by Aristotle's works, which then became accessible in Europe through the Latin translations of the Greek texts. *Caius Plinius Secundus*, or **Pliny the Elder**,[20] wrote the *Historia naturalis* about 77 A.D. It deals with an enormous variety of subjects and is a congested and uncritical compilation from credible and incredible authorities and popular beliefs. E. Gibbon, in his *Decline and Fall of the Roman Empire* (London, 1789), called it "an immense register of the discoveries, arts, and errors of mankind." The works of but a few of the authorities quoted by Pliny are known.

The prosperity of the Roman Empire—which included England, France, Spain, and all the countries about the littoral of the Mediterranean Sea—was on the wane about 180 A.D. The Romans, satiated with conquest, became indolent and corrupt, and their intellectual activity slackened. Their empire was invaded by the uncivilized northern races—Goths, Vandals, and Huns. The destructive impulses of the invaders led to the complete disintegration of the empire; and about the fifth century, culture and civilization in Rome were crushed in a few dark years. Many of the records of science, literature, and art were deposited in monasteries, where they were preserved as sacred trusts until civilization again revived in Western Europe. Fortunately, however, Constantine transferred the Roman capital to Byzantium (Constantinople) in the fifth century, and the New Rome maintained a continuity of government and of civilization until the raid of the fourth crusaders in 1204. It is considered that more destruction and damage to ancient records were wrought in the sack of Constantinople by these Crusaders than by the Mahomedan conquest in 1453.[21]

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§ 11. The History of Chemistry in Syria, Persia, and Arabia

Very little advance in culture could be made even by the greatest man of genius if he were dependent for what knowledge he might acquire merely on his own personal observations. Indeed it might be said that exceptional mental ability involves a power to absorb the ideas of others, and even that the most original people are those who are able to borrow the most freely.—W. Libby (1917).

About the third, fourth, and fifth centuries, the Neo-platonic schools at Alexandria and at Athens included Ammonius Saccas, Plotinus, Porphyry, Iamblichus, Proclus, etc. These schools cultivated mysticism and magic. As with the Pythagoreans, they taught that the air is full of spirits and demons which control health and disease, and natural phenomena in general. It was said:

> God rules the world. He has demons under his control, some of which govern animals, some vegetables, and others minerals. . . . One demon governs the liver and another the heart.

When animals or vegetables were destroyed by fire, the gases which escaped were supposed to be subtle spirits returning to the air. With beliefs like these, natural phenomena could be investigated only by contact with the supreme divinity, and this could be attained only by certain mysterious ceremonies involving the use of secret symbols, incantations, and prayers. A knowledge of these ceremonies was regarded as a divine gift particularly reserved for the priests and the initiated. Somewhat similar ideas were later incorporated in the mystical forms of alchemy of the Middle Ages.

In the period between the first and fifth centuries, alchemy attracted the attention of many learned men, and authentic writings on alchemy began to appear. The first, **Zosimos** of Panopolia, lived in the third century, and most of his writings seem to have been lost. Some fragments attributed to him have been collected from Greek papyri, and he is often quoted by later alchemists. Zosimos described various forms of apparatus and furnaces, minerals, and alloys, and he frequently refers in more or less obscure language to the transmutation of the metals. Fragments of the writings of Zosimos, Africanus, Synesius, Olympiodorus, (pseudo) Theophrastus, (pseudo) Democritus, and several other Greek alchemists [1]—about

150 in all—were preserved in European museums—Venice, Rome, Paris, Munich, etc.—whither they drifted after the conquest of the Turks in 1453. The essays reproduced in M. Berthelot's *Collection des alchimistes grecs* are all composed in an enigmatical style with obscure chemical terms used in many different ways; they discuss magical and astrological formulæ; and give citations from mythical authors. The writers were acquainted with many ores, minerals, earths, salts, and animal and vegetable substances; there is no evidence of a scientific classification; and the writers were in ignorance of the mineral acids and their important derivatives. They were chiefly concerned with the operations of solution, distillation, and heating.

The conquests of Rome brought the Orient and the Occident, the East and the West, into close communication. At the beginning of the Christian era, Alexandria was the asylum of Eastern traditions, the centre of medical, alchemical, and philosophical culture; and the sanctuary of the world's learning. The Roman depredations in the fourth century led to a rapid decline; and as a result of the Mahomedan conquest of Egypt in the sixth and the seventh centuries, the Alexandrian philosophers and teachers were scattered, and some refugee Byzantine alchemists travelled to Constantinople; others settled in Persia and Syria, where they introduced the Greek and Egyptian philosophies. Some of the writings of the Greek philosophers were translated into Syrian.

In the seventh century, the Arabians overran Syria and Persia; and the Syrian schools languished and died. The Arabians then began to cultivate those very arts which they had done so much to destroy. Syrian scholars were employed by the rulers for positions demanding wisdom, knowledge, and judgment. Copies of two Syrian manuscripts are preserved in the British Museum; one is translated in M. Berthelot's *La chimie au moyen âge* (Paris, 1893). It contains various technical recipes, discussions on magic and mystic doctrines, the elixir of life, the adulteration of gold, and descriptions of some chemical apparatus. An Academy was founded at Bagdad about 800 A.D., and the Arabians began to collect and translate books from various countries—East and West. The works of Aristotle were translated from the Greek into Syrian, and re-translated from Syrian into Arabian. Consequently the alchemists of Arabia derived their ideas and knowledge from those of Syria; the Syrians in turn were largely dependent on the Greek works of the pseudo-Democritus, Zosimos the Panopolite, the pseudo-Cleopatra, and others who flourished at Byzantium. Historians generally consider that the Greek writers of this period, in turn, derived their ideas from the Egyptians.[2] In any case, the Arabians, like the Greek writers of the Alexandrian school, imparted mysticism into their versions of Hellenistic philosophy, so that there was a partial reversion to the first of Comte's three states. Instead of regarding natural phenomena as the workings of natural law, they were inclined to consider them to be subject to the capricious wills of superior intelligences, and creatures of an imagined demonology. As a result, physical science reverted to magic, astronomy to astrology, and philosophy to theosophy. The alchemical operations were described in mystic language. Hence too arose the philosopher's stone, the elixir of life, etc. The Arabians had a bias in favour of medicine and pharmacy rather than metallurgy, and they appear to have interpreted the alchemical writings from the Egyptians, in terms of medicine and pharmacy—a bias possibly derived from the Hindus. Consequently, the philosopher's stone of the Alexandrian school became the Arabian elixir of life.

The reputation of one **Geber,** an Arabian writer of the eighth century, loomed mightily in the alchemical world about the later half of the Middle Ages. He is credited with having been the first to give chemical knowledge a systematic form by publishing the first extant system of chemistry. It is very true that the ideas expressed in these writings are the earliest to stand in historical continuity with those of the present day. This fact has invested the writings of Geber with a special interest, and this interest is only quickened by a knowledge of their contents and style. The fragmentary information which is available respecting Geber is most disappointing; there is no agreement among the historians concerning his birth-place, his parents, his social or political relations, his rank, the events of his life or his death.[3] There are, however, quite a number of Latin treatises alleged to be translations of Arabic texts of Geber's writings. For example, up to recent years, the *Summa perfectionis magisterii* was credited to Geber, and it was said to have been the first work exclusively devoted to chemistry. The book is an attempt to summarize what was then known or believed with respect to chemical operations and processes. It is, however, disfigured by unintelligible matter which has wrongly led some to the idea that the term " gibberish " for unintelligible words, is a tribute to Geber's style of writing.

The Latin Geber was acquainted with alum, copperas, saltpetre, sal ammoniac, aqua fortis, oil of vitriol, aqua regia, etc.; he described the action of mercury on gold, and of sulphur on red-hot iron; and he supposed that there are three elementals —mercury, sulphur, and arsenic. The metals, said the Latin Geber, are compound bodies which are extracted from their earthy ores when the latter are mixed with carbonaceous materials and heated in a furnace in the absence of air. It seemed to him as if the calx got something from the furnace and so became a metal. According to the Latin Geber, the metals are compounds of the same substances—mercury and sulphur—united in different proportions. Geber also accepted as dogmas of his faith, the transmutation of the metals, and the influence of the planets on the metals—although he said:

> It is as impossible to transform the metals into one another as it is to turn a bull into a she-goat; for it has taken nature thousands of years to make the metals, and we cannot hope to effect the transformation when we rarely live a hundred years.

Many grave doubts have arisen as to the genuineness of the Latin writings which have been attributed to the eighth-century Geber. M. Berthelot has compared the texts of the Latin works, and translated the known Arabic texts preserved in the Museums at Paris and Leyden. He has also compared these works with those of contemporary writers. The style and standards of the Latin and Arabian works are altogether different; and, as a result, Berthelot concludes that *the Latin works attributed to Geber were the composition of one or more writers about the thirteenth century*, who forged the name of the Arabian Geber to crown the book with veneration and respect. The Latin version of Geber is not to be regarded as a translation from Arabic texts. The Latin versions, on which Geber's reputation rests, are sometimes called the thirteenth-century works of the **pseudo-Geber** to distinguish them from some Arabic texts which were probably the work of an unimportant Geber, or of some writer between the eighth and eleventh centuries. The Arabian Djaber (Geber) is reputed to have been the pupil of a Khâled ben Yezid ibn Moaouia, the first Mahomedan writer on alchemy. M. Berthelot's translation of the works of the Arabian Geber show that Geber used the hydrostatic balance; attempted to classify minerals; discussed the changes in volume which occur when substances are heated; and stated that he had seen many persons ignorantly attempting to manufacture gold and silver by wrong methods, and added: " I perceived these workers were divided into two categories, the dupers and the duped. I had pity for both of them."

A debate among the Arabians as to the possibility of alchemy is described in the writings of the Arabian **E. S. Avicenna** (980–1037). The doctrine was defended by **A. M. Rhases** (840–940), or *Rhazes*, whose writings are often quoted by mediæval alchemists. The Arabic physician Avicenna wrote on chemistry and medicine, and he also wrote commentaries on the works of Aristotle. Judging from the reports of his *Porta elementorum* and his *Dictiones*, his philosophical ideas closely followed those of Aristotle; his medical work, *The Canon*, was mainly a compilation of Hippocrates and Galen; and his general knowledge was but little in advance of the Greeks. Notwithstanding this, Avicenna's medical works were long revered as a code of science; but they sank into almost complete oblivion about the end of the seventeenth century. Similar remarks apply to the commentaries of

I. R. Averroes (1126–1198) upon the works of Aristotle; in fact, it was mainly through the commentaries of Averroës that Aristotle's scientific work became known in Europe in the Middle Ages.

There is a very important treatise, *The book of the balance of wisdom,* written in the twelfth century by the Arabian optician and physiologist **Al-Khazini,** or *Alhazan.*[4] It contains a memoir on the use of the balance for the determination of specific gravities, and is supposed to have been based upon a work by **Abu-r-Raihan** written about 1000. Al-Khazini said:

> The water-weight of a body visibly changes according to the difference between the waters of different regions in respect to variety and density, together with incidental difference due to variety of seasons and uses. . . . In winter one must operate with tepid, not very cold, water on account of the inspissation and opposition to gravity of the latter, in consequence of which, the water-weight of the body comes out less than it is found to be in summer. . . .

The temperature was apparently estimated by the distance a kind of hydrometer sank in water. The specific-gravity bottle was described, and an improvement on the floating hydrometer of Pappus (*c.* 400 B.C.) indicated. Gravitation seems to have been regarded as a force directed to the centre of the earth, and which diminished proportionally with the distance; it remained for Newton to show that it diminishes as the square of the distance. Both Abu-r-Raihan and Al-Khazini compiled tables of the specific gravities of various solids and liquids with which they were acquainted; and the numbers agree closely with those adopted to-day.

During the period of the intellectual darkness which prevailed in Europe after the decline and fall of the Roman Empire, the torch of learning was borne by the Arabians, but there is little to show that the Arabian alchemists—Avicenna, Anvenzoar, Averroës, etc.—who flourished between the eleventh and thirteenth centuries —did much to extend the chemical knowledge which they derived mainly from their contact with the Egyptians, Greeks, and Hindus. The Arabians borrowed freely; but they showed little genius for independent thought. In his posthumous *A History of Chemistry* (London, 1913), J. C. Brown sums up by saying: "far from crediting the Arabians with being the originators and improvers of chemistry, as stated by E. Gibbon (1789),[5] much of their knowledge was not understood, and they involved it in mystical confusion which hindered the progress of science for centuries;" and W. Whewell, by saying:

> The Arabians cannot claim in science or philosophy, any really great names, they produced no men and no discoveries which have materially influenced the course and destinies of human knowledge, they have tamely adopted the intellectual servitude of the nation which they conquered by their armies; they joined themselves at once to the string of slaves who were dragging the car of Aristotle and Plotinus.

About the eighth century, the Arabians amalgamated with the European settlers in Egypt, and under the name Moors, crossed into Spain, where they founded Academies at Cordova and Granada. These Moorish universities flourished between the eighth and eleventh centuries, and furnished the schools of Europe with many learned teachers. The power of the Moors in Spain was destroyed with the conquest of Granada by the Christians under Ferdinand and Isabella in 1492. The Arabian centre of learning at Bagdad was captured in the eleventh century by the Turks, a tribe which separated from the Mongols in the sixth century, and settled in Asia Minor. The Turks gradually extended their power westwards, and formed the Ottoman or Turkish Empire under the leadership of Othman (born 1258). The Turks crossed into Europe in 1356, and about a century later, 1453, captured Constantinople. The learned men congregated in that city then slowly drifted westwards with their manuscripts and learning.

The authors of the earlier Arabian alchemical books were directly or indirectly associated with the famous schools of Alexandria, the last resting-place of the secrets of the Egyptian priests. There can be no doubt that the chemical arts were well developed in old Egypt. The Egyptian origin of the term chemistry would harmonize with the prefixing of the article *al* (the) to the word *Khem* (Egypt) when the Arabians overran Egypt, and thus learned many of the secrets of the temple laboratories of the Egyptian priests. No doubt also the contact of the Arabians with Persia made them acquainted with some chemical knowledge derived by the Persians from India. The Arabians also learned from the Grecian philosophers through the Syriac translations. The learning derived by the Arabians from East and West was probably distorted, modified, and adapted to suit their own particular dogmas, and carried to Europe partly by the currents of returning crusaders, and partly by the Moors *viâ* North Africa and Spain.

The origin of the term chemistry.—Chemistry had no special name prior to the sixth century, before which it was variously known as the *art of Hermes*, the *Hermetic art*, the *Sacred art*, the *Occult art*, or the *Black art*. Many have tried to trace the origin of the name chemistry, and the quest has led etymologists to suggest several different hypotheses; accordingly, the student has the choice of a number of plausible guesses at his disposal.[6]

(1) The various attempts which have been made to make the root a Greek word have not been very successful. H. Barbarus, in his *Compendium scientiæ naturalis* (1547), and A. Libavius, in his *Alchymia* (Francofurti, 1606), consider it possible that the term is derived from *χύμος*—a juice or menstruum—in reference to the use of various solvents by the early alchemists; or from *χέω*—to fuse or melt; and J. A. Quercetanus, in his *De priscorum medicina* (c. 1600), uses the term *halchymiam* for a fused salt—*ἅλς*, salt; and Alexander the Aphrodisian (c. 200 A.D.) speaks of the use of *χυικὰ ὄργανα*—a kind of crucible for melting substances. While this derivation of the word was in fashion, alchemy was spelt *alchymy*, and chemistry, *chymistry;* but this spelling was dropped when it was recognized that the Greeks had neither the name *chemia* nor the science; it was only near the beginning of the Christian era that the new science began to attract attention in Europe. The scholars tell us that the word alchemy does not occur in Greek writings earlier than the third or fourth century, when J. F. Maternus mentioned the *scientia alchemiæ* in an astrological work entitled *Mathesis*, written about 337 A.D. He says, in the jargon of astrology: "If man be born in the house of Mercury, he will devote himself to astronomy; if in Venus, he will be fond of singing and pleasure: if in Mars, he will apply himself to arms; if in Jupiter, he will follow religion and law; if in Saturn, he will devote himself to alchemical knowledge. . . ." Zosimos of Panopolis (Egypt), a writer possibly contemporaneous with, or possibly earlier than, Maternus, refers to *χημία*, *chemia*—or *χημεῖα*, *chemeia*—as the art of making gold and silver. We are also told that the term was seldom or never used by subsequent writers before the ninth century, but thereafter somewhat frequently.

(2) It has been argued that the word is derived from the Hebrew word *Chaman* or *haman*, meaning a mystery or secret, in which case, chemistry would mean the *secret art;* and Zosimos (c. 400) considers that chemistry should be treasured as a religious secret to be known and jealously guarded by the priestcraft. S. Bochart (c. 1660) favours a derivation with a similar connotation, for he refers the word to the Coptic *kema* or *kemo*, obscure or hidden, or the Arabic *chema*, to hide. Hence the old designation the *occult science*, and the Arabic book of secrets called *Kemi*.

(3) It has been suggested by S. Bochart, in his *Geographiæ sacræ* (Cadomi, 1646), that the word may be derived from Noah's son *Cham*, whom he thinks was identical with Zoroaster the founder of the Magi. According to Diodorus Siculus' *Bibliotheca historica* (c. 30 B.C.), the word chemistry is derived from the name of an Egyptian king named *Chemnis* or *Chembes;* and, according to H. Goring's *De hermetica medicina* (Helmestadii, 1648), the god Chemnis was worshipped in the city of Thebes, which was famous for its metal and colour industries.

(4) Plutarch, in his *De Iside et Osiride* (c. 100 A.D.) implies that the word comes from the Egyptian *Kham* or *Khem* (Psalms, **105**. 27)—meaning black or dark—because the same word was applied to the country of Egypt. The term thus refers to the art of the black country, or the Egyptian art. The trend of opinion seems to favour this suggestion.

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§ 12. The History of Chemistry during the Middle Ages. Alchemy and Medico- or Iatro-chemistry

> The applications of chemistry to various kinds of industries are all buried in the tombs of many generations of artists who have left no other traces of their existence than a few of their productions.—P. LACROIX (1869).

The Middle Ages are sometimes taken to extend from about the seventh to the seventeenth centuries. During the fourth century Western Europe was ravaged by Teutonic barbarians—the Goths and the Vandals. The Roman Empire transferred its capital to Byzantium (Constantinople), on the banks of the Bosphorus, where Greek metaphysics mingled with Oriental mysticism; and intellectual Europe there managed to exist until the Turkish conquest of Constantinople in the fifteenth century. The traditions of the Greek philosophers were preserved in the schools of Alexandria and Byzantium,[1] and there was a succession of real though feeble students of philosophy, physical and natural science, mathematics, and medicine. Byzantium thus kept alive the thought and knowledge of the ancient world during a period when Western Europe was submerged in turmoil and strife.

During the fifth century, the Huns, under Attila, devastated the fairest provinces in the West about the time the Anglo-Saxons were conquering England. Natural science could make no progress under these turbulent conditions; and ignorance and superstition prevailed in the West. There was a gradual infiltration of ideas, knowledge, and art from Byzantium, the Greco-Roman Empire, into Western Europe between the fifth and the fifteenth centuries. The fall of Byzantium (Constantinople) in 1453 led to the westward migration of the scholars of the Eastern Empire. Europe also gained some hints of the chemical lore of the Arabians from the returning crusaders; and after the Moors had carried Arabian literature into Western Europe *viâ* Spain in the tenth century, some progress was made. The works of the Grecian and Egyptian writers were not directly known in the West until after the thirteenth century, although Latinized versions of Arabian translations, preserved in the Mahomedan libraries in Spain, were available. This gave rise to the erroneous impression that chemistry originated in Arabia.

Some Latin translations of the Arabic writings were collected and printed in the seventeenth century—for instance, the *Theatrum chemicum* (Argentorati, 1613–22) and J. J. Manget's *Bibliotheca chemica curiosa* (Genevæ, 1712). M. Berthelot found in these works whole passages taken from the older Greek alchemists. The meaning of the original writings seems to have been distorted and perverted during the many translations and re-translations; as a result, the mediæval chemists or alchemists started their work with mutilated and incoherent descriptions of the technical and philosophical works of the Greeks and the Egyptians; and the literary productions of the alchemists of this period are characterized by much obscurity, either in unconscious mimicry, because their mutilated models were similarly tainted, or else to hide their real meaning from a hostile community, or from the vulgar. It was said: "A profound secret should not be revealed in the vulgar tongue, the true adept can sufficiently comprehend the mystical language, and it would not be right that it should be understood by the people."

Historians tell us that the tardy growth of science in the early Middle Ages was largely due to the constitution of society. The chief elements of feudal society were the barons and the priests. The barons were perpetually at war, and the study of natural science and philosophy was eminently distasteful to them. The priests were often men of great learning, but they devoted their energies mainly to theology. They possessed great power over society, for on them devolved both the spiritual and the temporal teaching of the people. Except in rare cases, the priests did not devote special attention to the physical and chemical sciences. Aristotle's works were considered sufficient for all purposes, and speculations in reference to natural phenomena were discountenanced, and in some cases forbidden. Ignorance appeared to be a sacred duty. It was generally thought impious to attempt to draw aside the veil enshrouding nature's mysteries, and man shrank from all inquiry into the perplexed ways of the universe. What a reversion from the intellectual fearlessness with which the Greek unwearyingly interrogated nature, and wrestled with her secrets ! What a contrast with Euripedes' hymn (*c.* 450 B.C.) :

> Happy is the man who has learned to search into the reasons of things, and to discern the deathless and ageless order of nature—whence it arose, how, and why.

The alchemical school.—The most celebrated alchemists during the twelfth and the thirteenth centuries were Albertus Magnus, Thomas Aquinas, Roger Bacon, Arnold Villanovanus, and Raymond Lully. Their works serve as milestones indicating the state of alchemy at that period. Very few important additions to chemical knowledge were made, since the general tendency of the age was towards magic, sorcery, and the transmutation of the base metals into gold. Albertus Magnus and Thomas Aquinas were Dominican friars ; Roger Bacon was a Franciscan monk ; and Arnold Villanovanus was a university professor at Barcelona. Some of the works attributed to these men are no doubt spurious.

Some religious orders sought to spread a knowledge of the arts and sciences, but they unfortunately also attempted to control the progress of science in predetermined channels ; and the promulgation of hypotheses, or the discovery of facts which did not harmonize with accredited authorities, or orthodox beliefs, was regarded as a serious offence against the State or Church. The students of alchemy were believed to be magicians, and were supposed to be in communication with beneficent or malignant spirits ; and, although Albertus Magnus denied this assumption when he declared that "all those stories of demons prowling in the regions of the air, and from whom secrets of futurity may be ascertained, are absurdities which can never be admitted by sober reason," yet, the fear and dread of magic took complete possession of the popular mind ; even "the church service books gave agonizing petitions for averting these dire influences, and prescribed impressive exorcisms for thwarting the occult powers."[2] The first step to be taken by a student of nature was thought to be to league himself with Satan by bartering his soul for knowledge and occult power, and whenever a mediæval thinker appeared to be inspired by a love of knowledge and freedom of thought, the disease was ascribed to diabolic agency.

One of the oddest and oldest tricks of the human mind, in ancient and modern times, is to invoke spirits, in time of need, to explain ill-understood phenomena. In accord with the beliefs and customs of the times both Roger Bacon and Arnold Villanovanus were prosecuted for being in league with demons, and in 1317, the inquisition of Tarragona condemned the writings of Arnold to be burned on account of their heretical sentiments. Both Albertus Magnus and Thomas Aquinas were astute enough to escape the severe persecution which befell many of their brother monks who studied the alchemical arts.

It must be confessed that the authorities probably had some justification for their attitude against the "unholy quest of alchemy," just as to-day it is necessary to limit the activity of fortune-tellers, etc., by legislation. In the fifteenth century severe interdicts against the practice of alchemy were issued in the Roman provinces, in England, and elsewhere; indeed, Duke Frederick I of Württemberg is said to have kept a special gallows for hanging the alchemists [3]—but the alchemists still continued their labours.

The views of the eminent German alchemist, *Albert of Bollstädt*, or **Albertus Magnus** (1193–1280),[4] were mainly derived from those of Aristotle. The alchemical writings attributed to Albertus Magnus have been shown by the scholars to be in the main compilations from Arabian sources, although he introduced several novelties. Albertus Magnus specially studied the union of sulphur and the metals; and, like the Arabian Rhases, he considered the metals themselves to be compounds of different proportions of the three principles or elementals: arsenic, mercury, and sulphur. Sulphur, said he, "blackens silver and burns the metals on account of the *affinity* which it has for these substances." The term affinity was thus used for the first time to designate the unknown cause of chemical action. Silver was supposed to be the metal most closely allied to gold, so that he considered the transmutation of silver into gold would be the easiest to realize. Albertus Magnus knew how to separate the noble from the base metals by fire, and how to separate gold from silver by *aqua regia*. Some suppose that the treatise on alchemy ascribed to Albertus Magnus is spurious. The canonized scholar, **Thomas Aquinas** (1225–1274),[5] was a pupil of Albertus Magnus. It has been said that while the master was a student of nature and philosophy, the pupil was a student of man and society. Both are considered to have excelled as exponents of theology rather than as students of natural science. From the little knowledge which is available concerning the alchemical labours of Thomas Aquinas, he would appear to have been particularly attracted by the action of mercury on the metals—lead, tin, etc.—and he applied the term *amalgam* to the liquid or paste which is formed when these metals are opened up with mercury.

Among the foremost in substantial knowledge in the thirteenth century stood **Roger Bacon** (1214–1294). He saw far beyond his age; and his reputation among his contemporaries was so great that he was styled *Doctor Mirabilis*. His knowledge was thought to be uncanny; his insight was mistaken for wizardry. Roger Bacon's knowledge of physical science was probably derived from Arabian and Greek sources,[6] for no new principle has been traced to Bacon himself. S. Vogl has pointed out that, during a great part of his life, Roger Bacon was practically without the means of prosecuting experimental research; and he was thwarted in his aspirations at every turn by his superiors. It is therefore not surprising that he failed to enrich science by any striking original discoveries. Nevertheless, his critical examination of the science of his time was conceived in a broad philosophical spirit which showed that he had made a great advance in the methodology of science. Bacon was not exactly an admirer of Aristotle, for he said:

> If I had all the books of Aristotle in my power, I would cause every one of them to be burnt, because studying them is only a loss of time, and a cause of error, and a multiplication of ignorance, beyond what can be explained.

In his *Opus majus*, R. Bacon emphasized very clearly the importance of *scientia experimentalis*, which, in his opinion, is the mistress of all the sciences—*domina est omnium scientiarum*. Indeed, he actually claimed an equal rank for observation and experiment. True enough, towards the end of the Grecian epoch, there dawned an era of experiment, for C. Galen experimentally investigated the nerve system, and C. Ptolemy, the refraction of light; consequently the experimental method was not a new thing. R. Bacon's merit lies in having explicitly indicated the importance and bearing of experiment as a universal instrument of research. The more important scientific works of Roger Bacon are: the *Opus majus* written in 1266, and the supplementary *Opus minor*, with its introductory *Opus tertium*, completed within a year of the publication of the *Opus majus*. The last-named work contains very little about alchemy, but much more occurs in the two subsidiary works.

Alchemy, said R. Bacon, falls into two divisions—speculative and operative. Operative alchemy includes the practical and industrial processes pursued, with more or less wisdom, by men who have a definite purpose in view. *Alkimia speculativa* treats of the transformations of matter from its simplest to its most complicated form, and in this sense the problem of R. Bacon's speculative alchemy approaches that of modern chemistry. Roger Bacon was necessarily ignorant of the fundamental truths of chemical science, and he could do little more than compile a number of empirical facts. He believed that air is the food of flame, for if a lighted lamp be placed in a closed vessel, the flame is extinguished. Like Albertus Magnus, he supposed the best and basest of metals to differ only in the relative proportions of their constituent parts—mercury and sulphur—and their degree of purity. He also devoted special attention to the properties of saltpetre and gunpowder. **Arnold Villanovanus** (1234–1312)[7] specially studied distillations, and he prepared many essential oils—turpentine, rosemary, etc. The fanatical **Raymond Lully** (1235–1315) enjoyed an ephemeral reputation; he led a turbulent restless life, and although an enormous number of books have been attributed to him, it is certain most are spurious.[8] There is also the probability that there are two different Raymond Lullys—one the fanatic, one the alchemist. Lully is reputed to have made spirit of wine which he called *aqua vita ardens*, and he seems to have rectified it by distillation from potassium carbonate.

This quintet may be taken to represent characteristic types of alchemists during the twelfth century. Arnold Villanovanus ascribed any successes which he obtained in his experimental work to the favourable position of the planets and stars, and to suitable prayers; these conditions seemed to him to be more important than a mastery of the controllable conditions under which the operations were performed. This was rather unsatisfactory because no science is possible if the phenomena under consideration are subject to the capricious wills of beneficent or malignant spirits, for science postulates that natural phenomena are but links in an endless chain of cause and effect, and that in experimenting "the same antecedents are invariably followed by the same consequents." The intellect of man now began to assert its claim for independent thought; and a general yearning for progress was apparent. Learning revived in Italy, the land whence it had been almost blotted out of existence a thousand years before. A few literary societies appeared during the fifteenth century, and in the sixteenth century these societies became quite numerous. Their chief work was the study of the philosophy of Plato, and the development of the Italian language. Scientific societies were also founded.

The invention of printing, about the middle of the fifteenth century, gave an impetus to the pursuit of literature. There was also a spirit of social unrest. The voyage of Columbus opened up the New World for those who sought new fields of discovery, fortune, or adventure. Martin Luther's revolt was inaugurated in 1517 by the posting of his thesis upon the church door at Wittemburg. That versatile genius **Leonardo da Vinci** (1452–1519), whose compendious manuscripts were so long thought to be written in secret script because written backwards, has been but recently appreciated, and his notes in part transcribed and edited. He was a pioneer of the modern spirit of investigation and practised the inductive method a century before Francis Bacon. The foundations of astronomy, mechanics, and physics were laid about this time; **Nicolas Copernicus** had published his *De revolutionibus orbium cœlestium* in 1543. During the next fifty years fuller and more accurate data were compiled by **Tycho Brahe** (1546–1601). About 1608, the astronomical Don Quixote, **Johann Kepler** (1571–1630), published voluminous works[9] which have been styled "a most singular medley of sound thoughts and unmitigated nonsense." Kepler, however, did submit his ridiculous conceptions to the test of observation, and rejected those which did not stand the trial. Among the wildest of guesses on the motions of the planets and their satellites, he discovered those truths which have long been known as Kepler's laws. **Galileo Galilei** made important experiments on the laws of motion, towards the end of the sixteenth century; and a century later, **Isaac Newton** demonstrated the all-embracing law of gravitation in his epoch-making *Philosophia naturalis principia mathematica* (London, 1686).

A Latin compilation on technological chemistry, entitled: *Compositiones ad tingenda*, was published towards the end of the eighth century, and about the tenth century one entitled: *Mappæ clavicula*. These works contain recipes for industrial processes closely resembling those of the ancient Greek papyri. The term *vitriol* for impure ferrous sulphate was used for the first time in the eighth-century work. Reference is made to the use of the hydrostatic balance in the analysis of alloys of gold, and this has been taken to show that the knowledge of this instrument did not pass through Arabian channels to Western Europe, but came direct from the writings of Archimedes of Syracuse (287–212 B.C.), which were carried west by the fugitives from Constantinople after its capture by the Turks in 1453.

A large number of alchemists—P. Bonus, N. Flamel, Isaac of Holland, G. Ripley, T. Norton, T. Charnock, E. Kelley, John Dee, M. Sendibogius, M. Maier, J. Boehme, T. Vaughan—who wrote under the *nom de plume*, Eupenius Philathes—and another —who wrote under the pseudonym, Erenaeus Philathes—laboured with some skill, between the fourteenth and seventeenth centuries, although the alchemical school was perhaps at its zenith in the fifteenth century. About this time there were three different types of alchemist. The first or *bookish type* spent his time commenting upon, elucidating, or unconsciously obscuring the views of the earlier writers; this type might also include the mystical chemists who hinted at a secret doctrine of a spiritual order. The second or *mercenary type* hoped to find unlimited riches when he had succeeded in converting the base metals into gold; and the third or *investigating type* sought to discover the properties and combinations of the metals, and the best means of extracting them from their ores. The last formed the prototype of the modern chemist, although representatives of all three types still survive. The majority of the alchemists were diligent experimenters, and although they worked in a stupendous chaos of phenomena, their indefatigable zeal will long be remembered for the multitude of primary facts which they discovered, even though the names of the discoverers are forgotten. The alchemists crystallized and calcined, digested and distilled, filtered and fused, just as chemists do to-day.

Auguste Comte [10] has said that it is difficult to understand how the early investigators could have had the energy and perseverance to discover the chief chemical phenomena had they not been constantly incited by unbounded hopes arising from their chimerical notions of the constitution of matter. The alchemists were indeed stimulated and guided in their work by a logical system of hypotheses. For instance, they accepted the older *prima materia hypothesis* of the ultimate constitution of matter. The changes which were observed in the different forms of matter appeared as the outer clothes of an unchangeable all-pervading essence. The qualities of the elements, not their essences, are changeable; some of these qualities are more easily removed than others, thus the four elements were regarded as firmly clinging coverings, while heat and cold, moistness and dryness, were more easily removed. The different varieties of matter were the different vestments or wrappings of the one universal entity, the quintessence of things. The universal essence was regarded as the perfect thing—*The One Thing*. This one thing was given many different names—*e.g.* the stone of wisdom or the philosopher's stone,[11] a term which, according to M. Berthelot, appeared in alchemical writings about the seventh century, although the central idea is much older.

The property of matter which enabled it to withstand the action of fire was attributed to its possessing the quality of fixidity later symbolized by salt; if it possessed the principle of volatility—later symbolized by mercury—the substance would volatilize; if it possessed the principle of combustibility—later symbolized by sulphur—the substance would burn; the principle of redness gives matter a red colour; and so on. To the Romans, lead and tin were differently coloured varieties of the same metal, and called dark and light lead respectively. Thus, the variations in the different forms of matter were supposed to depend on the qualities or principles with which it was endowed. The chemical properties of matter were but dimly recognized even in the Middle Ages; and the differences between bodies were considered to depend essentially on their physical qualities. Hence, it was assumed that the properties of a body could be modified by the abstraction or addition of qualities and forms. It was argued that just as the hardness, colour, fusibility, and other properties of certain metals can be altered, so must it be possible to change all the properties of one metal into those of another, and thus produce a veritable transmutation. Consequently, the alchemists believed in **the transmutation of the metals.**

The idea of transmutation occurs in the pre-Christian Greek writings, but the idea of transforming the base metals into gold developed near the beginning of the Christian era when the Egyptian goldsmiths seem to have carefully studied the diplosis—διπλώσις—or doubling of gold; in other words, the art of increasing the weight and bulk of gold by adulteration with cheaper metals. In M. Berthelot's *Collection des anciens alchimistes grecs* (Paris, 1887–8) quite a number of works on this subject are cited—one by Moses (not the law-giver of Israel, though possibly by one who adopted this name as a *nom de plume*) is entitled περι διπλώσεως χρύσον, or *The diplosis of gold*, is preserved in the collection of alchemical writings at Venice; another by Cleopatra (not the celebrated queen), entitled κλεοπάτρας χρυσοποίια (*c.* 50 B.C.) or *The chrysopoeia of Cleopatra*, is in the collection at Leyden; etc. The last-named manuscript deals with the preservation of beauty; with weights and measures; and with the making of gold. In the *Collection des anciens alchimistes grecs* there are drawings of digesters, aludels, alembics, and a variety of apparatus for distillations, and of water baths [12] for heating in the laboratory. It may be added that the water bath was in use, 500 B.C., in Egypt, and was called the *bath of Isis*: the name was later altered to the *bath of Mary*—or the *bain marie*, as it is still called in France—after an Egyptian Jewess, Mary, a writer on alchemical subjects.

In the opinion of M. Berthelot [13] the idea of alchemy, as a method for transmuting the base metals into gold, was a development from the fraudulent practices of the goldsmiths in Egypt as an accidental accretion to chemistry, either from a misreading or misunderstanding of ancient manuscripts. As a result, the working recipes for adulterating gold were regarded as directions for the transmutation of the metals. This is shown by the fact that some of the Egyptian papyri—*e.g.* the Leyden papyrus—contain elaborate prescriptions for the falsification of the precious metals, and these recipes reappear later obviously copied as formulæ for the transmutation of the base metals into gold. Hence H. Kopp could say: *Die Geschichte der Alchemie ist die Geschichte eines Irrtums.*

According to the transmutation hypothesis, the baser metals were diseased and imperfect; gold was the most perfect of the metals. The process of transmutation consisted in healing and ennobling the diseased metals. It was postulated that a stone of wisdom, or philosopher's stone, could be found which would heal the diseased metals, for, said W. Salmon, in his *Bibliothéque des philosophes chimiques* (Paris, 1672–8), the philosopher's stone is "the universal medicine for all imperfect metals, it fixes that which is volatile, purifies that which is impure, and gives colour and lustre more brilliant than nature herself." This hypothesis is quite legitimate, but the questions which the alchemists asked from nature appear to have been too profound; they could not understand her responses. The idea of a *universal medicine* for diseased metals was extended and the philosopher's stone was invested with all kinds of mystic properties by extravagant visionaries. The Arabian pharmaceutists supposed it to have the power of elevating man's diseased and sickly body into a state of golden health, and thus arose the idea of an *elixir of life* [14] or *elixir vitæ*—or universal medicine capable of curing all curable diseases, and which later developed into an elixir of immortality. Still later, in the old age or dotage of alchemy, the alchemists sought a philosopher's stone which would preserve health, raise the dead, rejuvenate the old, make cowards brave, etc. The enthusiastic visionaries gave still further play to their fancies, and Paracelsus imagined an **alkahest** or universal irresistible solvent which would dissolve every substance with which it came into contact; there was also the *perpetual lamp* which would burn for ever;[15] *perpetual motion;* etc. The series of facts which nature revealed to the first experimenters in chemistry were so unlike anything already known that the ordinary principles of belief were shaken or subverted; and their mind became so exceedingly credulous that J. Playfair, in an essay *On the progress of mathematical and physical science* (Edinburgh, 1853), could say that one who professed to be in search of truth ever wandered over the regions of fancy in paths more devious and eccentric.

The medico-chemical or iatro-chemical school.—In the sixteenth century, alchemy received an impetus in another direction—medicine. Philip Hoehener, who, on commencing his professional career, styled himself **Philippus Aureolus Theophrastus Paracelsus Bombastus,** was born at Zurich in 1493,[16] and he seems to have developed the amazing arrogance, insolent presumption, and swelling vanity now implied by the term "bombast." It has been pointed out that it is not generally the calm, cautious, common-sense men who do the new and great things of the world, for it seems to require vigorous impulses and certain extravagances of character to institute drastic reforms. W. Ostwald, in his *Grosse Männer* (Leipzig, 371, 1909), attempted to arrange men of genius in two classes which he called respectively *romanticists* and *classicists*. The classification is based on mental reaction velocity—or mental temperature, so to speak. The romanticist has a high and the classicist a low mental reaction velocity. The latter is inclined to be phlegmatic and melancholic, and the former sanguine and choleric. The romanticist with his agile mind reads everything, he is interested in everything and everybody, and, as a result of his enormous consumption of facts, he writes a great deal. On the other hand, the classicist works more silently and more alone, and he writes comparatively little. W. Ostwald would undoubtedly have classed the wayward erring Paracelsus among the romanticists. Paracelsus seems to have combined in himself the personality of two men: there is the daring reformer and incessant observer, and there is also the mystic hypnotized by conceit who claimed that he was privileged above all others, and received knowledge direct from God or by inspiration from the Divine.

The works of Paracelsus embrace many subjects—chemistry, botany, philosophy, physics, astrology, theosophy, magic, and most important of all, medicine. His style is generally clear, and characterized by energy and vigour, but suffused with mysticism. Paracelsus maintained that each disease has its own specific symptoms and cause, and must be combated by specific remedies—every disease, said Paracelsus, must have a remedy. The development of this idea led to his being called the Luther of medicine since, previously, all diseases were considered to result from an excess of phlegm, bile, or blood. Paracelsus introduced many new remedies, and he directed the attention of medical men to the importance of chemical preparations and medicines; he taught that the direct object of chemistry is not to make gold, but to cure disease; and he gave a bias to the quest for the essences or quintessences of things—*e.g.* he investigated the active principles of plants which he used medicinally in the form of tinctures, extracts, essences, etc.— and thus he prepared tincture of opium or laudanum.

There is little evidence to show that Paracelsus contributed any important discovery to chemical science. There are, however, references in his writings to zinc and bismuth which he characterized as bastard metals because, though resembling the metals in general appearance, they lacked the characteristic ductility and malleability of the seven metals known from ancient times. Paracelsus prepared arsenic acid by the action of nitre on arsenious oxide; he discriminated between the alums and vitriols by showing that the former had an earth and the latter a metal as base; he prepared copper amalgam by the action of mercury on copper precipitated from its sulphate by iron; he noted the development of a gas during the action of oil of vitriol on iron; he used an infusion of nut-galls for detecting iron in mineral waters; he mentioned the bleaching action of the fumes from burning sulphur on red roses; and he described the separation of hydrochloric from nitric acid by means of silver. Paracelsus promulgated some astounding, even childish hypotheses on the slenderest of evidence, so that the wildest vagaries were promulgated by the followers of the mystic Paracelsus during the succeeding century. The great merit of Paracelsus lies in his having undermined faith in the traditions which had previously corrupted and demoralized the thought and works of most of the earlier alchemists.

Soon after Paracelsus' degraded death in 1541, the alchemists seem to have parted ways. The **palæo-alchemical school**—παλαίος, ancient—still pursued the transcendental and ever-vanishing images of alchemy which could not be brought into harmony with the inflexible world of fact. It is characteristic of a science in its early stages, said S. Brown (1843) and A. N. Whitehead (1916),[17] to be both ambitiously lofty in its aims, and trivial in its handling of details. This statement is very true of the mediæval alchemists, and "their successors still tried to scale to heavenly heights; but their vitality was gone and they degenerated into fanatical inanities of no historical significance; and their compilations are usually mystical anonymities fathered on to the potentates of old." The **neo-alchemical school**—νέοφς, new—soon renounced the unattainable sublimities of the earlier alchemists, they dropped the Arabian *al*, and sagaciously pursued the sober and attainable aims of a truer chemistry. They sought knowledge, not gold; they confined their attention to phenomena and reactions which could be realized experimentally; and they assiduously devoted themselves to the discovery of primary facts, without dissipating much energy on attempts at transmutation. In fine, they were undoubtedly the working chemists of their day, and they laid the foundations of experimental chemistry.

Masses of information were rapidly accumulated by **George Agricola** (1491–1555)—the father of metallurgy, and author of the painstaking *De re metallica* (Basil, 1556),[18] on mining and metallurgy; by **Andreas Libavius** (1540–1616),[19] the discoverer of tin tetrachloride or *liquor fumans Libavii;* and by **Angelo Sala** (1575–1640),[20] who severely criticized the old mystic hypotheses, and who would have chemists cease from trifling with sublimities. To the alchemists who professed to extract from antimony a mercury which would effect the great transmutation, A. Sala said: "Show me only one drop of your wonderful mercury and I will believe you; but meanwhile I am deaf to your nonsensical claims." A. Libavius proved that the acid obtained by distilling alum and green vitriol (ferrous sulphate) is the same as that obtained by burning sulphur with saltpetre; he studied the action of nitric acid on sulphur; and prepared artificial gems by tinting glass with metal oxides. A. Sala specially studied ammonia; and he synthesized ammonium chloride by treating ammonium carbonate with muriatic acid. A. Sala recognized that iron is not changed to copper when dipped in a solution of blue vitriol, for he saw that the copper comes from the blue vitriol. Paracelsus had given a bias to alchemy which led its followers to study diligently the preparation of medicines rather than pursue an emasculated alchemy in the quest for the unattainable. The new school of medico-chemists and pharmaceutists made a mistake in attempting to explain the changes and processes which occur in the human organism by fanciful hypotheses founded upon their ignorance of the facts. Paracelsus himself seems to have made the childish assumption that a demon named Archæus resided in the stomach, and changed bread into blood, etc.

The talented **J. B. van Helmont** (1577–1644) of Brussels, began his career an enthusiastic alchemist, and ended a worthy chemist; he also specialized in medicine, and helped to carry on the medical reform inaugurated by Paracelsus. Consequently, his posthumous collected works [21]—*Ortus medicinæ* (Amsterdam, 1648)—appear to be both alchemical and chemical. J. B. van Helmont is particularly noted for distinguishing clearly between *air* and *gases;* for his work on carbon dioxide which he did not distinguish sharply from sulphur dioxide, ammonia, and nitrogen peroxide; for wholeheartedly advocating Thales' doctrine that water is the *prima materia* out of which all things are made—although Paracelsus had something to say in the same direction; and for his denying the elemental nature of fire which he considered was not a material substance at all. J. B. van Helmont is also noted for first using melting ice and boiling water as fixed points in thermometry; for his use of the term *saturation* to signify the combination of an acid with a base; for emphasizing the imperative claims of the balance for a premier place in the chemical laboratory; and for showing that although a metal can enter into many combinations, yet it does not lose its own peculiar nature since it can always be again separated unchanged—no metal can be obtained from a salt if it is not already present therein. The clear recognition of this fact was a necessary condition for progress in chemistry. It was previously supposed that a change in the appearance of a metal constituted a veritable transmutation. It was not until the chemical properties had been studied that it became possible to realize that the differences between the various kinds of matter depend on differences in their chemical composition, and are not produced solely by the addition or abstraction of certain qualities or principles.

The famous **J. R. Glauber** (1604–1668) was a laborious and diligent chemist who studied the preparation and properties of several salts—*e.g.* he prepared blue vitriol by the action of sulphuric acid on verdigris; various acetates by the action of wood vinegar on alkalies, earths, or metals; ammonium sulphate, or as he called it *secret sal ammoniac*, by the action of sulphuric acid on sal ammoniac; ammonium nitrate which he called *nitrum flammaris;* etc. J. R. Glauber prepared nitric acid by distilling a mixture of nitre and alum or sulphuric acid; and hydrochloric acid by distilling common salt with sulphuric acid. The term *muriatic acid* for this acid was also coined by him. The residue in the last-named operation is known to this day as *Glauber's salt*, or sodium sulphate, which J. R. Glauber regarded as a most wonderful salt—*sal mirabile*—for he ascribed to it extraordinary curative properties when used as a medicine. He said:

> This salt is the beginning and end of all things, and it increases and exalts their powers and virtues; it is the true universal medicine; not that I would have any man persuade himself, that in these words I would assert immortality, for my purpose tendeth not thither, seeing that I am not ignorant there is no medicine against death.

J. R. Glauber[22] also studied the products of the distillation of bones, and of wood. He described the preparation of *pyroligneous spirit* or *wood vinegar—acetum lignorum*—by the destructive distillation of wood, and stated that it could be made as virtuous as wine vinegar—*acetum vini*—by re-distillation. He also noted the preservative action of wood tar. J. R. Glauber recognized the law of chemical exchange—double decomposition—in the action of sulphuric acid on common salt, and of potassium silicate on gold chloride. He said that the potash of the silicate neutralizes the acid of the gold salt, so that the silica and gold are both deprived of their solvents, and are precipitated.

F. Sylvius de la Boé (1614–1672), C. Glaser (1615–1673), O. Tachen (1620–1690), Robert Boyle (1627–1691), J. Kunckel (1630–1715), N. Lemery (1645–1715), J. K. Dippel (1673–1734), and many other interesting chemists flourished during this period. Their work will be discussed more specifically later on. Most of these men believed in the alkahest, the philosopher's stone, and in the transmutation of the metals. Their faith may have been largely founded upon J. B. van Helmont's assurance that he had verily witnessed the transformation of mercury into gold.[23] Fortunately, these men were indefatigable workers, and did not fritter away much time on fantastic fictions. Said S. Brown (1851): It is never the originators of a great but useful scientific error, nor yet its true believers, but it is the indolent perpetuators, who will not move to the music of a new fact and the new time, that are ridiculous, shifty, ambiguous, and not respectable.

Some important works, written under the *nom de plume* **Basil Valentine,** probably in the sixteenth or seventeenth century, were for a long time wrongly supposed to have been the work of a fifteenth-century Benedictine monk, before Paracelsus. On account of the many parallel statements in the writings of Basil Valentine and Paracelsus, J. B. van Helmont and others assumed that the latter was indebted to the former for many of his ideas and facts. The truth is more probably the direct converse of this, and the imposition of Basil Valentine as a pre-Paracelsian writer has been called " a seventeenth-century hoax." Anachronisms in the supposed writings of Basil Valentine show that these could not have been written so early as the fifteenth century. In common with the later views of H. Kopp, J. Ferguson, K. Sudhoff, M. Berthelot, F. Strunz, C. W. G. Kastner, etc., W. Hommel says that all the evidence indicates that the name was a pseudonym for Johann Thölde who, in 1603–1604, first published the works of Basil Valentine, and pretended that he had translated them from an old Latin manuscript which he had discovered.[24] The writings are characterized by some clearness, particularly when describing the results of experiments. The masterpiece, *Triumph-Wagen des Antimonii*, published at Leipzig, in 1624, seems to include almost all that was known about antimony up to the seventeenth century. Basil Valentine precipitated gold from its solution by the addition of mercury ; copper from its solution by means of iron ; and iron from its solution by potash ; he obtained metallic mercury by the distillation of corrosive sublimate with chalk ; and he is sometimes regarded as one of the founders of analytical chemistry. A number of other works are attributed to the same writer.

Special attention should be directed to **Robert Boyle,** who, more than any previous worker, emphasized the importance of the science or, as he called it, the philosophy of chemistry.[25] He has accordingly been called "the father of chemistry," although the same cognomen has been applied to several others. R. Boyle claimed that those who had previously studied chemistry regarded it as a means of preparing medicines or improving the metals, while he considered the art neither as a physician nor as an alchemist, but rather as a philosopher. Chemistry, he claimed, had been too often practised by illiterate arrogant impostors who wrote in a language which could scarcely be understood by a philosopher.

> Without seeking the grand elixir, chemistry may greatly promote our knowledge of the works of nature. It is certain that some meliorations of metalline and mineral bodies may be made, useful medicines prepared, and various productions serviceable in particular trades may be obtained by means of chemistry, and therefore this subject may be studied to advantage.

R. Boyle further claimed that he had a larger view in cultivating the science—no less a purpose, indeed, than the general advancement of natural philosophy.

> Chemistry is eminently conducive to extend the empire of mankind by enlarging our views, and giving us a command of nature. Just as the Bologna stone would never become luminous unless it were chemically prepared, so many natural bodies would never afford light to philosophy unless it be struck to them by chemical operations.

In his remarkable *Sceptical Chymist* (Oxford, 1661), Robert Boyle introduced the modern conception of an element, and dropped the four principles or elements of the peripatetic school, and the *prima tria* of the alchemists. In 1660, Boyle designed a new air pump based upon that of O. von Guericke. Between 1660 and 1672, R. Boyle tried the effect of a reduced pressure upon the properties of many substances, and he made many experiments on the elasticity of gases. He demonstrated what is now known as Boyle's law ; he showed that air expanded by heat (1662) ; he studied the action of alkalies on vegetable tinctures (1663) ; and attempted a classification of substances into acids, bases, and salts (1680). He also studied the calcination of metals in sealed vessels (1673), and assumed that during the calcination " a subtle fluid is able to pierce into the compact and solid bodies of metals " imparting to them " no despicable weight." Robert Boyle had a clear conception of the ponderable character of air, for he several times attempted to determine its weight, and showed that the weight of a bladder of air appears to be greater in vacuo than in air.

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§ 13. The Evolution of Ideas regarding the Nature of Calcination

> Let all the greatest minds in the world be fused into one mind and let this great mind strain nerve beyond its power; let it seek diligently on the earth and in the heavens; let it search every nook and cranny of nature; it will only find the cause of the increased weight of the calcined metal in the air.—JEAN REY (1630).

The principle operations of the earlier chemists were performed by fire, and one of the many names applied to chemistry in its early days was *Pyrotechnia*—πῦρ, fire; τέχνη, art. Calcination has always been one of the most important operations in the chemical laboratory. Paul de Canotanto,[1] about the middle of the fifteenth century, defined this operation as involving "the incineration of the metals, or the destruction of the igneous principle."

The term **calx** (calcis) is the Latin word for lime, but the meaning was extended by the alchemists to anything produced in the same way as quicklime—namely, by roasting to a powder or friable substance. The operation of heating or roasting was called **calcination**. Consequently, as the Latin Geber expressed it in his *De alchemia*, calcination is the pulverization of a thing by fire by the deprivation of the humidity consolidating its parts—in illustration, the ash of wood, the oxide of a metal, and the ignited residue of a substance dissolved in acid were all calces. The alchemists regarded the calx as the purest and most refined residuum of a substance which remained after the coarser parts had been dispelled by heat.

It was probably known very early that limestone loses weight during its conversion into a calx, and it came as an incredible surprise to find that an increase in weight occurs when the metals are converted into calces. Near the end of the fifteenth century—November, 1489—P. Eck de Sultzbach [2] was probably the first to demonstrate experimentally that when a metal is calcined in air, the resulting calx—or *cineris fixi*, as he called it—is heavier than the original metal. He also showed that an amalgam of silver and mercury increased in weight 50 per cent. when heated for eight hours in air. The increase in weight, which many later observers also noticed, seems to have puzzled the earlier chemists. P. Eck de Sultzbach attributed the increase to the union of a spirit (gas) with the metal; and, as will soon appear, he was nearly right. No notice seems to have been taken of P. Eck de Sultzbach's surmise, and many probable and improbable explanations of the increase in weight, and of the change in the appearance of the metal, were made during the sixteenth and seventeenth centuries. Two sets of hypotheses now struggled for existence.

One set of hypotheses assumed that the metals are naturally compounded of a substance lighter than air which buoys up the metals, so to speak, against gravitation; during calcination this component is driven from the metal and the calx remains. Thus, H. Cardan, in his book *De subtilitate* (Basil, 1553), stated:

> The metal during calcination dies, for the celestial heat—*calor cœlestis*—which gave it life and rendered it light, is dissipated, and the metal consequently becomes heavier during calcination.

Paracelsus expressed a similar idea a short time previously: Calcination, said he, separates watery moisture, fat, natural heat, odour, and whatever else is combustible. Accordingly, terms like *terra damnata* and *caput mortuum* were applied to the residues left after the spirit had been driven from the metals by calcination, and the *residua* were often symbolized pictorially by a skull and cross-bones.

In another set of hypotheses, it was assumed that something ponderable is absorbed by the metal. R. Boyle attributed the increase in weight to "the arresting of *igneous corpuscles*," and N. Lemery,[3] to the assimilation of *corpuscles de feu* by the metal. In R. Boyle's essay, *Fire and flame weighed in the balance* (London, 1672), a number of experiments are described showing the actual gain in weight which occurs when metals are calcined in air; thus, an ounce of copper filings gained 49 grains in two hours, and an ounce of lead gained 28 grains in the same time. R. Boyle inferred that "glass is pervious to the ponderous parts of flame" because tin or lead are partially calcined when heated in hermetically sealed vessels; and he stated that the increase in weight arises from the assimilation of the "extinguished flame" by the calx. It is rather remarkable that R. Boyle did not attribute the increase in weight to the action of the air on the heated body, because, shortly afterwards, in an essay entitled *Suspicions about some hidden qualities of air* (London, 1674), apparently following R. Hooke's experiments, *q.v.*, R. Boyle suggested that "air contains some odd substance, either of a solar, astral, or other foreign nature; on account whereof the air is so necessary to the subsistence of flame;" and he further added that "this substance is not improbably *a volatile nitre* akin to that which seems so necessary for the maintenance of other flames." In opposition to H. Cardan, Boyle also says that **the calx of a metal must be the metal plus, not minus, something acquired during calcination,** and not its *terra damnata*. J. Kunckel (1677), J. J. Becher (1690), J. Homberg (1700),[4] and others also attributed the increase in weight of a metal during calcination to the absorption of what J. Kunckel called *particulæ igniæ*. In an analogous manner, O. Tachen (1666)[5] assumed that the increase is due to the absorption of an acid existing in the flame, and he found that when lead burns to red lead, it increases its weight one-tenth, and returns to its former weight when reduced to the metallic state. H. Boerhaave (1732)[6] must have suspected that something was wrong, since he kept mercury at a slightly elevated temperature for fifteen years in order to find if there was any increase in weight due to the absorption of the alleged fire particles; and, in opposition to Boyle's hypothesis, no increase due to this cause could be detected. He also demonstrated that the weight of certain metals—*e.g.* silver—was the same whether at ordinary temperatures or at a red heat.

A. Cæsalpin, in his *De metallicis* (Romæ, 1596), summarily dismissed the subject by assuming that the increase in weight is due to the deposition of soot in the interior of the metal during calcination, and others supposed the increase was due to the retention of the vapours of charcoal, or the volatile salt of charcoal or the matter removed from the calcining vessel. J. Hartmann, in his *Praxis chymiatrica* (Lipsiæ, 1625), showed that the increase could not be due to the assimilation of soot, or the vapours of charcoal, because antimony increased in weight when heated in the focus of a burning lens with sunlight; and N. le Febvre[7] supposed that when the metal is calcined by means of a burning glass, the increase in weight is due to the absorption of the *matter of light*, which J. Mayow called *particulæ nitro-aeræ*, and which were supposed to be derived, not from the air but from the sun, which he regarded as a chaos of these particles.

Jean Rey appears to have been the first to critically examine the different hypotheses which had been proposed to explain the increase in weight which occurred when the metals are calcined. J. Rey's work was published in an obscure pamphlet entitled *Essays de Jean Rey, docteur en médécine, sur la recherche de la cause pour laquelle l'éstain et le plomb augmentent de poids quand on les calcine* (Bazas, 1630),[8] which at that time does not seem to have attracted much attention from those interested in the subject, since the discovery of the pressure of air, shortly afterwards, diverted the minds of investigators away from a study of the chemistry of air.

1. The facts.—In order to clarify the mind, the facts must be reviewed.

Investigators of nature, said D. Sennertus in his *Epitome naturalis scientiæ* (Oxford, 1664), are warned not to look for the causes of phenomena before there is a complete agreement as to the facts. Four things are present during the calcination of the metal in air: (1) The containing vessel or crucible; (2) The metal being calcined; (3) The air; and (4) The source of heat. Again the metal weighs more after the calcination than it did before.

2. The hypotheses.—In applying the inductive method of investigation to these facts, *it is necessary to review every rational explanation consistent with the facts, and to examine each hypothesis rigorously and impartially*, since, as emphasized above, it is necessary to show that the explanation finally selected is *alone* consistent with the facts. This extension of the inductive process might be called the **method of exhaustion**; its importance was recognized by Epicurus (*c.* 300 B.C.).[9] **It is a mistake to confine the attention to one hypothesis, because that might seriously limit the range of the inquiry.** The mind unconsciously assimilates evidence in favour of a pet hypothesis; and a pet hypothesis is apt to grow from a favoured child to a tyrannical master. Four plausible hypotheses may be suggested to explain the cause of the increase in weight: (1) the gases, etc., from the source of heat unite with the containing vessel; (2) the air unites with the containing vessel; (3) the gases from the flame penetrate the crucible, and unite with the metal; and (4) the air unites with the metal.

3. Testing the hypotheses by experiment.—By heating the crucible alone, without the metal no change in weight occurs. This **blank, dummy, or control experiment** shows that neither the first nor the second hypothesis will account for the increase in weight of the metal. The third hypothesis can be tested by heating the crucible and the metal out of contact with the air. There is then no change in the weight of the metal. The third hypothesis is therefore untenable. This method was not practicable for the early chemists, and hence J. Rey employed a less decisive test. It might be expected that if the results depend upon the absorption of the flame gases, different results must be obtained by using different sources of heat—sun-glass, etc.—but the same results are obtained in every case, and accordingly, the third hypothesis is probably wrong.

4. The conclusion.—Rey thus examined all the previously suggested explanations, and rejected them one by one; the remaining unchallenged factor was air. **The sole invariable antecedent of a phenomenon is probably its cause.** Hence, unless something has been overlooked, it is concluded that **when metals are calcined in air the increase in weight is due to the fixation of air by the metal,** and not to the absorption of furnace gases, nor to variations in the weight of the vessel in which the calcination is made. The idea was not far from F. M. A. de Voltaire's mind[10] a century later, for in 1737 he said:

> Il est très possible que l'augmentation du poids soit venue de la matière répandue dans l'atmosphère, donc dans toutes les autres opérations par lesquelles les matières calcinées acquierent du poids cette augmentation pourrait aussi leur être venue de la même cause, et non de la matière ignée.

Similar remarks apply to R. A. Vogel's *Experimenta chemicorum de incremento ponderis corporum quorundam igne calcinatorum examinat* (Göttingen, 1753) made in ignorance of J. Rey's work.

J. Rey attempted to explain how air alone could produce an increase in the weight of a metal during calcination. J. Rey *imagined* that when air is heated, it separates into a heavier and a lighter part, and that when a metal is calcined in air, the lighter part of the air is distilled off, and the denser portion—*l'air épais*—alone attaches itself to the metal and forms an ash or calx. J. Rey did not prove this subsidiary hypothesis, viz. that only a part of the air attaches itself to the metals to form a calx. The increase in weight which occurs during calcination was compared to the wetting of sand with water—most of the water can be drained away, but a little remains adherent to the sand:

> The condensed air becomes attached to the calx, and adheres, little by little, even to the smallest of its particles. Thus the weight increases from the beginning to the end. When all of it is saturated, it cannot take up more.

J. Rey's explanation proved to be fallacious. The great merit of J. Rey's work lies in his demonstration that air is a ponderable fluid; and the analogy between air and a liquid regarded as ponderable fluids enabled him to grapple with an intangible body, and to reason on that which from its subtlety had hitherto eluded the grasp of the philosophers of all previous ages.[11]

5. Confirmatory experiments.—S. Hales [12] and J. Juncker also explained the increase in weight by assuming that particles of air were absorbed by the metal, and S. Hales showed that when "1922 grains of red lead is heated there arises 34 cubic inches of air." He did not consider it necessary to test the gas expelled from the red lead since he assumed that it was elemental air. J. Rey's idea that the increase in weight which occurs when a metal is calcined in air is due to the fixation of air by the metal, was confirmed by the work of P. Bayen [13] early in 1774. Bayen showed that mercurial calx owes its "calcined state" to its intimate combination with an elastic fluid, the weight of which, in adding itself to that of mercury, "constitutes the cause of the observed increase in weight" of the mercury during calcination. The experiment was made by reversing J. Rey's procedure and heating the calcined mercury until it decomposed into the original mercury and an elastic fluid. The mercurial calx and the revived mercury were weighed before and after the calcination:

Mercurial calx	576 grains
Revived mercury	518 „
Difference	58 „

P. Bayen added: "I cannot state positively that the 58 grains represent the true weight of the elastic fluid, liberated from the 576 grains of mercurial calx, but clearly everything leads to that conclusion."

J. Rey also made the interesting unforeseen observation that "nature, in her inscrutable wisdom, has set limits which she does not overstep"; in other words, **however long a metal may be heated in air, a definite weight of each metal can combine with only a definite maximium amount of air.** Students to-day regularly repeat J. Rey's experiments on the metals, under various guises, as class exercises—Table I. for example.

TABLE I.—ACTION OF AIR ON THE CALCINATION OF THE METALS.

Metal.	Weight of metal (gram).	Weight of calx (gram).	Increase in weight (gram).	Ratio weight air absorbed : metal used.
Magnesium . .	1	1·658	0·658	1 : 1·52
Zinc	1	1·246	0·246	1 : 4·06
Aluminium . . .	1	1·890	0·890	1 : 1·12
Copper . . .	1	1·252	0·252	1 : 3·97
Tin	1	1·269	0·269	1 : 3·72

Hence, one gram of the absorbed air is respectively equivalent to

(Absorbed air).	Magnesium.	Zinc.	Aluminium.	Copper.	Tin.
1	1·52	4·06	1·12	3·97	3·72 grms.

6. Anticipation of new phenomena.– A good hypothesis ought to predict phenomena which have not been observed, and to foretell the results of new experiments; because, if the hypothesis be true, it ought to include all other cases. **A hypothesis which is not illogical and which does not contradict known facts is to be judged by its usefulness. The end justifies the means.** G. J. Stoney has expressed the idea neatly: "A theory is a supposition which we hope to be true;

a hypothesis is a supposition which we expect to be useful. Fictions belong to the realm of art; when allowed to intrude elsewhere, they become either make-believes or mistakes." When the consequences of a hypothesis are logically deduced, **a good hypothesis should not only explain, but it should anticipate new facts.** Rey's hypothesis can be used to predict new results. In his *Mémoire sur la calcination de l'étain dans les vaisseaux fermés, et sur la cause de l'augmentation du poids qu'acquiert ce metal pendant cette opération* (1774), A. L. Lavoisier [14] wrote:

> Thus did I at the beginning reason with myself. . . . If the increase in weight of a metal calx (calcined in a closed vessel) be not due to the addition of fire matter, nor of any other extraneous matter, but to the fixation of a portion of the air contained in the vessel, the whole vessel after calcination must be heavier than before, and must merely be partly void of air, and the increase in the weight of the vessel will not occur until after the air required has entered.

A. L. Lavoisier confirmed this inference experimentally on November 12, 1774, although the gifted Russian chemist, M. W. Lomanossoff,[15] had come to the same conclusion in 1756, eighteen years before A. L. Lavoisier.

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§ 14. The Evolution of Ideas regarding the Nature of Burning

> Step by step we cross great eras in the development of thought; there is no sudden gigantic stride; a theory proceeds by slow evolution until it dominates or is destroyed. —G. F. Rodwell (1869).
>
> Slowly, gradually and laboriously one thought is transformed into a different thought, as in all likelihood one animal species is gradually transformed into a new species. Many ideas arise simultaneously. They fight a battle for existence not otherwise than did the Ichthyosaurus, the Brahmin and the horse. Thoughts need their own time to ripen, grow, and develop.—E. Mach.

The beautiful fiction of Greek mythology, as related by Æschylus, tells how Prometheus stole fire from heaven, and gave the sacred gift to man as the most useful of all his necessaries. To many ancient worshippers, fire was a thing divine, the supreme manifestation of God himself, and it soon became the one visible symbol of God. Even to-day the *sacred fire* exists among the races of the Balkans. Accordingly, the Zoroastrian fire worshippers called their god *the one fire*, or *the pure fire*;[1] and the sun was worshipped first as an emblem of the deity—fire—and afterwards as itself a god.[2] Fire thus came to be the first and most potent of all the elements, and it is easy to understand how Heracleitos regarded subtle fire as the sole primal element from which all things were created; and how fire was canonized by Pythagoras and Empedocles as one of the four indispensable and all-sufficient components of the universe.

Some of the early philosophers promulgated a dynamical theory of heat and fire. Epicurus (*c.* 300 B.C.) regarded heat as a result of the rapid motion of minute spherical particles which insinuated themselves in the pores of the densest substances; cold was likewise produced by angular particles moving more slowly. Lucretius (*c.* 80 B.C.) similarly referred heat to the motion of primary particles which penetrated every material thing. H. Cardan[3] (1557) spoke of a *motus ignis* and a *motus caloris*. R. Fludd (1617), F. Bacon (1620), A. Kircher (1644), and others have propounded views which amount to a denial of the elemental nature of fire, since they virtually assumed that heat is a violent motion of the particles of bodies, or that fire is air which has been made to glow by the vehement collision of its particles, and that the heat so generated changes combustible matter into flame.

René Descartes, in his *Principia philosophiæ* (Amsterdam, 1644), assumed that originally all matter consisted of square particles endowed with two kinds of motion: a rotation of each particle about its own centre; and a rotation of groups of particles about a common centre. The angles of the particles were abraded by collisions producing three kinds of particles which he called elements: (1) *Materia primi elementi*, or fine dust, which he also called *materia subtilis*, or *materia cœlestis*, because the sun, stars, and fire were supposed to be composed of this material. (2) *Globuli secundi elementi*, or rounded particles which were supposed to make up the atmosphere and everything between the stars and the earth. (3) *Particulæ tertii elementi*, or particles which retain some of their angles and are partially rounded; these were assumed to make up the earth and all terrestrial bodies. The particles of the *materia cœlestis* were supposed to be in far more rapid motion than the other particles. The different forms of matter were supposed to be determined by the relative proportions and motions of these three elements; and every natural phenomenon, the result of the conduction of motion from one body to another. Fire, according to R. Descartes, consisted of the third element rapidly agitated by the *materia cœlestis*; and the particles of combustible bodies were supposed to be peculiarly adapted to receive the motions of the *materia cœlestis*. It was all a transmission of motion, not substance. N. Lemery adopted the main tenets of thè Cartesian theory in his famous *Cours de chimie* (Paris, 1675):

> I understand by igneous corpuscles—*corpuscles ignées*—a subtle form of matter which having been thrown into rapid motion, still retains the capacity of impetuous motion when it is enclosed in grosser matters; and when it finds bodies which by their texture or figure are easily put in motion, it draws them about so strongly that their parts develop heat by being rubbed violently against one another. . . . The particles of sulphur, for instance, are very susceptible to motion . . . and it seems probable that fire is only violent motion of minute bodies about their common centre.

Flame, said R. Descartes, is directed upwards because it contains much *materia cœlestis* which is lighter than air, and the cause of lightness in bodies generally. Descartes' *materia cœlestis* approximates to the modern conception of an æther more subtle than air, and filling the interstices between the molecules of air with a continuous series of globules which pervade the pores of glass, and of the densest substances without interruption; and propagating light by communicating impulses from one molecule to another so as to produce a kind of pressure without locomotion.

Isaac Newton[4] postulated a similar æther "pervading and lurking in dense bodies, but not yet sufficiently manifested by experiments." R. Hooke introduced the notion of vibratory impulses in this medium, and the idea was elaborated by C. Huygens and T. Young into the undulatory theory of light which is now generally accepted. The communication of the vortex motion of the *materia cœlestis* to the atoms is thus described by R. Boyle:[5]

> The restless agitation of the *materia cœlestis* wherein the particles of air swim, so whirls

> them round that each corpuscle endeavours to beat off all others from coming within the little sphere requisite to its motion about its own centre . . . their elastic power is made to depend upon the vehement agitation which they receive from the fluid æther (*materia cœlestis*) which swiftly flows between them.

Several early observers noticed that fire cannot subsist without air. Theophrastus,[6] for instance, in the fourth century B.C., in his treatise *On Fire*, noticed that air plays an important part in the maintenance of flame; Hero of Alexandria (*c.* 117 B.C.) demonstrated this by placing a lighted lamp in a closed vessel, and showing that under these conditions the flame was extinguished—Hero said that the fire consumed and rarefied the air; and from a similar experiment in the thirteenth century, Roger Bacon inferred that *aer est cibus ignis*—air is food of flame—in agreement with Theophrastus—315 B.C.—who said, "It is not at all irrational to believe that flame is maintained or supported by an aëriform body." Near the beginning of the sixteenth century (*c.* 1500), Leonardo da Vinci[7] clearly recognized that air is necessary for the sustenance of the flame of a burning candle, for he said: "There is smoke in the centre of the flame of a wax candle because the air which enters into the composition of the flame cannot penetrate to the middle. It stops at the surface of the flame and condenses there." Leonardo da Vinci also showed that air is necessary for respiration; and that air is not an element because one part of it alone is concerned in combustion. R. Fludd[8] noticed in 1617 that when a candle is burnt in a glass vessel over water, the water rises in the vessel as the air is consumed, for "air nourishes fire, and in nourishing consumes it." H. Cardan also, in his *De rerum varietate* (Basil, 1557), classified different substances as *combustible* or *incombustible*. Flame, said he, is nourished by a gas—*flatus*—which will ignite a glowing splint, and which exists in saltpetre. H. Cardan was here very near to the discovery of facts which in the hands of A. L. Lavoisier produced *une révolution immense dans la science.*

After his discovery of the air-pump in 1650, one of the first experiments tried by O. von Guericke[9] was to ascertain if a candle would continue burning in an exhausted receiver, and it was found that owing to the want of air the flame of a lighted candle expired more quickly under the exhausted receiver of an air-pump than when the receiver was not exhausted; fire, said Guericke, consumes air. In his first treatise on pneumatics, *New experiments, physico-mechanical, touching the spring of air* (London, 1660), R. Boyle mentions several proofs that combustion cannot proceed in a space void of air; and in 1672, R. Boyle, in an essay *On the difficulty of preserving flame without air* (London, 1672), showed that when placed under the receiver of an air-pump, the flame of burning gas, derived from the action of an acid on iron, is suddenly enlarged on exhausting the air, and finally is extinguished; and he showed that sulphur does not burn if heated in vacuo. These, and other experiments on similar lines, clearly showed that **air is necessary for combustion.**

Robert Hooke outlined a theory of combustion in his *Micrographia* (London, 1665). He noticed the similarity in the actions produced by air and by saltpetre,[10] and hence suggested that **air is mixed with a substance which is like, if not identical with, that which is fixed in saltpetre, and that only this portion of air is required to support combustion and respiration.** A similar conclusion had been hinted at by R. Fludd,[11] who said: "The substance of saltpetre is nothing but air congealed by cold." Again, in his *Lectiones cutlerianæ* (London, 1674–9), Robert Hooke assumed that burning is produced by the solvent action of the surrounding air which is dissolved by the burning body much as water dissolves salt. He said:

> Air is a menstruum that dissolves all sulphurous bodies by burning, and without air, no such dissolution will follow, though the heat applied be never so great, which was particularly tried by charcoal enclosed in an iron case with a screw stopper, which though violently heated yet the coke was not burned nor wasted when taken out. . . . That shining transient body we call flame is but a mixture of air and volatile sulphurous parts of combustible bodies which are acting upon each other as they ascend. . . . The action is performed with so great violence and does so minutely act, and rapidly agitate the

smallest parts of the combustible matter, that it produces in the diaphanous medium of air the action or pulse of light.

J. Mayow (1669)[12] subjected the guess or hypothesis of Hooke to the test of observation. The following experiment is a more refined form of one made by J. B. van Helmont, *circa* 1640 :—

J. Mayow arranged a candle in water so that the wick was between 9 and 10 cm. above the surface of the water. A glass cylinder, *A*, Fig. 6, was lowered over the burning candle so that the level of the water inside and outside the cylinder was the same. A small syphon, *B*, was used for the purpose. Immediately the cylinder was in position, the syphon was removed. The flame of the candle soon expired, and water rose in the jar. Some gas still remained in the jar, but it could not be air because one of the characteristic properties of air is to support the burning of the candle, and the flame of the candle is extinguished in the residual gas. Mayow obtained analogous results by confining a mouse under the jar. The mouse died, and the water rose in the jar.

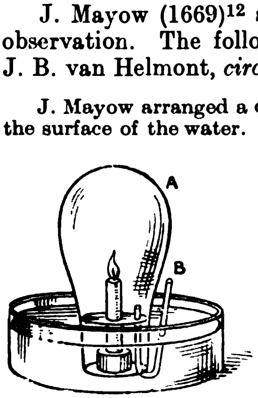

FIG. 6.—Mayow's Experiment on Combustion.

Hence, Mayow inferred that **air contains two kinds of particles, one of which—the nitro-aërial particles—is withdrawn and destroyed by the burning candle.** J. Mayow also stated :

> Though the particles of air are very minute, and are vulgarly taken for an element of the greatest simplicity, it appears to me necessary to judge them to be a compound. . . . It is manifest that the air is deprived of its force by the respiration of animals much in the same manner as by the deflagration of flame.

Mayow does not seem to have quite grasped the idea that the nitro-aërial particles which support combustion actually combine with the burning body, although he correctly inferred that air was a mixture containing nitro-aërial particles as one constituent. The nitro-aërial particles were indiscriminately called fire-air, nitre-air, and nitro-aërial spirit. Mayow's observations appear to show that **air is a mixture of two gases one of which is withdrawn during combustion, and the remaining gas does not support combustion.** Stephen Hales [13] also noticed that in the combustion of phosphorus under a bell-jar, white fumes are produced and air is absorbed. When the experimenters of the seventeenth century spoke of the *destruction of the elasticity of a portion of the air*, they meant that some of the air was lost—presumably by absorption by the confining liquid, etc.

Some modern commentators consider that J. Mayow's *nitro-aërial spirit* represented oxygen, and his *aërial spirit*, nitrogen. It has been said that J. Mayow's nitro-aërial particles were made to explain too much, for he applied them to all sorts of phenomena—*e.g.* the formation of acids, fermentation, the production of nitre, calcination, combustion, and respiration—rather is this a tribute to J. Mayow's genius. J. Mayow considered the nitro-aërial particles to be fixed as the acid component of nitre because the effects produced by nitric acid and by the burning glass on antimony were the same. He extended his views to other substances—particularly the acidification of sulphurous and fermenting substances by exposure to the atmosphere—and thus inferred that his nitro-aërial particles are the active agents in combustion and acidification. When J. Mayow regarded these same particles as the principle by which metals increase in weight when calcined in air ; the principle by which vegetables germinate and grow ; and by which the blood changes its colour in the lungs during respiration, he seems to have generalized with far greater precision from a few facts than the greater part of the next generation did from many.[14]

J. Mayow, however, did mix some fantastic hypotheses with his eminently logical interpretations of ingenious experiments, and in some cases the relevant matter is mixed with so many irrelevancies, that it is difficult to tell which is which unless his statements are interpreted in the light of what is now known to be true. To-day, J. Mayow's brilliant reasoning would be accepted as a logically conclusive proof of the existence of oxygen as a distinct substance; but his demonstration was a century ahead of its time. Instead of his unique experimental talents being encouraged by his contemporaries, they were damped by the coldest of receptions. His work was evidently above the heads of his contemporaries. The historian of science, said G. F. Rodwell,[15] should endeavour to grasp the precise mode of thought of the man of whom he writes, to think as he thought, to view the phenomena in the light of the age in which he lived, and then to reason on them as he reasoned. Evidently, then, R. Hooke and J. Mayow got very near to the present-day theory of combustion, but unfortunately, the latter's ingenious experiments had very little, if any, influence on the subsequent development of chemistry, because the lowering clouds of the phlogiston hypothesis appeared as a grey after dawn and gradually darkened the sky of chemistry until the chemical world appeared to be enveloped in an impenetrable fog. For another century more trust was placed in phantasms of the imagination than in facts obtained by precise observations.

It must be added that in the Far East, the Chinese philosopher Mao-Khoa, who flourished about the eighth century, is said to have had a fairly clear idea of the composition of air, and of the part played by oxygen—which he called *yin*—in combustion and respiration. This historical information, however, played no part in European discoveries since it is but a comparatively short time ago that Mao-Khoa's views were reported, and unfamiliarity with the language and literature has prevented many examining the claims of the Chinese scholar to a proud place in the history of chemistry.

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§ 15. The Phlogiston Theory

During the greater part of the eighteenth century, the doctrine of phlogiston was not only the lamp and guide of chemists but it remained the time-honoured and highest generalization of physical chemistry for over half a century.—S. P. LANGLEY.

Phlogiston died as an old king,—once infinitely dominant, somewhat tyrannical, not always just; now deposed, decrepit, utterly senile, forsaken by all.—W. ODLING.

Up to about the middle of the fourteenth century, combustion was explained by the aid of the assumption that all combustible bodies contained a common element, the essence of fire, that is, an inflammable principle which enabled them to burn. This obviously means little more than saying that substances burn because they are combustible. The idea of a subtle fire innate in matter has pervaded philosophy from the earliest times. Zeno (*c.* 450 B.C.) called it ἀτεκνέκον πῦρ—barren fire; Heracleitos (*c.* 450 B.C.), ἀναθυμίαις; Lucretius (*c.* 80 B.C.), *subtilis ignis*, *cœlestis ignis*, or *tenuis ignis;* Paracelsus (*c.* 1500), *sideric sulphur;* H. Cardan (*c.* 1553), *calor cœlestis;* and R. Descartes (*c.* 1664), *materia cœlestis*. The alchemists of the Middle Ages variously styled it *elemental fire*, *astral fire*, *sulphurous principle*, *or materia ignis*.

The empyrean[1] element of the ancient Greeks was consecrated under the classical name **phlogiston** by the hierophants of a newer chemistry. The word phlogiston is derived from the Greek φλογιζω, to inflame, and is related to φλέγω, to burn, and φλὸξ, flame. In some cases phlogiston was believed to resemble that subtle fiction we now call *æther*, and J. Juncker,[2] in 1744, called it *materia ignea ætheræ*. J. Kunckel (1676) thought that the inflammable principle must be sulphur, and wrote *ubi ignis et calor, ibi sulphur*—where there is fire and heat there is sulphur. Virtually all chemists of this period attributed the combustibility of a substance to the presence of sulphur. There were many *sulphurs*—*e.g.* the *sulphur of wood* (carbon), the *sulphur of wine* (alcohol), etc., and Robert Boyle in his essay *On the difficulty of preserving flame without air* (London, 1672), called the fume or gas which is evolved when an acid acts upon iron *the volatile sulphur of Mars;* and in his essay *On the producibleness of chemical principles* (London, 1680), he speaks of the sulphur of the chemist as being a combustible and inflammable principle.

Twenty-five years after the appearance of R. Descartes' *Principia*, and about the time of J. Mayow, J. J. Becher began to publish the chemical side of a theory analogous in many respects with the physical theory of René Descartes. The most important work of J. J. Becher is his *Physica subterranea* (Lipsiæ, 1669), and the three supplements dated 1671, 1675, and 1680 respectively—J. J. Becher's term *subterranea* is probably equivalent to the modern *inorganic*. J. J. Becher advocated the importance of experiment in chemical science. He rejected the four-elements and the quintessence of the ancients, but he did so only to promulgate four elements of his own devising—fire; the earthy principle; the combustible element; and the metallic one. This enabled him to classify material substances into fiery or imponderable bodies, earth, combustibles, and metals. The combustibles and metals were later grouped together, and his system was simplified into fire, the first kind of substance; earths, calces, and acids, the second; and combustibles and the metals, the third; otherwise expressed, J. J. Becher's triad included fire, the products of combustion, and combustibles. It was not the custom, in J. J. Becher's time, to keep one specific technical term for one specific thing. He seems to have used the terms vitrifiable earth—*terra lapida* or *terra vitrescibilis*—inflammable earth—*terra pinguis*—and mercurial earth—*terra fluida* or *terra mercurialis*—almost in the same sense that the alchemists spoke respectively of salt, sulphur, and mercury. He regarded his three elements as three varieties of sulphur; vitrifiable earth was called *fixed sulphur*, *mercurial earth*, or *volatile sulphur;* and *inflammable earth* was indiscriminately called *combustible sulphur*, *sulphur adustible*, *sulphur ardens*, or *phlogistic sulphur*. J. J. Becher said:

> Combustible sulphur is the innate heat of the metals. . . . The base metals contain an inflammable principle which by the action of fire goes into the air, leaving behind a metal calx.

This recalls the hypothesis promulgated by H. Cardan a century earlier. J. J. Becher supposed the different forms of matter to be compounds of one or more of these elements differently arranged with or without water. G. F. Rodwell,[3] in a valuable article *On the theory of phlogiston*, says that J. J. Becher never used the word φλογίστον as a noun to designate the matter or principle of fire. It was reserved for J. J. Becher's disciple G. E. Stahl, near the beginning of the eighteenth century, to employ the term phlogiston for the *materia ignis* of the early writers.

Towards the end of the seventeenth century, G. E. Stahl sketched an outline of the theory of phlogiston in his *Zymotechnia fundamentalis* (Franckfurth, 1697); and in his *Specimene Becheriano* (Franckfurth, 1702), he elaborated J. J. Becher's *Physica subterranea*, a work which he rated very highly, and vaunted it to be *opus sine pari*—a work without a peer; *primum ac princeps*—first and foremost; *liber undique et undique primus*—a book everywhere supreme; etc. G. E. Stahl also wrote his *Fundamenta chymiæ dogmaticæ et experimentalis* (Norimbergæ, 1723) as a text-book of phlogistic chemistry, and he described in his *Experimenta, observationes, animadversiones, CCC numera, chymicæ et physicæ* (Berlin, 1731), a number of experiments in support of the theory, and answers to some questions. Like the ancients, G. E. Stahl believed in the existence of two kinds of fire: (i) ordinary visible fire, or mundane fire, or gross earthy fire which he called *ignis* or flame; and (ii) pure, subtle, invisible fire, *materia ignis*, or phlogiston, which became *ignis* only when associated with material particles which assimilated its motion. It therefore follows that J. J. Becher's *terra inflammibilis*, *terra pinguis*, *combustible sulphur*, *sulphur ardens*, or *phlogistic sulphur*; and G. E. Stahl's *phlogiston* are new names for an old time-honoured principle. The dominant functions of Descartes' *materia cœlestis* were conferred on phlogiston, and some new properties were added. Phlogiston, said G. E. Stahl, is the *materia aut principium ignis, non ipse ignis*. Although the real nature and properties of phlogiston were unknown, its existence was pure conjecture, yet G. E. Stahl did not hesitate to speak very definitely about this creature of the imagination. He said:

> Phlogiston is a very subtle matter capable of penetrating the densest substances; it neither burns, nor glows, nor is visible; it is agitated by a rapid motion—*igneo motu*—and it is capable of communicating its motion to material particles adapted to receive it. The particles when endowed with this rapid motion constitute visible fire. . . . Fire is an aggregate of a great number of particles in vehement motion. The *materia* of fire is phlogiston—a thin all-pervading medium composed of movable particles—the *forma* is the motion itself; the *materia* is passive, the *forma* is active. The motion of phlogiston is *gyratorius seu verticillaris* and not progressive. . . . Heat is an intestine motion of the particles of matter.

G. E. Stahl taught that in the act of combustion, phlogiston, an intrinsic constituent of every combustible body, was set at liberty. Oxidation was said to be due to the escape of phlogiston; deoxidation or reduction to the absorption of phlogiston. When a metallic oxide was heated with a substance rich in phlogiston —*e.g.* charcoal or reducing agents generally—the charcoal supplied the calx or metallic oxide with phlogiston, and reproduced a compound of phlogiston with the metallic oxide which was the metal itself. Metals were thus supposed to be compounds of phlogiston with their calces or oxides. The noble metals were supposed to have their phlogiston so firmly fixed that nothing can take it from them. While the base metals are turned to calces when roasted in air, the royal metals remain intact during the fiercest trial. If phlogiston escaped, the metallic oxide or calx remained. The idea is symbolized

$$\text{Metal} \rightleftharpoons \text{Phlogiston} + \text{Metal calx or oxide}$$

The body from which phlogiston escapes, when no longer capable of supporting combustion, was said to be *dephlogisticated*, and conversely, the body—solid, liquid, or gas—with which the phlogiston was combined, or by which it was absorbed, was said to be *phlogisticated*. Apparently overlooking the theories of R. Hooke (1664) and J. Mayow (1674), which were developed while Stahl was in the nursery, M. E. Chevreul[4] claimed that *on doit à Stahl la première explication de la combustion*.

The phlogistians are said to have been most assiduous in collecting *instantiæ convenientes*, but very reluctant in accepting *instantiæ inconstantiæ*. G. E. Stahl, by denying that the calx of mercury weighed more than the mercury from which it was derived, sacrificed fact to theory. Phlogistic chemistry was thus established in opposition to facts which at first sight appeared to carry its own refutation, for if the calcination of a metal be attended by the expulsion of phlogiston, the calx should weigh *less* than the metal. When the facts that the loss of phlogiston is always associated with a *gain* in weight, and *vice versa*, became too insistent, and could no longer be denied, G. E. Stahl, in his *Fundamenta chymiæ* (Norimbergæ, 1723), frankly evaded the difficulty by introducing another perplexity. He said:

> The fact that metals when transformed into their calces increase in weight, does not disprove the phlogiston theory, but, on the contrary, confirms it, because phlogiston is lighter than air, and, in combining with substances, strives to lift them, and so decreases their weight; consequently, a substance which has lost phlogiston must be heavier than before.

Thus, the phlogistians said that phlogiston also embodied the principle of levity, and conferred a negative weight upon bodies. Consequently, when phlogiston is associated with matter, the weight is lessened, just as inflated bladders lessen the water-weight of a swimmer.

It may not seem rational to postulate the existence of a substance weighing less than nothing. It will be observed, however, that the assertion, *all matter is heavy and possesses weight*, is one way of saying that the attraction of gravitation exists between all masses of matter. This is by no means a self-evident principle, because it is just as easy to conceive of two masses of matter repelling one another, and easier still to imagine two masses of matter neither attracting nor repelling one another. Thus, G. B. Airy [5] said: "I can easily conceive that there are plenty of bodies about us not subject to this mutual action, and therefore not subject to the law of gravitation." Hence, the assumption of a phlogiston weighing less than nothing is not so silly as is sometimes supposed. If phlogiston be a principle of levity, however, with a negative gravity, it would not be attracted but rather repelled by other substances. Consequently, in order to explain how phlogiston becomes fixed in combustible bodies, it would be necessary to invent another force stronger than gravitation. It is quite true that no form of matter with a negative gravity has been detected, and accordingly, it is assumed that a form of matter weighing less than nothing does not exist, and that, other things being equal, **an increment in weight is necessarily an effect of an increment of matter.**

The era of phlogiston presents serious claims to be regarded as the period when chemistry began to take shape as a definite science. It represented a definite attempt to group diverse chemical phenomena about a rational principle which seemed adequate to embrace the then known facts. The doctrine of phlogiston was invented to render chemical phenomena intelligible to the mind; it was founded on fact; and it owed its value in the minds of a race of eminently practical chemists, to the facts which it represented. New facts soon began to accumulate which could not be explained in terms of the original simple hypothesis, and auxiliary hypotheses were framed in quick succession; these made the theory contradictory and unmanageable. In his *Réflexions sur le phlogistique* (Paris, 1783), A. L. Lavoisier [6] said:

> Chemists have turned phlogiston into a vague principle, one not rigorously defined, and which consequently adapts itself to all the explanations for which it might be required. Sometimes this principle has weight, sometimes not; sometimes it is free fire, sometimes it is fire combined with the earthy element; sometimes it passes through the pores of vessels, sometimes the vessels are impervious to it; it explains both causticity and non-causticity, transparency and opacity; colours and their absence; it is a veritable Protean, changing in form each instant.

A. L. Lavoisier's explanation of the increase in weight which occurs when lead is calcined, seems so obvious that it is now difficult to appreciate the difficulty as set forth by P. J. Macquer (1769) [7]:

> The phenomenon is *un vrai paradoxe chimique*. While it is easy to prove the fact, it

> is difficult to find a satisfactory explanation. The phenomenon is outside all physical ideas which we have formed, and it is only in the future that a solution of the difficulty can be expected.

The chief difficulties encountered in the application of the theory of phlogiston were : (i) The increase in weight which occurs when metals are calcined ; (ii) The necessity for the presence of air during combustion ; (iii) The change of mercury calx into a metal without the addition of phlogiston. In the latter case, P. J. Macquer, indeed, used the fact that mercury calx can be converted into a metal by merely heating it *per se* in the absence of a body containing phlogiston, to argue that the mercury calx is not a real calx, but merely a substance which has acquired *par l'action du feu l'apparence d'une chaux métallique*. P. J. Macquer endeavoured to remove the objection by assuming that phlogiston is light and that during combustion, light and air mutually precipitate one another ; during the calcination of a metal, the air unites with the metal and disengages phlogiston ; and during the reduction of a metal calx, light unites with the metal and liberates air. C. W. Scheele[8] supposed that heat, light, and inflammable air were compounds of air and phlogiston which are convertible into one another by the addition or subtraction of phlogiston—inflammable air was assumed to contain most, and heat least phlogiston. During calcination, the metal either attracted air by means of its phlogiston and thus formed heat, or else communicated phlogiston to the air, and attracted heat from the fire ; in either case the air remained in the calx and imparted an overplus of weight. When a calx is reduced by inflammable air, heat, or light, the latter is decomposed and the phlogiston remains united to the reduced metal. The fact that oxygen supported combustion better than air led to the hypothesis that air contains more phlogiston than oxygen, which was hence called *dephlogisticated air*. At one time H. Cavendish (1766)[9] assumed that inflammable air is itself the phlogiston of the ancient chemists, and that a certain amount is fixed in all combustible bodies. Inflammable air, *i.e.* hydrogen gas, was accordingly called *phlogisticated air*. This hypothesis substituted a definite tangible material for a vague principle, but many of the properties of G. E. Stahl's phlogiston were utterly at variance with those of hydrogen, and the hydrogen hypothesis completely failed.

About 1770, it had been definitely proved that there is an increase in weight during the conversion of a metal into a calx by calcination of the metal in air. The fact was qualitatively explained, somewhat clumsily, by the phlogiston hypothesis which was based upon the *subtilis ignis* of the ancients, or the *materia cœlestis* of R. Descartes. R. Hooke, J. Rey, and J. Mayow had recognized that air somehow plays an important part in the process of calcination and combustion, but while their ideas on the general principle were clear, the details were somewhat hazy and indefinite.

References.

[1] *Empyrean*—the highest heaven where the ancients supposed pure fire subsisted.

[2] J. Juncker, *Conspectus chemiæ theoretico-practicæ*, Magdeburg, 1744 ; J. von Löwenstern Kunckel, *Nützliche Observationes*, Hamburg, 1676.

[3] G. F. Rodwell, *Phil. Mag.*, (4), **35**. 1, 1868.

[4] M. E. Chevreul, *Compt. Rend.*, **59**. 977, 1864.

[5] G. B. Airy, *Gravitation*, London, 1885; R. Hare, *Amer. Journ. Science*, (1), **42**, 260, 1842; W. Whewell, *Cambridge Phil. Soc.*, **7**. 197, 1842.

[6] J. B. Dumas, *Leçons sur la philosophie chimique*, Paris, 161, 1837.

[7] P. J. Macquer, *Mém. Acad.*, 153, 1769 ; *Éléments de chimie pratique*, Paris, 1751.

[8] C. W. Scheele, *Chemische Abhandlungen von der Luft und dem Feuer*, Leipzig, 1782.

[9] H. Cavendish, *Phil. Trans.*, **56**. 141, 1766 ; R. Kirwan, *An Essay on Phlogiston and the Constitution of Acids*, London, 1789 ; *Phil. Trans.*, **72**. 236, 1782 ; W. Nicholson, *The Controversy between Kirwan and the French Academicians on Phlogiston*, London, 1787.

§ 16. Lavoisier's Experiments on Combustion and Calcination

Nature is ever making signs to us, she is ever whispering to us the beginnings of her secrets; the scientific man must be over on the watch, ready at once to lay hold of nature's hint, however small: to listen to her whisper, however low.—M. FOSTER.

The beginning and end of every exact chemical process is weighing.—W. NICHOLSON (1808).

In 1772, Antoine Laurent Lavoisier began to publish accounts of a brilliant series of investigations which in a few short years banished phlogiston completely from chemical science. Chemistry had grown too great to be governed by the mystic phantom—phlogiston. In his *Opuscules physiques et chimiques* (Paris, 1774), A. L. Lavoisier first showed that phosphorus and sulphur increase in weight and absorb large volumes of air when they are burnt, and he obtained similar results with lead and mercury in closed vessels. A. L. Lavoisier pursued the subject further in a *Mémoire sur la calcination de l'étain dans les vaisseaux fermés, et sur la cause de l'augmentation de poids qu'acquiert ce métal pendant cette opération* (1774). He found that the vessel containing the air and tin did not increase in weight, although part of the air was absorbed. When the flask was opened, air rushed in, and the increase in the weight of the vessel was found to be equal to the increase in weight which the tin alone had suffered. Hence, A. L. Lavoisier concluded, with J. Rey, that the increase in the weight of the tin was solely due to an absorption of the air in which the calcination had occurred. There was not sufficient air in the flask to saturate all the tin, and yet some air always remained as a residue. Hence, A. L. Lavoisier concluded further that only **part of the air can combine with the metal during the calcination**; he also found that the increase in the weight of the tin during calcination is equal to the decrease in the weight of the air. Hence, it seems as if air contains at least two constituents, only one of which is absorbed by the heated metal. This inference was tested by an important experiment described in his *Traité élémentaire de chimie* (Paris, 1789).

The mercury was confined in a glass retort with an S-shaped neck which dipped under a bell-jar in a trough of mercury, as illustrated in Fig. 7. The air in the retort was in communication with the air in the bell-jar. The level of the mercury in the bell-jar was adjusted at a convenient level, and its position "very carefully marked with a strip of gummed paper." By means of a charcoal furnace, the mercury in the retort was heated—not quite to its boiling point (357°). A. L. Lavoisier said: "Nothing of note occurred during the first day. The second day I saw little red particles swimming over the surface of the mercury, and these increased in number and volume during four or five days; they then stopped increasing and remained in the same condition. At the expiration of twelve days, seeing that the calcination of the mercury made no further progress, I put the fire out." The red particles were identified with the calx of mercury now called red oxide of mercury, or mercuric oxide, and then called *mercurius calcinatus per se*.

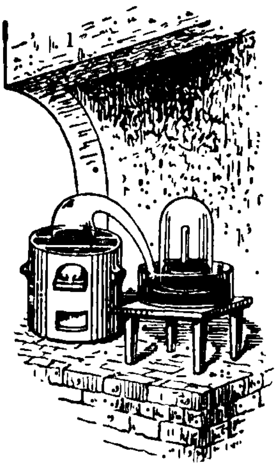

FIG. 7.—A. L. Lavoisier's Experiment on the Combustion of Air.

After making allowance for variations of temperature and pressure, A. L. Lavoisier found that when mercury was calcined with a given volume of air in a closed vessel, 50 cubic inches of air were reduced to between 42 and 43 cubic inches; the difference, 7 to 8 cubic inches, that is, one-fifth or one-sixth of the total volume of the air, was absorbed by the mercury, forming the red calx of mercury. The air which remained in the retort was not absorbed by the excess of hot mercury; it was rather less dense than ordinary air; it extinguished the flame of a burning candle immersed in the gas; and a mouse was quickly suffocated when placed in the gas. Hence, A. L. Lavoisier first called the gas *moufette atmosphérique*, and later **azote,** "from the α privative of the Greeks, and ζωή, life." In France, the gas is still called *azote*, though in Britain it is called *nitrogen*.

By collecting the red mercury calx, and re-heating it in a suitable retort (probably to 400°), Lavoisier obtained between seven and eight cubic inches of a gas which had been previously removed from the air by the hot mercury. The gas was exactly analogous in properties with the *dephlogisticated air*, discovered on August 1st, 1774, by Joseph Priestley, by heating *mercurius calcinatus per se* by means of a burning lens. When a burning candle was immersed in the gas, the candle burnt with *éclat éblouissant*—blinding brilliancy—as Lavoisier expressed it; a smouldering splinter of wood burst into flame when plunged in the gas; and the gas did not suffocate a mouse like azote. A. L. Lavoisier first called this gas *l'air éminemment respirable*, *pur*, *ou vital*, and afterwards *oxygen*. The latter term is its present-day designation. In this manner, A. L. Lavoisier proved that **atmospheric air is made up of two gases—oxygen and nitrogen—of different and even opposite natures, the oxygen alone combines with the metal during calcination, and is the cause of the increase in weight.**

A. L. Lavoisier further showed that the sum of the weights of the mercury and oxygen obtained by heating mercury calx is exactly equal to the weight of the calx; and that the increase in the weight of the mercury in the formation of the calx is equal to the weight of the oxygen taken from the air. In his *Réflexions sur le phlogistique* (Paris, 1783) A. L. Lavoisier said that during the combustion of phosphorus in oxygen gas (vital air):

> There is a total absorption of vital air, or rather of oxygen, in the combustion of phosphorus, and the weight of the phosphoric acid obtained is found to be rigorously equal to the weight of the phosphorus, added to that of the vital air employed in the combustion. The same agreement of weights is observed in the combustion of inflammable air, in the combustion of charcoal, etc.

Hence, the mechanism of combustion according to A. L. Lavoisier is: Metal + Oxygen = Metal calx, and not, as G. E. Stahl supposed to be the case: Metal − Phlogiston = Metal calx. The phenomenon which occurs when oxygen unites with a metal to form a calx is called **oxidation,** and the resulting calx is called an **oxide.** A. L. Lavoisier thus showed that it is not the calces that are simple and the metals compound, but just the reverse; so that the phlogistians have therefore been said to have perceived the relations between these two classes of bodies upside down. In all reductions with charcoal, said A. L. Lavoisier, fixed air is obtained owing to the union of the charcoal with the pure portion of the air—oxygen—which was fixed in the calx during the oxidation of the metal.

> If I take a metallic calx and heat it with carbon in a closed vessel, at the moment the calx is reduced to the metallic state—at the moment, for example, when litharge, the calx of lead, is changed into metallic lead, there reappears the air, which had become fixed when the metallic lead had been made into a calx, and an aerial product—fixed air—can be collected at least a thousand times more bulky than the solid litharge employed. This experiment appears to be one of the most interesting which has been made since the time of Stahl.

Assuming that this interpretation of the experiments is correct, A. L. Lavoisier inferred that by mixing azote and oxygen in the right proportions, it ought to be possible to reproduce atmospheric air. This A. L. Lavoisier did, and the mixture was found to behave with respect to "combustion, respiration, and the calcination of metals similar in every respect to atmospheric air." Lavoisier similarly showed that if the calcination of the metal is attended by the union of the vital air—oxygen—of the atmosphere with the metal, then, when the calcination is effected in an inverted glass vessel containing vital air, the whole should be absorbed. This deduction was "proved by weight and measure."

According to the phlogistians, a lighted candle burns because it is a compound of candle-matter and phlogiston. The compound is decomposed little by little, as the candle burns from tip to base, and the phlogiston passes into the surrounding atmosphere. A. L. Lavoisier inverted *l'ancienne hypothèse.* He supposed the hydrogen and carbon of the candle, during the burning, to unite with the oxygen of the air to form the oxides of carbon and of hydrogen; and generally, when a substance is burned, it does not give out an imaginary levitative phlogiston, but rather takes in real gravitative oxygen.

In his *Mémoire sur la combustion en général* (Paris, 1777), A. L. Lavoisier altogether rejected the principle of combustion advocated by G. E. Stahl, and argued that his own hypothesis "seemed to be more probable, more conformable with the laws of nature, and to involve less strained explanations and fewer contradictions" than the doctrine of G. E. Stahl. About ten years later, A. L. Lavoisier collected and organized such an array of facts in defence of his proposition that he was able to write with much greater confidence in his *Réflexions sur le phlogistique* (Paris, 1783), and he claimed the phlogistic doctrine to be an error fatal to the progress of chemistry:

> If in chemistry everything can be satisfactorily explained without the aid of phlogiston, it thereby becomes eminently probable that phlogiston does not exist, that it is a hypothetical being, a gratuitous assumption.

It is easier to make new discoveries than to eliminate old prejudices. Chemists were painfully slow to recognize the part played by air in combustion and calcination. In his *Réflexions sur le phlogistique* (Paris, 1783), A. L. Lavoisier said:

> Chemists have turned phlogiston into a vague principle, one not rigorously defined, and which consequently adapts itself to all the explanations for which it might be required. Sometimes this principle has weight, sometimes not; sometimes it is free fire, sometimes it is fire combined with the earthy element; sometimes it passes through the pores of vessels; sometimes the vessels are impervious to it; it explains both causticity and non-causticity, transparency and opacity, colours and their absence; it is a veritable Protean, changing in form each instant.

A. F. de Fourcroy began to teach A. L. Lavoisier's theory in 1787; C. L. Berthollet joined the new cause about the same time. Then followed L. B. Guyton de Morveau, and nearly all the French and British chemists. The Berlin Academy abandoned phlogiston in 1792, and the controversy which had waged for some years between the phlogistians was virtually at an end.[1] The downfall of phlogiston, a relic of Egyptian and Chaldean lore, was celebrated by Madame Lavoisier, habited as a Greek priestess, burning the writings of G. E. Stahl upon an altar dedicated to the new positive science. At the beginning of the new century a few petrified spirits, unable to march to the music of the new chemistry, still lingered behind. Robert Boyle's admonition in his *Considerations touching experimental essays in general* (1661), may have been forgotten:

> It ought to be esteemed much less disgraceful to quit an error for a truth than to be guilty of the vanity and perverseness of believing a thing still because we once believed it. . . . Until a man is sure he is infallible it is not fit for him to be unalterable.

The observed facts were sterile and barren before they were vivified by the fire of Lavoisier's genius. Indeed, enthusiasts have said that chemistry as a science was not born until A. L. Lavoisier's theory of burning had been demonstrated. Many writers—*e.g.* S. Brown (1858)[2]—have emphasized that tradition and prejudice were all against A. L. Lavoisier, and however much he owed to his predecessors and contemporaries—J. Rey, P. Bayen, J. Priestley, H. Cavendish, and C. W. Scheele—he scarcely owed them one glimmering ray of thought—rather the reverse. The legacies of fact inherited by A. L. Lavoisier were beclouded and distorted by the false hypotheses through which their discoverers saw them, and it required a master mind to co-ordinate the facts accumulated by many workers into one system. We can feel with A. Wurtz when—following A. F. de Fourcroy (1797)—he opened his *Histoire des doctrines chimiques* (Paris, 1869) thus: *La chimie* *est la science française, elle fut constituée par Lavoisier d'immortelle mémoire;* otherwise expressed, chemistry is a French science, it was founded by Lavoisier of immortal memory. This statement seems to have needlessly irritated some of our own historical writers. Can we wonder that Frenchmen are proud of their Lavoisier? Surely "we can amiably pass without protest this ardent hero-worship."

At first sight, it does seem curious that such a long period of time should have been required to work from P. E. de Sultzbach's note in 1489 to the effect that metals increase in weight when calcined in air, to A. L. Lavoisier's proof in 1774 that the increase in weight is due to the absorption of oxygen from the air. This will occasion no surprise when we remember the difference between the properties of air which cannot be seen, and the properties of solids and liquids which can be readily seen and handled. As G. F. Rodwell has emphasized, the most obvious property of matter is its visibility, and the conception of matter divested of this quality is no small effort to a mind untutored in invisible bodies, which exercise no apparent effect on surrounding objects, and it belongs to an advanced order of experimental philosophy. There were no means of recognizing even the more salient properties of air at the disposal of the chemists until a comparatively late period, and the earlier chemists, accordingly, believed air to be intrinsically different in its essence from more familiar visible substances. To illustrate the ideas about air which prevailed at the end of the eighteenth century, the opening words of A. L. Lavoisier's *Mémoire sur la nature du principe qui se combine avec les métaux pendant leur calcination et qui en augmente le poids* (Paris, 1775) may be quoted:

> Do different kinds of air exist? Is it enough that a body should be permanently expanded for it to be considered a particular kind of air? Are the different airs found in nature or formed by us specific substances, or are they modifications of atmospheric air?

Again, altogether apart from the skill required in the manipulation of gases, it is not at all surprising that writers on chemistry in the Middle Ages failed to interpret the mechanism of the burning of a candle in air when the knowledge required to explain the chemical side of the phenomenon is recalled:

> (i) Air is composed of two gases both sparingly soluble in water; (ii) During combustion one of the gases unites and the other does not unite with the burning body; (iii) Air contains four volumes of the inert gas, and one volume of the gas which unites with the burning body; (iv) A gas soluble in water is produced during the combustion; and (v) The increase in weight of the combustible body during the burning is equal to the decrease in the weight of the air.

The phlogiston hypothesis is sometimes held up to ridicule. It must be borne in mind that the hypothesis was adopted by nearly all the leading chemists in the earlier part of the eighteenth century when it appeared to be as firmly fixed among the root principles of chemistry as the kinetic theory does to-day. Thus, the ardent and devoted J. Priestley could say:

> If any opinion in all the modern doctrine concerning air be well-founded, it is certainly this, that nitrous air is highly charged with phlogiston. If I have completely ascertained anything at all relating to air, it is this;

and the diplomatic P. J. Macquer, in his *Éléments de chymie pratique* (Paris, 1751), that

> We cannot say how phlogiston is fixed by substances; but without pretending to guess the cause of the phenomenon, let us rest contented with the certainty of the fact.

The phlogiston theory represented the most perfect generalization known to the best intellects of its day, and J. J. Becher and G. E. Stahl were the prophets of a new mode of viewing chemical mutations. The doctrine served to give coherence to the thoughts and work of a race of chemists extending from J. J. Becher and G. E. Stahl down to H. Cavendish, J. Priestley, and C. W. Scheele.

The phlogistic hypothesis enabled chemistry to escape in part from mystic and mediæval empiricism,[3] for it introduced a certain amount of order among a chaotic mass of facts. Like phenomena were grouped together, and chemistry thrived and multiplied its proportions while under its sway. Phlogiston prepared the way for A. L. Lavoisier's balance, just as the balance heralded J. Dalton's arithmetic. There is what A. Comte[4] called *la loi de succession* running through history. The early struggles of man in quest of knowledge and truth were not in vain. The sun-worshipper and the phlogistian, each in his own way, had been working to a common end. All generations—past and future—thus seem to be linked in one common service.

It is inconceivable that men like T. Bergmann, H. Cavendish, J. Priestley, and C. W. Scheele would counsel what they considered to be an inconsistent doctrine. Phlogiston was regarded by them, not as a temporary hypothesis, but as a permanent acquisition, an enduring conquest of truth. To-day the word is but an empty symbol.

It must be added that H. St. C. Deville (1860), C. Brown (1866), and W. Odling (1871)[5] have pointed out that phlogiston occupied a similar position in the chemistry of the eighteenth century that potential energy does to-day. Said Deville : *On arrive à admettre que l'affinité (en intensité) n'est pas autre chose que la quantité de chaleur latente ou phlogistique enfermée dans les corps.* Even A. L. Lavoisier, in his *Traité élémentaire de chimie* (Paris, 1. 60, 1793), considered oxygen to be made up of caloric and the matter of oxygen. Lavoisier's *caloric* —a veritable ghost of phlogiston—was supposed to be the matter of heat possessing no weight whatever. Ordinary oxygen thus contained the principle of oxygen plus caloric. The latter has also been identified with potential energy. Here then the old revives in the new. The chemistry of to-day is not materialistic, for it is concerned with both energy and matter.

Theories perish, facts remain.—Much of what we think best in the theories of to-day may to-morrow be rejected, with phlogiston, worthless. There is no reason to suppose that fewer errors are believed to-day than in the days when phlogiston reigned supreme ; and it is not at all improbable that posterity will smile at our inexplicable ignorance in some departments of science. This need cause the student no embarrassment. A fallacious theory may be a valuable guide to experiment. Experiment and labour applied to the explication of the most extravagant hypothesis are not always lost. Guided by wrong hypotheses, men haves ought one thing and found another ; Columbus sought the Indies and found America. W. Whewell has pointed out that when a theory, which has been received on good evidence, appears to fail, the really essential and vital part of it survives the fall, that which has been discovered continues to be true. It is necessary, however, to follow René Descartes advice : **Give unqualified assent to no proposition which is not presented to the mind so clearly that there is no room for doubt.** As Aristotle would have said, we do not need to cultivate the art of doubting, but rather the art of doubting well ; for the art of doubting well is the necessary antecedent of progress. Doubt is the parent of inquiry.

It is not always expedient to follow the history of each hypothesis and each conquest of truth, step by step, as in the case of air. That of course would be an ideal plan of work ; but it is not always a waste of time to study the exploded fallacies once cherished by the potentates of old. The right attitude of mind towards an hypothesis or law can be developed only when history has taught how man has had to climb with slow faltering steps until he obtained a clear view of each new principle of chemical science. J. W. Goethe was quite right : The history of a science is the science itself : The past is key to the present ; although, as A. Comte (1839) expressed it : *On ne connait pas complètement une science tant qu'on n'en sait que l'histoire.* Unfortunately, time cannot always be spared to wander with the original investigators into the byways of knowledge, and a more economical plan must usually be followed. If every one had to pass through all the stages traversed by all who have gone before, it would be impossible to reach the vantage ground gained by the labours of his predecessors.

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CHAPTER II

COMBINATION BY WEIGHT

§ 1. What is an Element?

The elements count as simple substances not because we know that they are so, but because we do not know that they are not.—J. von Liebig (1857).

A. L. Lavoisier showed that atmospheric air is no more an elementary principle than the water of the ocean, for it can be resolved into two simpler gases—oxygen and nitrogen. It is further possible to resolve all known substances—air, water, etc.—into about eighty distinct elemental or primitive forms of matter. The present-day concept of an element is one of those ideas which has gradually grown into chemistry. Epicurus, about 300 B.C., held that corporeal things are either composite, or else they are the constituent parts of which the composite things are compounded; and that the continued division of the composite must at last furnish ultimate, indivisible, unchangeable particles of the elements. Aristotle, in his *De cœlo* (**3**. 3), also defined an element. He said:

> Everything is either an element or composed of elements. . . . An element is that into which other bodies can be resolved, and which exists in them either potentially or actually, but which cannot itself be resolved into anything simpler, or different in kind.

This precise and accurate concept was soon beclouded with the idea that all the different varieties of matter observed in nature are composed of a primitive element with varying proportions of wetness or dryness, or of coldness or hotness. This quaternary of attributes gradually materialized into earth, water, air, and fire. All the different forms of matter were vaguely supposed to have been compounded in some inscrutable manner from varying proportions of this quartet.

In 1661, Robert Boyle's attention was arrested by the loose way in which the term element was employed, and in his *The Sceptical Chymist* (Oxford, 1661), he gave a clear concept for an element. He said:

> I mean by elements, as those chymists that speak plainest do by their principles, certain primitive and simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the ingredients of which all those called perfectly mixt bodies are immediately compounded, and into which they are ultimately resolved. . . . I must not look upon any body as a true principle or element, which is not perfectly homogeneous, but is further resolvable into any number of distinct substances.

N. le Febvre,[1] whom J. B. Dumas called *l'homme d'imagination*, flourished in the seventeenth century about the time of Robert Boyle. N. le Febvre showed that Empedocles' analysis of wood into four elements—flame or fire, smoke or air, moisture or water, and ashes or earth—does not include all the principles of which this form of matter is compounded. By the destructive distillation of wood, he found that water charged with acetic acid and an oily inflammable liquid condensed in the receiver; a gas escaped; and charcoal remained. The charcoal burnt in air, giving fire and ashes; and the ashes were resolved by water into a soluble salt, and an insoluble earth. N. le Febvre thus resolved wood into six ingredients, and he got very near to recognizing that the only proof of an elementary principle is the fact of its yielding nothing else to analysis. He maintained that chemistry is not the doctrine of the four elements, an art of transmutation, or a science of mixts ; but is rather the art of analysis with a view to discover *la connaissance de toutes les choses que Dieu a tirées du chaos par la création*—a knowledge of all the ingredients of all the various kinds of matter which God has created out of chaos.

Even as late as the latter part of the eighteenth century, fire, air, water, and earth were regarded as elemental. Thus, P. J. Macquer, in his *Dictionnaire de chymie* (Paris, 2. 4, 1778), gave a *juste* definition of an element, and added :

> Although fire, air, water, and earth are reputed to be simple, it is possible that they are not so ; they may be very complex, and may result from the union of several other more simple substances . . . but as experience teaches us absolutely nothing on this subject, we may consider without inconvenience, and indeed in chemistry we ought to consider fire, air, water, and earth as *les corps simples*, because they really act as such in all chemical operations.

We are also indebted to A. L. Lavoisier (1789) for further clarifying the concept of an element. A. L. Lavoisier, quite logically, considered lime, magnesia, baryta, and alumina to be elements. We now know that these elements of A. L. Lavoisier are compounds of oxygen with calcium, magnesium, barium, and aluminium respectively. This was not known to Lavoisier, and he rightly said : " We are certainly authorized to consider them simple bodies until, by new discoveries, their constituent elements have been ascertained." Again, in 1811, the question whether chlorine—then called oxymuriatic gas—was really an element or a compound of oxygen with some other element was raised by Humphry Davy. H. Davy claimed that chlorine is an element because, although oxygen was believed to be present, none could be found. " Hence," added H. Davy, " we have no more right to say that oxymuriatic gas (*i.e.* chlorine) contains oxygen than to say that tin contains hydrogen. . . . Until a body is decomposed, it should be considered simple."

It is not possible to improve upon Lavoisier's conception of a chemical element, and I feel compelled to quote his words, although written before 1789 : [2]

> When we apply the term elements or principles to bodies to express our idea of the last point which analysis is capable of reaching, we must admit, as elements, all substances into which we are able to reduce bodies by decomposition. Not that we are entitled to affirm that these substances which we consider as simple, may not themselves be compounded of two, or even of a greater number of more simple principles ; but since these principles cannot be separated, or rather, since we have not hitherto discovered the means of separating them, they are, with regard to us, as simple substances, and we ought never to suppose them compounded until experiment and observation have proved them to be so.

The definition of an element is not founded upon any intrinsic property of the elements, but rather upon the limited resources of the chemist. To find if a given substance is an element or a compound, it is usual to assume that it is a compound and then to apply all known methods for resolving compounds into simple substances. If the methods fail to effect a decomposition, the substance is said to be an element. Hence, the statement that any given substance is an element has been said to be a confession of the impotence of human powers. In fine, element is a conventional term employed to represent the limit of present-day methods of analysis or decomposition.[3] We may, therefore, summarize these ideas in the definition : **An element is a substance which, so far as we know, contains only one kind of matter.** To say the substances we call elements *cannot* be decomposed may be regarded as an unwarranted reflection on the powers of our successors. The moment Auer von Welsbach (1885) proved that didymium was a mixture of praseodymium and neodymium, one element ceased to exist, and two elements were born. If it were found to-morrow that the element chlorine is really a compound of two new elements previously unknown, the fact would be important and it would change the face of chemistry, but it would not render useless any facts we know about chlorine.

The old alchemists sought to transform some of the common metals into gold. Whenever the attempt has been made with materials known to be free from gold, no transmutation has been observed. There is nothing intrinsically absurd in the notion, but at present, no authentic transmutation has been deliberately, or rather intentionally, accomplished. Works like P. J. von Lewinheim Sachs' *Aurum chymicum* (Genevæ, 1702) and K. C. Schmeider's *Geschichte der Alchemie* (Halle, 1832) professed to examine critically the authenticity of the legendary reports by the alchemists of the reality of the transmutation of the metals, and concluded that in some cases the legends are above suspicion, and this in spite of the fact that H. von Osten, in his *Eine grosse Herzstärkung für die Chymisten* (Berlin, 1771), had exposed some forty-five tricks and deceptions practised by alchemical knavery. All the reports now stand discredited. K. C. Schmeider criticized the legends imperfectly, and failed to recognize that fictions may be plausible as well as extravagant. When the evidence has permitted a critical examination, every recorded instance has been traced to a mal-observation; and evidence which cannot be tested is outside the range of scientific methods. In the words of J. M. Wilson (1917), in science, there is no statement of fundamental importance that depends on history or on any testimony which cannot be verified.

The next inquiry arises from the question: What relations subsist between the weights and volumes of the different elements which make up the different kinds of matter known to man ?

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§ 2. The Law of Constant Composition—Proust's Law

Nature in her inscrutable wisdom has set limits which she never oversteps.—JEAN REY.

The proportion in which one element can unite with another is fixed by nature, and the power of augmenting or diminishing this *pondus naturæ* is not given to man.—J. L. PROUST (1801).

Attention must now be directed to the singular observation made by Jean Rey (1630) that during the calcination of a metal in air, "the weight of the metal increased from the beginning to the end, but when the metal is saturated, it can take up no more air. Do not continue the calcination in this hope: you would lose your labour." The examples previously quoted—Cap. I, Table I—have shown that one gram, and only one gram, of air is absorbed by definite amounts of the given metals under the conditions of the experiment, and Lavoisier's work proves that the *oxygen* of the air is alone absorbed. Accordingly, one part by weight of oxygen is equivalent to 1·52 parts magnesium; 4·06 of zinc; 1·12 of aluminium; 3·97 of copper; and 3·72 of tin. Instead of taking the weight of oxygen unity, it will be more in accord with general usage to make oxygen 8. Hence, multiply the preceding numbers by 8:

Oxygen.	Magnesium.	Zinc.	Aluminium.	Copper.	Tin.
8	12·16	32·48	8·96	31·96	29·76

When magnesium is calcined in the presence of oxygen, or air, the metal always unites with the oxygen in the proportion of one part of oxygen per 1·52 parts of magnesium, or 8 parts by weight of oxygen per 12·16 parts by weight of magnesium. The same principle obtains when magnesium oxide is made in several different ways; and likewise with the other metallic oxides. The proportions in which two elements unite together do not vary in a fortuitous manner, but in fixed and definite proportions. Hence, as P. J. Hartog[1] puts it: **two like portions of matter have the same composition.** The converse of this statement is not necessarily true, for two portions of matter compounded from the same proportions of the same elements are not necessarily alike.

The exact work of J. S. Stas[2] and T. W. Richards and many others has firmly established the constancy of the composition of the regular type of chemical compounds. J. S. Stas, in his famous *Recherches sur les lois des proportions chimiques* (1860–65), for example, studied among other things, the composition of silver chloride prepared by four different processes at different temperatures. He found that 100 parts of silver furnished 132·8425, 132·8475, 132·8480 parts of silver chloride; and that neither the temperature nor the method of preparation had any influence on the composition of the chloride. The difference between the two extremes is less than 0·006 part per 100 parts of silver. This shows that the errors, incidental to all experimental work, are here remarkably small. J. S. Stas likewise proved that ammonium chloride prepared from quite different sources, and purified in different ways, always contains exactly the same proportion of chlorine. Still further, he proved that *the combining weight of an element is not affected in the slightest degree by the various elements with which it might combine.* For example, silver combines with iodine to form the iodide, and with iodine and oxygen to form the iodate. The ratio of silver to iodine in both compounds is the same, and is not modified by the large quantity of oxygen present in the iodate. Hence, J. S. Stas stated: "If the recognized constancy of stable chemical compounds needed further demonstration, I consider the almost absolute identity of my results has now completely proved it."

The law of constant proportions, however, can never be proved with mathematical exactness. However skilful a chemist may be, it is impossible to make an exact measurement without committing an error of observation or an error of experiment. It is assumed that the small difference 0·005 per cent. between the two extreme results of J. S. Stas (1) is wholly due to the unavoidable errors of experiment, for we cannot expect an exact solution of the problem; and (2) is not due to a very slight inexactitude in the law of constant proportions. In 1860, J. C. G. de Marignac considered that the experiment did not prove definitely that the composition of compounds might not vary within very minute limits:

> I do not consider that it has been absolutely demonstrated that chemical compounds do not normally have an excess of one of the constituents. It is true that this excess is very minute, but it is still appreciable in very delicate measurements.

The composition of a definite compound appears to be independent of its mode of formation, and therefore it is inferred that substances always combine in definite proportions. If an excess of one substance be present, the amount in excess remains uncombined as extraneous matter. This deduction from the observed facts is called **the law of definite proportions,** or **the law of constant composition.** The law is sometimes enunciated: *a particular chemical compound always contains the same elements united together in the same proportions—by mass.* This statement, if interpreted literally, holds good for a particular mixture, as well as for a particular compound; and it has nothing to say as to the distinction between a mixture and a compound. Probably no generalization in chemistry is more firmly established than that like compounds possess the same quantitative composition. So great is the faith of chemists in the truth of this generalization that a few accurate and careful experiments are considered sufficient to settle, once for all, the composition of a substance. For instance, if a substance possessing all the properties of magnesium oxide be given to a chemist, without taking any more trouble, he knows that it will contain 12·16 parts of magnesium for every eight parts of oxygen. The law of constant composition furnishes a kind of *a priori* control over quantitative analysis. Constancy in composition is regarded as a proof of purity, and purity is attended by constancy in composition. Hence arose the concept of a **chemical compound** as distinct from a mixture.[3]

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§ 3. History of the Law of Constant Composition

Ce n'est que du conflit des opinions contraires que jaillit la vérité.—F. Hoefer (1843).

The law of constant composition was not discovered by any particular man, but it gradually grew among the doctrines of chemistry. The law was tacitly accepted by many before it was overtly enunciated. This is shown by J. Rey's views (1630), previously stated. In 1699, G. Homberg,[1] in his *Observations sur la quantité d'acides absorbés par les alcalis terreux*, described measurements of the amounts of different acids (vinegar, spirits of salt, aqua fortis, and vitriolic acid) required to saturate a given amount of potassium carbonate (salt of tartar); he evaporated the saturated liquid to dryness and weighed the resulting solid. His results were compiled in the form of a table which has been regarded as embodying the first hint of the law of definite proportions. G. Homberg considered that the quantity of an acid which unites with an alkali is *la mesure de la force passive de cet alcali*, and further added that by *la force des acides* he means the solvent action of the acid, and similarly for the alkalies. F. Hoefer (1843) suggests translating G. Homberg's "solvent action" by "neutralizing," and "solubility" by "neutralizable." Isaac Newton referred to the saturation capacity of acids for different metals in the thirty-first query of his *Opticks* (London, 1704). G. E. Stahl also in his *Fundamenta chymiæ* (Norimbergæ, 1723) spoke of the *pondus naturæ* as the proportions which ought to exist between the masses of the different ingredients in order that a determinate compound be produced. In 1717, E. F. Geoffrey analyzed saltpetre and stated its quantitative composition. A. S. Marggraf (1749); H. T. Scheffer (1750); T. Bergmann (1775-84); R. Kirwan (1790-1800); J. Black (1794); M. H. Klaproth (1795); V. Rose (1803-5); C. F. Bucholz (1799-1802); and L. N. Vauquelin (1812) all based analyses of chemical compounds on the tacit assumption that this law is valid; and W. Higgins' theory of atoms (1789) implies that chemical compounds must have a constant composition. A. L. Lavoisier appears to have had no doubts on the subject. In every oxide, said he, the relation of oxygen to the metal is constant.

In 1767, H. Cavendish said that those quantities of bases—*e.g.* potash and lime—are equivalent which neutralize the same amount of acid; and, in 1788, he showed that this equivalency is independent of the nature of the acid. C. F. Wenzel (1777) had a fairly clear idea that a definite weight of a base neutralized a definite amount of a given acid, and in his *Lehre von der Verwandschaft der Körper* (Dresden, 1777), he gave measurements of the weights of over twenty metals and bases which were required to saturate about a dozen acids; and he also examined quantitatively the products of some reactions—*e.g.* copper sulphate and lead acetate; mercuric sulphide and silver chloride; etc. Shortly after C. F. Wenzel's book had appeared, J. B. Richter, in an important study of this subject, published evidence in his *Ueber die neueren Gegenstände der Chemie* (Breslau, 1791-1802), and in his *Anfangsgründe der Stöchyometrie oder Messkunst chymischer Elemente* (Breslau, 1792-4), which demonstrated conclusively that the weights of the various acids which neutralize certain fixed weights of the bases are the same; and the same numbers hold good for the neutralization of all acids by the bases; otherwise expressed: **Acids and alkalies unite in constant proportions to form salts**—this is **Richter's law of proportionality,** or *Richter's law of equivalent ratios.* Consequently, it is possible to assign equivalent numbers to the acids and bases. For instance, using modern data and terms :

Acids.	Equivalent weight.	Bases.	Equivalent weight.
Hydrofluoric acid	20·01	Ammonium hydroxide	35·05
Hydrochloric acid	36·47	Calcium hydroxide	37·06
Sulphuric acid	49·04	Sodium hydroxide	40·01
Nitric acid	63·02	Potassium hydroxide	56·00

J. B. Richter gave separate tables for the neutralization equivalents of each acid and each base ; but G. E. Fischer, in an appendix to his German translation of C. L. Berthollet's *Recherches sur les lois de l'affinité,* showed that J. B. Richter's data could be reduced to a single table containing twenty-one numbers divided into two columns as just indicated. These tables can be regarded as the first **tables of equivalent weights** published. The weights of the acids in one column represent the amounts required to neutralize the quantity of any of the bases indicated in the other column ; and conversely, the weights of the bases in the second column represent the amounts required to neutralize the quantity of any one of the acids indicated in the first column. Thus 56 grams of potassium hydroxide will neutralize 20·01 grams of hydrofluoric acid, 36·47 grams of hydrochloric acid, 49·04 grams of sulphuric acid, 63·02 grams of nitric acid, etc., and 63·02 grams of nitric acid will neutralize 35·05 grams of ammonium hydroxide, 37·06 grams of calcium hydroxide, etc. Richter claimed that the rule he gave is a true touchstone—*Probierstein*—for the proportions wherewith the acids and bases neutralize one another, because if the observed numbers do not agree with those demanded by the rule, they may be regarded as erroneous.

J. B. Richter mixed up much valuable work with several fantastic hypotheses ; he supposed that the weights of the bases required to neutralize a constant weight of acid are in arithmetical progression ; and the weights of the acids required to neutralize a constant weight of any base are in geometrical progression. Richter appears to have cooked some of his results to make them fit his erroneous hypothesis so that the numbers represent what he thinks he ought to have obtained rather than what he actually observed. Such a procedure is quite antagonistic to the spirit of science, and made chemists reasonably sceptical about the accuracy of the whole of Richter's work. It was thought, wrongly as it happens, *falsus in uno, falsus in omnibus* (false in one, false in all). Consequently, the above generalization did not attract the attention it deserved. On reading J. B. Richter's work on chemical ratios, said J. J. Berzelius (1827), we are astonished that the further study of the subject could ever have been neglected.

It must be added that the validity of the law of definite composition was the subject of an interesting controversy during the years between 1800 and 1808. J. L. Proust [2] maintained that constant composition is the invariable rule ; C. L. Berthollet did not assert that cases of constant composition are non-existent, but he argued that these instances were due to special circumstances, and maintained that constant composition is the exception, variable composition the rule. J. L. Proust's words are worth quoting :

> According to my view, a compound is a privileged product to which nature has assigned a fixed composition. Nature never produces a compound even through the agency of man, other than balance in hand, *pondere et mensura.* Between pole and pole compounds are identical in composition. Their appearance may vary owing to their manner of aggregation, but their properties never. No differences have yet been observed between the oxides of iron from the South, and those from the North ; the cinnabar of Japan has the same composition as the cinnabar of Spain ; silver chloride is identically the same whether obtained from Peru or from Siberia ; in all the world there is but one sodium chloride ; one saltpetre ; one calcium sulphate ; and one barium sulphate. Analysis confirms these facts at every step.

It might be thought that positive assertions of this kind, backed by accurate experimental work, would leave no subject for disputation; but, surveying the battlefield in the light of the present-day knowledge, it seems that another quite different phenomena was confused with the law of constant composition; and the methods of analysis were not very precise. Some, probably from the unfounded belief that "Proust deservedly annihilated Berthollet," call the generalization discussed in this chapter, **Proust's law.** The arguments against the law of constant composition was silenced not by J. L. Proust, but by the work which developed from J. Dalton's atomic theory.[3] J. L. Proust did not satisfactorily answer all C. L. Berthollet's objections.

According to C. Daubeny (1850) it has been stated that something like the theory of constant composition can be found among the dogmas of the old sage Pythagoras (*c.* 520). This philosopher is sometimes supposed to have derived what is the most valuable part of his philosophy from the Egyptian priests during his sojourn in Egypt. Pythagoras taught that number—whatever was meant by that term—is a bond sustaining by its power the permanent existence of everything on the earth. The influence of Pythagoras has been traced in the doctrine laid down by Philo the Jew—or who ever wrote the apocryphal book of wisdom—God ordained all things by measure, number, and weight. It is, however, certain that European chemistry is in no way indebted to the Egyptian priesthood or to the Pythagorean philosophy for the concept of the law of constant composition. It would indeed require the exercise of a good deal of ingenuity to disentangle the law of chemical combination from the conflicting statements which have been made as to the meaning to be attached to Pythagoras' doctrine of numbers.

F. Wald (1895–9)[4] argues that the composition of chemical compounds is variable, and that the observed constancy in the composition of chemical compounds must be attributed to the selection by chemists of special preparations. Hence, says F. Wald, the statement of the law of constant composition is quite empirical, and the assumption that these selected preparations are alone true compounds is quite arbitrary.

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§ 4. Pure Substances

> Pure water is never found in nature. One may even say that no man has ever seen or handled absolutely pure water. It is an ideal substance, to which some specimens of highly purified water have nearly approached.—M. M. P. MUIR.
>
> It is only in "tall talk" or in advertisements that any human preparation, elementary or not, can be spoken of as *chemisch rein*.—P. G. TAIT (1881).

The substance we call water has its own properties, but sea-water, spring-water, rain-water, and distilled water show certain differences in their properties. The differences, however, are not due to the water, but to the substances—impurities—which the water has dissolved from its surroundings. If sea-water be distilled, the "impurities"—sodium chloride, magnesium chloride, etc.—remain behind. Sea-water is therefore a homogeneous substance, but, rightly or wrongly, it is often stated to be a mixture, because water and various salts can be separated by simple evaporation or by freezing. Table salt is more or less impure sodium chloride. The presence of a little magnesium chloride in table salt makes the salt more hygroscopic, so that the contaminated table salt deliquesces more readily than if magnesium chloride were absent.

The term **deliquescence**—from *deliquescere*, to melt or dissolve—refers to the process of absorbing moisture from the air so that a salt becomes moist, or even dissolves in the moisture it has absorbed from the air; *e.g.* when potassium carbonate is exposed to the atmosphere it rapidly gains in weight. The term **hygroscopic**—from *ὕγρος*, wet—refers to the absorption or adsorption of moisture from the atmosphere. Most substances, particularly when powdered, are hygroscopic, even if they do not deliquesce. The term **efflorescence** from *efflorescere*, to blossom, refers to the formation of a crust—generally white—on the surface of a body. The phenomenon is very often due to the loss of water from the surface of certain crystalline salts; *e.g.* when crystals of washing soda are exposed to a dry atmosphere, they gradually lose weight.

Air is a mixture of oxygen and nitrogen, with a little carbon dioxide, and it is habitually moist owing to the presence of a varying proportion of water vapour. In a chapter contained in J. B. Porta's *Magiæ naturalis* (Naples, 1589), on the extraction of water from air, it is shown that if a large glass flask be filled with a mixture of ice and nitre, water condenses from the air to the outer walls of the vessel, and trickles down into a basin below as receiver. Isaac Newton[1] said that potassium carbonate deliquesces in air because of an attraction between the salt and the particles of moisture in the atmosphere, and asked: Why does not common salt or nitre deliquesce in the same way except for want of such an attraction? In H. B. de Saussure's *Essais sur l'hydrométrie* (Neuchatel, 1783) there is an excellent study of the moisture which is normally present in atmospheric air. He exposed "equal quantities of salt of tartar, quicklime, wood, lime, etc., all dried as perfectly as possible," to the same air, and found that they "imbibed water and increased in weight in unequal quantities." The salt of tartar took more than the lime, and the lime more than the wood. H. B. de Saussure said that "these differences can only proceed from the different degrees of the affinity of these bodies for water," and he called this affinity, the *hygroscopic affinity* of the bodies for the vapour, so that the amount of vapour imbibed by different substances from the air "is proportional to their affinity for water vapour." H. B. de Saussure also showed that the thirst or the attractive force of the body for aqueous vapour diminishes from moment to moment "in proportion as it drinks the vapour," otherwise expressed, the hygroscopic activity of the body diminishes in proportion as it approaches the point of saturation.

Lavoisier's experiments on the transformation of water into earth.—A compound may be contaminated with impurities in many ways—from the raw materials used in preparing the compound; from the vessels in which it was prepared or stored; by exposure to the atmosphere; by the partial decomposition of the substance when exposed to light, etc. It was once believed that air can be condensed to water, as was thought to be proved by the falling dew; and that water can be changed into an earth, as is evidenced by the residue obtained when rain-water or distilled water is evaporated to dryness in glass vessels. Thus, O. Borrichius in his *Hermetis, Ægyptorum et chemicorum sapientia* (Hafniæ, 1674), said that "when 100 pounds of snow, hail, or of rain-water, are evaporated, the water is transformed into a dusty earth which contains some common salt;" R. Boyle[2] found on distilling and re-distilling pure rain-water, time and again, in glass vessels, a white powdery substance was obtained each time the water was evaporated; and the more the water distilled from a given glass vessel, the larger the amount of white powder. He added that a friend, of unsuspected credit, had distilled water two hundred times "without finding the liquor grow weary of affording the white earth." It seemed to him as if water "might be very nigh totally brought into earth, since out of an ounce of distilled rain-water he had already obtained nearly three-quarters of an ounce, if not more, of the often-mentioned earth." A. L. Lavoisier[3] first traced the true source of this earth. In his paper *Sur la nature de l'eau et sur les expériences par lesquelles on a prétendu prouver la possibilité de son changement en terre* (1770), A. L. Lavoisier described experiments with the object of "settling by decisive experiments whether water can be changed into earth as was thought by the old philosophers, and still is thought by some chemists of the day." By heating water in hermetically sealed glass vessels, after some days, the water became turbid and little white specks separated from the water and floated about. The hermetically sealed glass vessels were weighed before and after the experiment; it was proved: (1) The earth does not come from outside the vessel, because the weight of the vessel *and* its contents does not alter. This is against Boyle's hypothesis that fine igneous particles are able to pass through the glass, and are precipitated in the form of a white powder when they come in contact with water.

> Consequently, I conclude that nothing can pass through the pores of the glass, and these little white particles, be they caused by what they may, are not caused by igneous particles passing through the glass.

Still further, it was shown (2) The earth does not come from the water, because the weight of the water remains the same before and after the experiment; (3) The earth comes from the vessel, because the vessel loses in weight; and (4) The earth comes *wholly* from the vessel, because the loss in weight of the vessel is virtually equal to the weight of the earth formed. Hence, adds Lavoisier, "it follows from these experiments that the greater part, possibly the whole of the earth separated from rain-water by evaporation, is due to the solution of the vessels in which the water has been collected and evaporated." C. W. Scheele (1777) [3] deduced a similar conclusion from other experiments. He analyzed the earth produced during the evaporation of water in glass vessels and showed that it has a similar composition to the stuff of which the vessel was made.

R. F. von Walther (1915) has an interesting experiment to demonstrate the solubility of glass in water, 500 c.c. of water are placed in a common litre flask with sufficient alizarine to produce a pale yellow colour, the colour changes to a reddish-violet owing to the dissolution of alkali from the glass. By adding dilute sulphuric acid from a burette, the colour changes back to pale yellow when the alkali is neutralized. He found that after an hour's boiling, alkali equivalent to 18·3 c.c. of centinormal sulphuric acid had been dissolved from a glass vessel.

The purity of commercial compounds.—The term *pure* or *chemically pure*, is unfortunately used when it is desired to emphasize the fact that the substance has not sufficient impurity to influence appreciably the most exact work for which it is to be employed. There cannot be degrees of purity. A thing is either pure or impure. It may be convenient to use terms like highly pure, all but pure, very impure, etc., but the term, chemically pure, in the sense of nearly pure, is objectionable. This recalls Basil Valentine's statement that water exists in three degrees of excellence—the pure, the purer, and the purest! The labels on commercial reagents with their *pure*, *purissimum*, and *chemically pure*, are almost equivalent. F. Mylius [4] proposed distinguishing degrees of purity as of the first, second, and sixth grades according as they contain one part of total impurity in 10, 10^2, . . . 10^6 parts.

The terms *reagents* and *chemicals* are applied to the substances used in chemistry for producing special reactions with other substances. The former term is more particularly used in analytical work. Chemically pure substances, paradoxical as it may seem, are sold with a statement on the labels indicating what impurities are present as well as how much of each. *Commercial* reagents, on the other hand, have not been specially purified, and hence are sold at a cheaper rate than the chemically pure substances. Purification is an expensive operation, and the cheaper commercial reagents are used whenever specially purified materials are not required. Some hold that "perfectly pure substances are unknown." This is possible, but to establish the proposition, we should be involved in a metaphysical discussion, and we might be led to say with A. Laurent: "Chemistry is the science of substances which do not exist," or perhaps with G. W. F. Hegel: "Pure being is pure nothing."

Positive and negative evidence.—One positive proof may demonstrate an indefinite number of negatives. Thus, if a test proves that a given substance is silver chloride, it at the same time proves that the substance is not metallic copper, arsenic oxide, etc. On the other hand, **inability to prove a direct negative is not to be regarded as equivalent to a positive proof.** Thus, let it be asserted that a third substance, say moisture, must be present when two substances interact chemically. Against this, it can be shown that substances like mercury and chlorine do react when most carefully purified and dried; but it could be, and has been argued that this circumstance is due to the presence of an unrecognized impurity. Similarly, some argue that if the elements could be obtained absolutely free from unknown impurities their atomic weights would be whole numbers. Negative arguments of this type are invulnerable in controversies because they cannot be controverted by proofs to the contrary. True, the most skilful workers with the most refined instruments cannot find an impurity, but still, it can be asserted that better equipped searchers *might* be more successful. This *might*, however, does not prove the thesis in question. Nevertheless, the argument is often used. For instance, H. Davy's quest for oxygen in chlorine; T. Bergmann's proof of the individuality of nickel; W. Ostwald's statement that catalytic agents can change only the velocity of existing reactions; etc.

The effect of traces of impurity on the properties of a compound.—It may be well to emphasize, just here, that sometimes a minute trace of impurity is of vital importance. Some reactions proceed quite differently in the presence, and in the absence of traces of moisture or maybe other impurities. The properties of many substances, too, are modified in a remarkable manner by small traces of impurity. H. Vivian says that $\frac{1}{1000}$th part of antimony will convert the best selected copper into the worst conceivable; Lord Kelvin, that the presence of $\frac{1}{1000}$th part of bismuth in copper would reduce its electrical conductivity so as to be fatal to the success of the submarine cable; H. le Chatelier, that the absorption of a quite imperceptible weight of gas changes the melting-point of highly purified silver nearly 30°; G. le Bon (1900) that the presence of $\frac{1}{10000}$th part of mercury in magnesium makes the metal decompose water at ordinary temperatures; and W. C. Roberts Austin, that $\frac{1}{500}$th part of bismuth in gold will render gold useless from the point of view of coinage, because the metal would crumble under pressure in the die. J. F. W. Herschel (1851) considered the fact that such minute proportions of extraneous matter should be found capable of communicating sensible properties of a definite character to the bodies with which they are mixed, to be perhaps one of the most extraordinary facts that has appeared in chemistry.

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§ 5. Physical and Chemical Changes.

> **Most of the substances belonging to our globe are constantly undergoing alteration in sensible quantities, and one variety becomes as it were transmuted into another. Such changes, whether natural or artificial, whether slowly or rapidly performed, are called chemical. Thus, the gradual and almost imperceptible decay of the leaves and branches of a fallen tree exposed to the atmosphere, and the rapid combustion of wood in our fires, are both chemical operations.—H. DAVY.**

The early chemists did not clearly distinguish between uniform mixtures and homogeneous compounds so that many substances now known to be mechanical mixtures were classed with substances known to be homogeneous compounds; again, owing to the fact that they were seldom able to prepare compounds of a high degree of purity, the properties of compounds seemed more or less variable. Even so late as the end of the seventeenth century, chemists were not all clear that substances could be obtained with fixed and invariable properties. The properties of a substance are those qualities, or attributes, by which its nature is manifested. About 1730, H. Boerhaave distilled mercury five hundred times with the idea of finding if its properties thereby suffered any change. About this time, it was recognized that a homogeneous pure substance always has the same properties and behaves in the same way, when the conditions are the same; and generally, that **one element or compound is distinguished from all other elements or compounds in possessing certain specific and characteristic properties**; or, in the words of an old alchemist: " God hath sealed each substance with a particular idea."

First and foremost, a chemical compound has a fixed and definite composition; then again, a compound or element usually melts and boils at definite temperatures; its specific gravity, specific heat, crystalline form, colour, odour, behaviour when in contact with other substances, etc., are characteristic of one particular chemical compound. When the melting-point of, say, pure silver chloride has been once accurately determined, it follows that all other samples of pure silver chloride will melt at the same temperature under the same conditions. Many changes in the properties of matter are not immediately perceptible to the senses; and in the majority of cases, the processes for the identification and differentiation of the different forms of matter are based upon their behaviour towards certain reagents. The more salient characteristic properties of an element or compound are employed for its identification—that is, for distinguishing it from other known elements or compounds. Thus, a student would be probably correct in stating that a solution contained a silver compound if it gave a white precipitate when acidified with hydrochloric acid, and the precipitate was insoluble in hot water, and soluble in aqueous ammonia; and if the spectrum of a burning body has a yellow line in a particular part, the presence of sodium would be inferred. About 1661, Robert Boyle[1] noticed many examples of the use of chemical reagents for the detection or identification of certain substances, and in 1780, T. Bergmann collected together a number of reagents useful for detecting the commoner elements or acids, and described the effects produced. M. H. Klaproth, L. N. Vauquelin, J. J. Berzelius, F. Wöhler, H. Rose, C. R. Fresenius, and others built upon this foundation the present system of qualitative analysis.[2]

Physical changes.—When liquid water becomes ice or steam there is no change in the *chemical* nature of the substance, for the matter which makes steam and ice is the same in kind as that of liquid water. A substance can generally change its state, as when liquid water becomes steam or ice. The idea is further emphasized by the fact that in most cases a substance is called by the same name, whether it be in a solid, liquid, or gaseous state of aggregation. For instance, we speak of *liquid* oxygen, *liquid* air, *molten* silver chloride, etc. Again, matter may change its *volume* by expansion or contraction; it may change its *texture*, as when a porous solid is fused to a vitreous mass; it may change its *magnetic qualities*, as when a piece of soft iron in contact with a magnet attracts other pieces of iron, etc. It is conventionally agreed to say that in none of these cases of physical change is there any evidence of the formation of a new substance; and that the matter does not lose or change those properties which distinguish it from other forms of matter. **A physical change involves an alteration in the properties of a substance without the formation of a new substance.**

Chemical changes.—When magnesium metal is heated in air, a white powder is formed, and when mercuric oxide is similarly treated, mercury and oxygen are obtained. The action of heat in both cases furnishes forms of matter with very different specific properties from those forms of matter employed at the start. **A chemical change involves the formation of a fresh substance with different**

specific properties from the original substance or substances. In both chemical and physical changes the total *weight* of matter before and after the change remains constant, but in chemical changes alone the *kind* of matter alters.

It is not always easy to distinguish between physical and chemical changes, because the only real distinction between the two turns on the question: is there any evidence of the formation of a new substance during the change? The evidence, as we shall soon see, is not always conclusive. When red mercuric iodide is heated above 126° it turns yellow, and the red colour is resumed on cooling. Two chemical changes are involved, because the new substance produced on heating the iodide re-forms the original compound on cooling. So, when water is heated, complex aggregates of simple particles are riven asunder to again coalesce or associate together on cooling. To the physicist, with his attention fixed on the temperature, or volume, the heating of water is a physical process; to the chemist, with his attention on the nature of the constituent particles, it is a chemical process, because when heated the particles of water become less and less complex as the temperature rises. What we call a body, said E. Mach, is a complex of properties which affects the senses in different ways. . . . One or more properties of the complex are altered in a physical change, while in a chemical change, the whole complex is affected.[3]

The distinction between chemical and physical changes is a subject for the end, not the beginning of chemistry. It is remarkable that the first principles of a science are really the most difficult to grasp, because, said J. F. Ferrier, that which is first in the order of nature, is last in the order of knowledge:

> The apotheosis and final triumph of the human reason will be, when, having traversed the whole cycle of thought, she returns—enriched only with a deeper insight and clearer consciousness—to be merged in the glorious innocence of her primitive and inspired *incunabula*.

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§ 6. Compounds and Mixtures

> The common operations of chemistry give rise in almost every instance to products which bear no resemblance to the material employed. Nothing can be so false as to expect that the qualities of the elements shall be discoverable, in an altered form, in the compound.—W. WHEWELL (1840).

In his *De generatione et corruptione*, Aristotle regarded the difference between what we call to-day physical and chemical mixtures, as dependent on the distinction between what is potential and what is actual. Aristotle recognized a form of combination—now called physical mixture—in which the elements were supposed to exist actually; and another—chemical combination—in which the elements were supposed to exist potentially—*e.g.* the elements oxygen and hydrogen exist actually as such in a free state, but in water they exist potentially, for they can be educed and become actual only by the destruction of the water or of that special form which in water they actually possessed.[1] Consequently it may be said what is actually one substance may be potentially another. In a mere mixture, said Aristotle, you have only mixture, juxtaposition or σύνθεσις; but in chemical combination you have a mingling or μίξις where the elements disappear as such, but they still remain potentially. This kind of combination—chemical combination—is defined very well by Aristotle as "the unification of mingled elements that have changed their nature as elements."

1. The constituents of a compound are combined in definite proportions.—The law of constant proportions is of fundamental importance in forming a conception of the meaning of the term "chemical compound." If a substance produced in different ways be not constant in composition, it is not considered to be a chemical compound, but rather a mixture. R. Bunsen (1846), for example, showed that the proportion of oxygen to nitrogen in atmospheric air is not constant, because the oxygen varies from 20·97 to 20·84 per cent. by volume, by methods of measurement with an error not exceeding 0·03 per cent. Hence, the oxygen and nitrogen in atmospheric air are said to be simply mixed together, and not combined chemically. The so-called eutectic mixtures and cryohydrates show that substances with a definite composition are not always chemical compounds.

2. Compounds are homogeneous, mixtures are usually heterogeneous.—It is comparatively easy to detect particles of sugar and sand in a mixture of the two; and a simple inspection of a piece of Cornish granite will show it is a mixture of at least four constituents—silvery flakes of mica; black patches of schörl; whitish crystals of felspar; and clear glassy crystals of quartz. Although the particles of felspar, mica, schörl, and quartz differ from one another in size and shape, no essential difference can be detected in the composition and properties of different samples of pure quartz, felspar, mica, and schörl. Hence, it is inferred that the sample of granite is a mixture of schörl, felspar, quartz, and mica; and that each of these minerals is a true chemical compound. Very frequently the constituents of a mixture are too small to be distinguished by simple inspection, and the body appears homogeneous. A microscopic examination may reveal the heterogeneous character of the substance. Blood and milk, for instance, appear to be homogeneous fluids, but under the microscope the former appears as a colourless fluid with red corpuscles in suspension; and milk appears as a transparent liquid containing innumerable white globules (fat). Naturally, too, the stronger the magnification, the greater the probability of detecting whether the body is homogeneous or not. Sometimes the microscope fails to detect non-homogeneity under conditions where other tests indicate heterogeneity.

Before constant composition can be accepted as a proof of chemical combination, it must also be shown that the substance is homogeneous. Chemical individuals are homogeneous. **A homogeneous substance is one in which every part has exactly the same composition and properties as every other part.** A substance may have a fixed and constant composition and yet not be homogeneous—*e.g.* cryohydrates and eutectic mixtures to be described later. A substance may be homogeneous, for all we can tell to the contrary, and yet not have a constant composition—*e.g.* atmospheric air; a solution of sugar in water, etc. This simply means that **all chemical compounds are homogeneous, but all homogeneous substances are not chemical compounds.** Indeed, it is sometimes quite impossible to tell by any single test whether a given substance is a mixture or a true chemical compound. It is therefore not satisfactory to classify matter into (i) homogeneous bodies (meaning elements and chemical compounds), and (ii) mixtures, because some mixtures would have to be included with homogeneous bodies. It might also be added that the term *substance* is used in chemistry in two ways: It is employed as a synonym for body or matter, and also for a specific form of matter which is chemically homogeneous.[2]

3. The constituents of a mixture can usually be separated by mechanical processes.—The properties of a mixture of finely powdered iron and sulphur have been used in chemical text-books from the beginning of the nineteenth century in order to illustrate the difference between mixtures and compounds. It would be difficult to find a better example. If a mixture containing, say, 6 grams of iron and 4 grams of sulphur be rubbed in a mortar, (1) the colour of the mixture is intermediate between the colour of the iron and of the sulphur; (2) the particles of iron and sulphur can be readily distinguished under the microscope; (3) most of the iron can be removed without difficulty by means of a magnet; and (4) the two constituents can be separated quite readily by washing the mixture on a dry filter paper by means of carbon disulphide. The sulphur dissolves in the carbon disulphide; and the former can be recovered by evaporating the carbon disulphide from the filtered solution. Sulphur remains behind as a crystalline residue. The metallic iron remains on the filter paper. Here then the constituents of the mixture have been separated by the mechanical processes—(1) magnetting, and (2) the action of solvents.

In 1826, J. J. Berzelius published analyses of the precipitate obtained when hydrogen sulphide is passed into a slightly acid solution of a salt of tellurous acid, and these showed that the proportions of sulphur and tellurium satisfied the law of constant composition, and hence J. J. Berzelius inferred that a true chemical compound—tellurium sulphide—was formed. Accordingly, tellurium sulphide—with its method of formation and a description of its chemical and physical properties—was regularly described in chemical literature. This sulphide is now considered to be a myth, because half a century later, F. Becker (1876) discovered that when the material was digested with carbon disulphide, the sulphur dissolved and tellurium remained undissolved. Hence it was inferred that Berzelius' sulphide is not a chemical individual, but a mixture of sulphur and tellurium in constant proportions. The assumption is of course made that the carbon disulphide does not decompose the precipitate.

It is generally stated that " a solution of sugar or of salt in water is a mechanical mixture because, though homogeneous, the salt or sugar can be recovered unchanged from the water by the mechanical process of evaporation." This is an unwarranted assumption. The salt and water may have combined, and the product of the chemical combination may be decomposed into salt and water during the process of evaporation. The intervention of a **solvent** sometimes decomposes a compound into its constituents, or conversely, causes the constituents of a mixture to combine in such a manner as to produce compounds which previously did not exist.

The so-called mechanical processes of separation usually include: (1) *Magnetting, hand-picking, sieving,* etc. (2) *Elutriation,* or treatment with water flowing at different speeds such that the lighter particles are carried off by the slower streams, and the heavier particles by the faster streams. *Settling* and *lixiviation* are modifications of this type of separation. (3) *Flotation, or fractional levigation.* If some mixtures be placed in liquids of the right specific gravity, the lighter constituents will float and the heavier constituents will sink; and if some mixtures be treated with oils, etc., the oil so affects the particles of some substances that they are buoyed up in liquids where otherwise they would sink—such substances can be separated in this way from other substances not so affected by the oil. (4) *Fractional solution, or crystallization,* depend on differences in the solubility of the constituents in suitable solvents. (5) *Distillation, evaporation, freezing, liquation, melting, diffusion, cupellation,* etc.

4. A mixture usually possesses the common specific properties of its constituents; the properties of a compound are usually characteristic of itself alone.—The properties of a mixture are nearly always additive, *i.e.* the resultant of the properties of the constituents of the mixture. For instance, a *mixture* of equal parts of a white and black powder will be grey, whereas sodium metal and greenish-yellow chlorine gas give a white pulverulent *compound*—common salt.

Specific gravity is a number which expresses how much heavier a given substance is than an equal volume of a standard substance (say water at 4°) taken at a standard temperature and pressure. In the case of gases, either air=unity, oxygen=16, hydrogen =1, or hydrogen=2 is taken as standard; and in the case of liquids and solids, water at +4°, or at 0°, is taken as unity. The great value of specific gravity data lies in the fact that *specific gravity is a number which enables volume measurements to be converted into weights, and weight measurements to be converted into volumes,* for weight=specific gravity ×volume. Specific gravity may thus be regarded as the weight of unit volume if water =unity be taken as a standard, and the weights are reckoned in grams, and volumes in cubic centimetres. There is no need here to elaborate distinctions between density and specific gravity. The density is the mass of unit volume, so that if D, m, and v respectively denote the density, mass, and volume of a substance, $D=m/v$.

The specific gravity of a mixture of equal volumes of two substances of specific gravity 3 and 5 will be 4, because if one c.c. of water weighs one gram, there will be a mixture of 0·5 c.c. weighing 1·5 gram of one substance; 0·5 c.c. of the other substance weighing 2·5 grams; and $1{\cdot}5+2{\cdot}5=4$ grams per c.c. It must be added that the specific gravities of compounds are not necessarily a mean of the specific gravities of their components; indeed, if elements mix without change in volume that fact alone is strong presumptive evidence that a compound has not been formed. It must be added, too, that a small contraction would not be considered a sufficient proof of chemical action because liquid chlorine and bromine contract a little when mixed together, and this reaches a maximum—2 per cent.—when the mixture corresponds approximately with the atomic proportions $Br + Cl$. The specific gravity of compounds may be greater or less than the average specific gravity of their constituents. This shows that the force which causes compounds to unite chemically is not an attractive force independent of the nature of the combining substances. Hence, although this force is sometimes called chemical attraction, the term is used metaphorically. Some properties of compounds —like weight—are additive, for they are the sum of the properties of their constituents.

EXAMPLES.—(1) What is the specific gravity of air containing a mixture of one volume of nitrogen when the specific gravity of oxygen is 16, and the specific gravity of nitrogen 14·01? One-fifth volume of oxygen weighs 3·2 units, and four-fifths volume of nitrogen weighs 11·2 units. Hence, one volume of the mixture will weigh 14·4 units.

(2) Ozonized air—a mixture of air and ozone—has a specific gravity 1·3698, and it contains 13·84 per cent. by weight of air, specific gravity unity, and 86·16 per cent. of ozone. What is the specific gravity of ozone? Here 13·84 grams of air occupy $13{\cdot}84 \div 1$ volumes; and 86·16 grams of ozone occupy $86{\cdot}16 \div x$ volumes, where x denotes the specific gravity of ozone. Hence, 100 grams of ozonized air occupy $100 \div 1{\cdot}3698 = 73$ volumes; and $73{\cdot}00=(86{\cdot}16 \div x)+13{\cdot}84$; or $x=1{\cdot}46$.

The **law of mixtures** may be stated in symbolic form. If a mixture of two substances contains x fractional parts of a substance of specific gravity s_1, it will contain $1-x$ fractional parts of the other substance of specific gravity s_2. Then if S be the specific gravity of the mixture, $xs_1+(1-x)s_2=S$.

EXAMPLE.—Lord Rayleigh and W. Ramsay (1895) found that a mixture of argon and nitrogen had a specific gravity 2·3102 (air unity), and the specific gravity of nitrogen alone is 2·2990; what is the specific gravity of argon if the mixture contained 1·04 per cent. of argon? Here $x=0{\cdot}0104$; $1-x=0{\cdot}9896$; $s_2=2{\cdot}2990$; $S=2{\cdot}3102$. By substituting these data in the above expression, $2{\cdot}2990+(2{\cdot}3102-2{\cdot}2990) \div 0{\cdot}0104=s_1$, or the specific gravity of argon (air unity), is $s_1=3{\cdot}376$.

If a portion of the mixture of finely divided sulphur and iron be placed in a hard glass test-tube and warmed over Bunsen's flame, the contents of the tube begin to glow and a kind of combustion spreads throughout the whole mass. When cold, break the test-tube, and note that (1) the porous black mass formed during the action is quite different from the original mixture; (2) the microscope shows that the powdered mass is homogeneous; (3) it is not magnetic like iron (provided the iron was not in excess); and (4) it gives up no sulphur when digested with carbon disulphide (provided the sulphur was not in excess). These facts lead to the assumption that there has been a chemical reaction between the sulphur and the iron. *When chemical combination occurs, the reacting constituents appear to lose their individuality or identity more or less completely, and each new substance which is formed has its own distinctive properties.*

5. Thermal, actinic (light), or electrical phenomena usually occur during chemical changes.—Attention must be directed to the fact that a great deal of heat was developed during the combustion of the iron and sulphur. The heat required to start the reaction does not account for the amount of heat developed during the reaction. This point is perhaps better emphasized by placing an intimate mixture of powdered sulphur and zinc on a stone slab. After the flame of a Bunsen's burner has been allowed to play on a portion of the mixture for a short time to start the reaction, the zinc and sulphur combine with almost explosive violence. Large amounts of heat and light are developed during the reaction.

If a plate of commercial zinc be placed in dilute sulphuric acid, bubbles of gas are copiously evolved, and if a thermometer be placed in the vessel, the rise of temperature shows that heat is generated during the chemical action. If the zinc be pure, very little, if any, gas is developed. It makes no difference if a plate of platinum be dipped in the same vessel as the zinc, provided the plates are not allowed to come into contact with one another. If the two plates are connected by a piece of copper wire, a rapid stream of gas bubbles arise from the surface of the platinum plate, and some gas also comes from the zinc plate. The platinum is not attacked by the acid in any way, but the zinc is rapidly dissolved. If a voltmeter and shunt or an electric bell be interposed in the circuit between the two plates, the deflection of the needle or the ringing of the bell will show that an electric current passes from the platinum to the zinc. The electric current is generated by the chemical reaction between the zinc and the acid, which results in the formation of zinc sulphate and a gas. The action will continue until all the acid or the zinc is used up.

For convenience, the zinc **plate** of the cell *B* is conventionally called the **positive plate** and is often represented by a short thick line, and the **platinum plate** is likewise called the **negative plate** and is represented by a longer thinner line as illustrated by the plan, Fig. 1. Here *G* represents the voltmeter or galvanometer and shunt. The vessel of acid with its two plates is called a **voltaic cell**, and this particular combination can be symbolized :

. Platinum | Dilute sulphuric acid | Zinc

The voltaic cell originally used by A. Volta (1800) had copper in place of platinum.

The chemical reaction just indicated is far from being the most economical mode of generating electricity, but all the different forms of voltaic cell on the market agree in this : **Electricity is generated during chemical action.**

The development of heat, light, or electrification are the usual concomitants of chemical action. The absence of such phenomena when substances are simply mixed together is usually taken as one sign that chemical action has not taken place. When nitrogen and oxygen are mixed together in suitable proportions to make atmospheric air, there is no sign of chemical action, and this fact is sometimes cited among the proofs that air is a mixture. The argument is not conclusive because the condensation of steam and the freezing of water are usually cited as physical changes although heat is evolved during both transformations.

The tests for distinguishing chemical compounds from mixtures involve answers to the following questions: (1) Is the substance homogeneous ? (2) Are the different constituents united in definite and constant proportions ? (3) Are the properties of the substance additive ? (4) Were thermal, actinic, or electrical phenomena developed when the substance was compounded ? (5) Can the constituents be separated by mechanical processes ? The list does not necessarily exhaust the available tests, but in spite of what we know, there is sometimes a lingering doubt whether a particular substance is a mixture or a true chemical compound. This arises from the fact that some of the tests are impracticable, others are indecisive. Owing to our ignorance, it is not always easy to state " the truth and nothing but the truth." As P. J. Hartog [3] has emphasized, C. L. Berthollet repeatedly asked J. L. Proust to furnish an experimental distinction between chemical compounds and mixtures, but without success. Even to-day, there is no experimental method of generally distinguishing the two. The usual definition is a theoretical distinction based on molecules, but one can also be adapted from the phase rule (*q.v.*).

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§ 7. Circumstantial and Cumulative Evidence

> To find the truth is a matter of luck, the full value of which is only realized when we can prove that what we have found *is* true. Unfortunately, the certainty of our knowledge is at so low a level that all we can do is to follow along the lines of greatest probability.—J. J. BERZELIUS.

Suppose a substance is suspected to be a chemical compound because it appears to be homogeneous; on investigation, we find that it has a fixed definite composition. This verifies our first suspicion, and the joint testimony gives a very much more probable conclusion than either alone. By piling up the evidence in this manner, for or against our suspicion, we can make a chain of circumstantial evidence which enables a highly probable conclusion to be drawn. Each bit of evidence by itself is not of much value, but all the evidence taken collectively has tremendous weight. A successful hypothesis is strengthened by the testimony furnished by diverse facts, and the more numerous and significant the particular instances embraced by the hypothesis the more nearly will their joint testimony mount to the altitude of proof, and plausible hypotheses neatly dovetailed may fit together so well as to apparently strengthen rather than weaken one another. However, it is easy to see that the probability of an hypothesis being valid becomes less as the number of unproved assumptions on which it is based becomes greater. We can even get a numerical illustration. *If* the definite-compound test be right nine times out of ten, the probability that a given substance of definite composition is a true compound is $\frac{9}{10}$; similarly, *if* the homogeneity test be right three times out of four, the probability that the given homogeneous substance is a chemical compound is $\frac{3}{4}$; and the probability that the given homogeneous substance of definite composition is a true compound is $\frac{39}{40}$. **Every bit of additional evidence in favour of a conclusion multiplies the probability of its being correct in an emphatic manner; and evidence against a conclusion acts similarly in the converse way.** Thomas Huxley has stated that one of the tragedies in science is the slaughter of a beautiful hypothesis by one *incongruent fact*; a conclusion based solely upon circumstantial evidence is always in danger of this Damoclean sword.

A writer has said: " When two facts seem to be in conflict, we may be driven to decide which is the more credible of the two." This statement may give rise to a misunderstanding. We cannot admit the possibility of two contradictory facts. Facts can, and often do, contradict hypotheses. Again, a fact is a fact and cannot be disputed; all facts are equally true. Scientific knowledge cannot be arranged in two compartments, one for truth and one for error. The degree of confidence to be placed in a statement can be made only after the evidence has been sifted and weighed. If there be any doubt about the truth of an alleged fact, something is wrong. The laboratory, not the study, is the place to decide if the alleged fact is the result of an incomplete or of a mal-observation. Facts *qua* facts cannot be graded in degrees of probability or credibility, since the difference between *probability* and *certainty* does not represent any quality of the objective fact, it merely describes a state or *attitude of the mind* which ranges from ignorance to knowledge.

§ 8. Analysis and Synthesis

> It is surely not fitting for a chemist to make a large number of experiments with the sole object of rapidly making new products, for he will then overlook phenomena and changes during the operations which might serve as important clues to an explanation of nature's secrets.—M. W. LOMONOSSOFF.

The earliest chemists were familiar with changes due to the *union* of distinct forms of matter to produce a different substance with new properties of its own; and also with the *separation* of two or more definite substances from another quite different substance. The term **spagyric art** (*σπάν*, to separate; *ἀγειρείν*, to assemble), applied to chemistry about the sixteenth century, emphasized the fact that chemical changes were regarded as involving either combinations or decompositions; and as the balance came into more and more extended use, it was gradually recognized that when elements or compounds have suffered a chemical change, the original substances can be recovered, qualitatively and quantitatively the same, by reversing the chemical operation.

The term *synthesis*—from *σύν*, with; *τιθέω*, I place—is employed for the operations involved in the formation of a particular compound from its constituents. The term *analysis*—from *ἀνά*, back; *λύω*, I loosen—is employed for the process of separating the constituents of a compound or mixture. Thus mercuric oxide is broken down into its constituents when heated. The object of the analysis may be to answer the question: What are the constituents of the mixture or compound? The analysis is then said to be *qualitative*. If the relative quantities of the different constituents are to be determined, the analysis is said to be *quantitative*.

There is one period in the history of chemistry when the discovery or synthesis of new substances was considered to be the main aim of the chemist; new substances were made unmeasured and unclothed with properties, which now require to be critically scrutinized all over again. The style of some old text-books on chemistry was not far removed from that of cookery recipe books, for they gave a long dreary list of modes of preparing different substances which led E. J. Mills (1876) to say: Chemistry has become an art of breeding (new compounds). The pioneer work has been useful, for it has furnished modern chemistry with raw empirical material to be worked up into science; indeed a great many more empirical data are now available than chemists have been able to co-ordinate and assimilate into their science. Consequently, we are beginning to recognize the truth of the inspired words of M. W. Lomonossoff, cited above, though written in 1751; and the growing use of tables of measurements and of squared paper in chemical text-books is a sign of the times. In the words of R. Fittig:

> We are now forced to increase the number of compounds, not merely in order to prepare new substances, but in order to discover natural laws.

The solution which remains when the dilute sulphuric acid can dissolve no more zinc, may be filtered and evaporated over a hot plate until a drop of the hot solution crystallizes when placed on a cold glass plate. Crystals of zinc sulphate will separate as the solution cools. By evaporating a large volume of the solution very slowly, crystals over a foot long have been obtained. This experiment illustrates the **synthesis** of zinc sulphate from metallic zinc and dilute sulphuric acid. The earlier alchemists assumed that when a metal dissolves in acid, the metal is destroyed. J. B. van Helmont[1] showed that this assumption is ill-founded because just as when a certain amount of common salt is dissolved in water, the same amount of salt can be recovered from the solvent, so, when silver is dissolved in *aqua fortis*, the metal passes into solution, but is not essentially altered. In the present case, the zinc dissolved by the acid can be recovered as zinc sulphate, and if need be as metallic zinc.

The analysis of aqueous solutions of zinc sulphate by the electric current.—An electric current is developed during the reaction between dilute sulphuric acid and metallic zinc which results in the formation of zinc sulphate and the evolution of a gas.

Place two platinum plates, *E*, Fig. 1, and pure distilled water in the clean glass jar, which will now be called the "electrolytic cell." Connect the two platinum plates with an accumulator or secondary battery, and a voltmeter and shunt as indicated in Fig. 1. The object of the accumulator is to generate an electric current. If the water is pure the needle of the voltmeter moves very little, if at all. Add a concentrated solution of zinc sulphate to the water in the glass jar. The jump of the needle of the voltmeter shows that a current of electricity is flowing through the circuit and hence also through the solution of zinc sulphate. If chloroform, benzene, or an aqueous solution of cane sugar had been used in place of the solution of zinc sulphate in the electrolytic cell, no current would pass through the circuit. Hence, liquids may be either conductors or non-conductors of electricity.

An electric current passing through an aqueous solution of zinc sulphate produces some remarkable changes: (1) a spongy mass of metallic zinc accumulates about one of the platinum plates; (2) if the solution be tested, particularly in the neighbourhood of the other platinum plate, sulphuric acid will be found to be accumulating in the solution during the process of electrolysis; and (3) bubbles of oxygen gas, easily tested by collecting some in a test-tube, rise from the same platinum plate about which the acid accumulates. If the experiment be continued long enough, metallic zinc and sulphuric acid will be produced in appreciable quantities. If the accumulator be disconnected, and the connecting wires be joined together, the zinc will redissolve in the acid, re-producing zinc sulphate; and an electric current will be generated during the dissolution of the zinc.

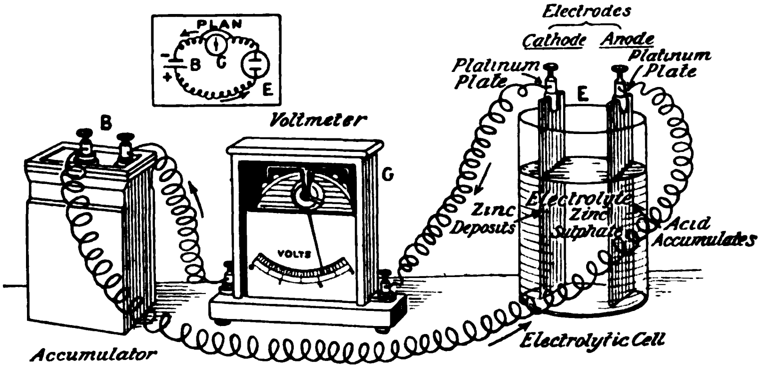

FIG. 1.—Chemical Action induced by Electric Current—Electrolysis.

The process of decomposition or analysis by the aid of the electric current is called **electrolysis.** The liquid which is decomposed is called the **electrolyte.** The passing of the electric current through the conducting copper wires, and through the conducting platinum plates, produces no change in these metals. Hence, we recognize two kinds of conductivity—in one the conducting medium is decomposed by the current—electrolyte; and in the other the conducting medium is not decomposed by the current—non-electrolyte. The plate at which the zinc collects is called the **cathode**—from κατά, down; ὁδός, a path—and the other plate, about which the acid collects, is called the **anode**—from ἀνά, up; ὁδός a path. The anode and cathode together are called the **electrodes.** These terms were suggested to M. Faraday by W. Whewell.[2] With the conventions already indicated as to direction, the electric current is said to enter the electrolytic cell *viâ* the anode, and to leave the cell *viâ* the cathode. The two electrodes are thus "the doors or ways by which the current passes into or out of the decomposing body." It seems as if the electric current first splits the decomposing liquid into two parts which pass to the electrodes. The term **anion**—from ἀνιόν, that which goes up—is applied to those parts of the decomposing fluid which go to the anode; those passing to the cathode are called **cations**—from κατιόν, that which goes down; and when reference is made to both the anions and the cations, the term **ions**—from, ἰών, traveller—is employed. **Ion is thus a general term for those bodies which pass to the electrodes during electrolysis; or for the two parts, no matter how complex, into which the electrolyte is primarily divided during electrolysis.** This notation was proposed by M. Faraday in 1834.

The experiments indicated above illustrate an important principle—**the principle of reversibility: If an antecedent event A produces an effect B, then an antecedent event B will reproduce the effect A.** Thus, chemical action can produce an electric current, and conversely, an electric current can produce chemical action, Fig. 1. The one can undo the work of the other. Many other examples of the principle will be recalled—for example, heat causes gases to expand; conversely, if a gas expands by its own elastic force, the gas will be cooled; a crystal of tourmaline is electrified by uniformly raising its temperature, and Lord Kelvin (1877) showed that the reverse effect can be induced, for a change of temperature occurs when the electrical state of the crystal is changed; etc.

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§ 9. Dalton's Law of Multiple Proportions

> If Dalton's hypothesis of multiple proportions be found correct, we shall have to regard it as the greatest advance chemistry has yet made towards its development into a science.—J. J. BERZELIUS (1811).

The formation of chemical compounds is not a capricious and fortuitous process, but it proceeds in an orderly fashion. Chemical combination is restricted to certain fixed proportions of matter. These limitations appear to have been prescribed by nature as part of her scheme in building the material universe. This fact arrested the attention of J. Rey in 1630. J. Rey's conclusion that in the calcination of the metals "nature has set limits which she does not overstep," agrees with many facts; but there are certain limitations. If one gram of lead be calcined for a long time at 500°, never more than 1·103 gram of a red powder—red lead—is obtained. Here, 64 grams of oxygen correspond with 621 grams of lead. If the lead be calcined at about 750°, one gram of lead will not take up more than 0·078 gram of oxygen to form a yellow powder—litharge; otherwise expressed, 64 grams of oxygen correspond with 828 grams of lead. Here then nature has set *two* limits; lead forms at least two definite oxides—a red oxide stable at a dull red heat, and a yellow oxide stable at a bright red heat. A puce oxide can also be obtained by treating the red oxide with nitric acid, and the puce oxide contains 414 grams of lead for 64 grams of oxygen. The relative proportions of lead and oxygen in the three oxides are as follows:

	Oxygen.	Lead.
Puce oxide (lead peroxide) . .	64	$414 = 207 \times 2$
Red oxide (red lead) . . .	64	$621 = 207 \times 3$
Yellow oxide (litharge) . . .	64	$828 = 207 \times 4$

This means that for a given weight of oxygen, the yellow oxide has four-thirds as much lead as the red oxide, and twice as much as the puce oxide. Similarly, carbon forms two well-defined oxides, called respectively carbon monoxide, and carbon dioxide. In these we have:

	Oxygen.	Carbon.
Carbon dioxide	8	$3 = 3 \times 1$
Carbon monoxide	8	$6 = 3 \times 2$

Perhaps the oxides of nitrogen furnish the most convenient illustration of the principles; at least six have been reported (the real existence of the hexoxide has not been established satisfactorily). In these, the relative proportions of nitrogen and oxygen are as follows:

	Nitrogen.	Oxygen.
Nitrogen monoxide	14	$8 = 8 \times 1$
Nitrogen dioxide	14	$16 = 8 \times 2$
Nitrogen trioxide	14	$24 = 8 \times 3$
Nitrogen tetroxide	14	$32 = 8 \times 4$
Nitrogen pentoxide	14	$40 = 8 \times 5$
(Nitrogen hexoxide	14	$48 = 8 \times 6$)

These six compounds of the same elements united in different proportions form a series of substances so well marked and contra-distinguished that it is questionable if the most acute human intellect would ever have guessed *a priori* that they contained the same constituents. Starting from the compound with the least oxygen, we see that for every 14 grams of nitrogen, the amount of oxygen increases by steps of 8 grams. Accordingly, in all six compounds of nitrogen and oxygen the masses of nitrogen and oxygen are to one another as $m \times 14 : n \times 8$, where m and n are whole numbers.

If an aqueous solution of sodium hydroxide be mixed with successive small quantities of hydrochloric acid, the relative proportions of the two substances can be varied at pleasure, but there is not an infinite variety of compounds of soda and acid. The one sole product of the reaction is sodium chloride, and this has always one fixed and definite composition. If an excess of either acid or soda be present, it is assumed that the excess remains uncombined, because, when the solution is concentrated by evaporation, crystals of sodium chloride are obtained along with the excess of soda or of acid if such be present. If sulphuric acid be substituted for hydrochloric acid, crystals of two distinct and definite products can be separated —the one is called *sodium bisulphate*, and the other *normal sodium sulphate*— according as the acid or alkali is in excess. Here then is an apparent exception to the old saw, *natura non facit saltum*, for nature does make jumps. The leaps are shown in the relations by weights between the soda and acid in the two products:

	Soda.	Acid.		Soda.	Acid.
Sodium bisulphate . .	52 .	160	or	52	160
Normal sodium sulphate .	52	80	or	104	160

Hundreds of cases equally simple might be cited. Similar facts helped to establish an idea deduced by J. Dalton (1802–4) from the atomic theory, and now called **the law of multiple proportions: when one substance unites with another in more than one proportion, these different proportions bear a simple ratio to one another.**

There is no difficulty in tracing the simple ratio $m : n$ in the cases which precede, but it is not always easy to detect the *simplicity* of this ratio in perhaps the larger number of cases. For instance, the ratio $m : n$ for compounds of carbon and hydrogen passes from 1 : 4 in methane, up to 60 : 122 in dimyrcyl, and still more complex cases are not uncommon; the methods of analysis are scarcely sensitive enough to distinguish the comparatively simple triacontane where carbon : hydrogen is as 30 : 62, from hentriacontane where this ratio is 31 : 64. Again, the masses of carbon which unite with one of hydrogen, in methane, ethylene, and acetylene are 3, 6, and 12 respectively, but in methane, ethane, propane, hexane, eicosane, and anthracene, they are 3, 4, 4·5, 5·143, 5·714, and 16·8 respectively. Several attempts have been made to get around the difficulty, by rewording the statement of the law. Thus, B. D. Balareff[1] recommends: "The masses of the different elements in a compound are directly proportional to their equivalent weights or to simple multiples of their equivalents," but E. Puxeddu has discussed these various forms and shown that they are intrinsically different in meaning from the original Daltonian law.

Still the Daltonian law is considered to be so well founded that it can be applied to predict the composition of compounds which have never been prepared. Thus, if an oxide of nitrogen containing rather more oxygen than nitrogen hexoxide be made, it may be predicted that it will contain $7\times8=56$ parts of oxygen for every 14 parts of nitrogen by weight. Again, if a substance be found to contain oxygen and nitrogen, not in the proportion 14 : 8 or a multiple of 8, it is in all probability a mixture, not a true compound. Again, air contains oxygen and nitrogen, but the proportions of nitrogen to oxygen is as 14 : 4·29. This is usually given along with other circumstantial evidence to show the probability that air is a mixture and not a chemical compound.

Are solutions chemical compounds or mixtures ?—Our definitions say mixtures, because the composition of solutions follows neither the constant nor the multiple proportion law. We might easily be led to **reason in a vicious circle**—*in circulo probando*—by a rigid application of the so-called constant and multiple proportion laws. Salts dissolve in water in all proportions up to a certain limiting value. The process of solution, in some cases, seems to be otherwise indistinguishable from chemical combination, and C. L. Berthollet (1803) [2] considered that " solution is a true combination " produced by " a feeble combination which does not cause the characteristic properties of the dissolved body to disappear." It is sometimes said that the process of solution cannot be a case of chemical combination because there are no signs of abrupt *per saltum* changes characteristic of combination in multiple proportions. **The composition of homogeneous solutions can vary continuously within certain limits while a chemical compound has one fixed and definite composition ;** accordingly, we refuse to call substances compounds which do not conform with this definition. Hence, in virtue of arbitrarily compiled definitions, solutions are said to be mixtures, not chemical compounds, and this in spite of the fact that the dissolution of salts may be accompanied by those very phenomena which are usually recognized as characterizing chemical combination —changes in volume, specific heat, temperature, etc.—so that the product of the reaction (solution) has different properties from the average of its components.

One writer has said : " Efforts have been made to find compounds which do not conform to the laws of chemical combination, but all attempts have resulted in failure ; " another writer says, " The law of multiple proportions has been tested by the analysis of thousands of compounds, and, like the law of constant proportions, it is one of the perfect laws from which no deviation has been discovered." From what has been said, **if exceptions to the laws of chemical combination were discovered, chemists would refuse to call them compounds, and the quest for exceptions must therefore end in failure.** For the same reason, the .appeal to experience is useless, it can neither establish nor refute the laws of constant and multiple proportions. More bluntly expressed : a prejudice in favour of the definitions in question may warp the judgment to such an extent as to lead to a denial of the possibility of contradictory phenomena. Such a perversion of the judgment must be detrimental to the progress of science. Hence the danger of cherishing a blind faith in our so-called laws of nature, which, at the present day, are little more than conventional definitions. With such definitions one can easily be deluded with the belief that he worships in the temple of certainty as indicated in the above two quotations.

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§ 10. The History of the Law of Multiple Proportions

Communities of atoms are called chemical combinations, and they possess every degree of stability. The existence of some is so precarious that the chemist in his laboratory can barely retain them for a moment; others are so stubborn that he can barely break them up. The more persistent or stable combinations succeed in the struggle for life and are found in vast quantities as in the cases of common salt and of the combinations of silicon. Stability is a property of relationship to surrounding conditions; it denotes adaptation to environment. Thus, salt is adapted to the struggle for existence on earth, but it cannot withstand the severer conditions which exist on the sun.—G. H. DARWIN (1905).

William Higgins, in his book *A comparative view of the phlogistic and antiphlogistic theories with inductions* (London, 1789), stated that one particle of sulphur and one of oxygen constitute sulphurous acid, while a particle of sulphur and two particles of oxygen constitute sulphuric acid; he also stated that in the compounds of nitrogen and oxygen, the particles of the two ingredients are to each other respectively in the ratio 1 : 1 or 2, 3, 4, or 5. According to C. Daubeny (1850), owing to imperfections in the available chemical analyses, W. Higgins could not have established the proposition as a general rule; and judging from the cursory manner in which Higgins refers to the relation between the proportions in which the constituents of these compounds unite to form compounds, he did not attach much importance to the principle. W. Higgins here appears to have followed Isaac Newton, who, in his *Opticks* (London, 1704), said:

> The smallest particles of matter may cohere by the strongest attractions and compose bigger particles of weaker virtue; and many of these may cohere and compose bigger particles whose virtue is still weaker, and so on for divers successions, until the progression ends in the biggest particles on which the operations in chymistry depend.

It has been suggested that Newton's idea of chemical affinity, dependent on the successive addition of atoms, may have given W. Higgins and J. Dalton the hint which they needed for producing the law of multiple proportions.

Even before John Dalton enunciated the law of multiple proportions, many observations had shown that compounds unite together in more than one proportion. Indeed, it now seems strange that chemists should have failed to notice the law of multiple proportions when numerous analyses were available. E. von Meyer[1] attributes this to the results being calculated in such a way as to hide the law, but A. N. Meldrum has shown that the data were frequently stated in precisely the way required. J. B. Richter (1792) noticed that certain metals have the power of combining with oxygen to form oxides with two different proportions of oxygen; J. L. Proust (1799) obtained a similar result in connection with copper, but partly owing to inaccurate analyses, and partly owing to the fact that he had no guiding principle, he failed to recognize the law of multiple proportions. A. L. Lavoisier (1789) knew that certain substances united with oxygen in several different proportions each of which corresponded with a fixed and constant relation between the weights of the combining elements. F. Clément and J. B. Désormes (1801) also analyzed carbon monoxide and found that it contained just half the amount of oxygen contained in carbon dioxide, and it afterwards struck J. Dalton as curious that the two French chemists did not take more notice of this remarkable result. J. Bostock's analyses of the lead acetates in 1805 were shown by J. Dalton to be in good agreement with the law. Between 1802 and 1807, J. Dalton gave a number of examples of the law of multiple proportions from his own analyses and those of others.

In 1808, in a memoir *On oxalic acid*, T. Thomson[2] showed that, in the formation of the two potassium salts of oxalic acid, the quantity of potash which reacts with a given amount of oxalic acid is in one case just double the proportion in the other; similar results were obtained with the two strontium oxalates—one of which is obtained by saturating oxalic acid with strontia water, and the other by mixing solutions of ammonium oxalate and strontium chloride. It is remarkable, said

T. Thomson, that thefirst contains just double the proportion of base contained in the second. In a paper *On super-acid and sub-acid salts* (1808), W. H. Wollaston also found that the amounts of carbonic acid relative to a given amount of potash in the two potassium carbonates are related as 1 : 1 and 1 : 2. These two papers are of historical interest, and they attracted some attention because, at that time, so few facts were known which could be employed to test the law of multiple proportions. In 1810, J. J. Berzelius began to publish a series of investigations designed "to find the fixed and simple ratios in which the constituents of inorganic nature are combined;" he gave a number of accurate analyses which enabled him to say that if two substances A and B unite in more than one ratio, the various masses of A which unite with a fixed mass of B bear a simple ratio to one another. These experiments played so important a part in establishing the law of multiple proportions that the law itself has been called *Berzelius' law*. Some years later, in reviewing J. Dalton's hypothesis, J. J. Berzelius said:

> It may be doubted if J. Dalton was sufficiently cautious in applying the new hypothesis to the system of chemistry. It appeared to me that the paucity of analyses given in support of the generalization indicated a desire on the part of the experimenter to obtain a certain result; but this is just the attitude which must be avoided when proofs for or against a preconceived theory are sought. Notwithstanding all this, to Dalton belongs the honour of discovery that part of the doctrine of chemical composition termed the law of multiple ratios, which no one had previously observed.

In the celebrated Proust *v.* Berthollet controversy, C. L. Berthollet showed that some elements unite in more than one proportion, and therefore he argued that compounds do not necessarily have a fixed and definite composition; but J. L. Proust demonstrated that when a metal unites with, say, oxygen in more than one proportion, the proportion in which the two elements combine do not vary in a continuous manner, but they proceed in jumps, *per saltum*, and each of the compounds has then a fixed and definite composition. J. L. Proust, however, failed to recognize the law of multiple proportions subsequently developed by J. Dalton.

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§ 11. Richter's Law of Reciprocal Proportions

After long centuries of painful and continuous effort, chemistry has discovered that the elements combine with one another in definite and unchanging ratios of quantity; and that, when their compounds are decomposed, they yield up those identical ratios.—S. BROWN (1843).

Between 1810 to 1812, J. J. Berzelius[1] published the results of a careful study of the quantitative relations of some of the elements—*Versuch die bestimmten und einfachen Verhältnisse aufzufinden nach welchen die Bestandtheile der unorganischen Natur mit einander verbunden sind*. He found that 100 parts of iron, 230 parts of copper, and 381 parts of lead are equivalent, for they unite with 29·6 parts of oxygen forming oxides, and with 58·73 parts of sulphur, forming sulphides. Hence, since 58·73 parts of sulphur and 29·6 parts of oxygen unite respectively with 138 parts of lead, then, if sulphur and oxygen unite chemically, 58·73 parts of sulphur will unite with 29·6 parts of oxygen, or, taking the law of multiple proportions into consideration, with some simple multiple or submultiple of 29·6 parts of oxygen. In confirmation, J. J. Berzelius found that in sulphur dioxide, 58·73 parts of sulphur are united with 57·45 parts of oxygen. The difference between 2 × 29·6 = 59·2 and 57·45 is rather great, but some of the methods of analysis were crude in the time of J. J. Berzelius, and very much closer approximations—very nearly 1 in 50,000—have been obtained in recent years.

J. B. Richter, some twenty years before J. J. Berzelius' work, proved that a similar relation held good for the combination of acids and alkalies. J. J. Berzelius extended J. B. Richter's law to combinations between the elements. The above relations are included in the generalization sometimes called the **law of reciprocal proportions,** or **the law of equivalent weights. The weights—multiple or submultiple—of the various elements which react with certain fixed weight of some other element taken abitrarily as a standard, also react with one another.** If each of two substances, A and B, combines with a third substance C, then A and B can combine with each other only in those proportions in which they combine with C, or in some multiple of those proportions. This law does not mean that if each of the elements A and B combines with C, then the elements A and B will combine with one another. A. L. Lavoisier, in his *Traité élémentaire de chimie* (Paris, **1.** 116, 1789), argued that if two elements have *une grande appétence* for a third element, they should have an affinity for one another: *quæ sunt eadem uni tertio sunt eadem inter se;* and he added: *c'est ce qu'on observe en effet.* Further knowledge has shown that the direct converse is more nearly in accord with facts.

The law of reciprocal proportions may be regarded as a corollary of the law of multiple proportions on the further assumption that A, B, and C can form binary compounds—AB, BC, CA—with one another. Consequently it follows that if a compound be formed by the union of two elements A and B, it is only necessary to find the proportions in which a third element C unites with one of the two elements, say A, to be able to predict the proportions in which C will unite with B; if the law of reciprocal proportions did not hold, this prediction would be impossible. These numerical relations come out very clearly by comparing the proportions in which the different members of a series of elements, selected at random, combine with a constant weight of several other elements. Suppose the analysis of a substance shows that its ingredients are not in those proportions which we should expect from the known combinations of each of its components with another substance, we might safely infer that the substance analyzed is a mixture, and not a single compound. At ordinary temperatures, alcohol mixes in all proportions with ether and with water, but ether and water cannot be mixed in all proportions.

Example.—If one gram of hydrogen unites with eight grams of oxygen to form water, and if one gram of hydrogen unites with 35·5 grams of chlorine to form hydrogen chloride, in what proportion will oxygen and chlorine be likely to combine? Ansr.—If oxygen and chlorine unite at all, they will be likely to do so in the proportion of 8 grms. of oxygen to 35·5 grms. of chlorine, or some multiple or submultiple of this ratio. As a matter of fact, 8 grms. of oxygen do unite with 35·5 grms. of chlorine to produce chlorine monoxide.

The laws of constant, multiple, and reciprocal proportions are wonderful examples of the beauty and harmony of nature; and yet, we have glimmering hints that these are but symbols of a sublimer generalization which, when discovered,

> Will make one music as before
> But vaster.

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§ 12. Combining, Reacting, or Equivalent Weights

> Since it is already settled for us by custom that quantities of different substances are to be called equal when or because they are equivalent gravimetrically, we have no choice. but also, from the chemical point of view, to call those quantities of substance equal which interact in single chemical changes.—E. Divers (1902).

The following numbers represent the results obtained by the chemical analysis of a number of substances selected at random :

		Per cent.		Per cent.
Silicon dioxide	Silicon	46·93 ;	Oxygen	53·07
Hydrogen chloride	Hydrogen	2·76 ;	Chlorine	97·23
Magnesium chloride	Magnesium	25·53 ;	Chlorine	74·47
Water	Hydrogen	11·18 ;	Oxygen	88·81
Silver chloride	Silver	75·26 ;	Chlorine	24·74
Silver fluoride	Silver	70·05 ;	Fluorine	29·95

Analyses are generally calculated so that the sum of all the constituents is 100 (per cent.) within the limits of experimental error. This is simply a convention of the analyst, for the results could be just as intelligibly summed to any other number. Taking any one of the elements as a standard, let us calculate what amount of each of the other elements will combine with a given quantity of the selected element. To save time, take oxygen = 8 as the standard. Starting with silicon, 53·07 parts of oxygen are combined with 46·93 parts of silicon. Consequently, we have the proportion $53·07 : 8 = 46·93 : x$; or, $x = 7·07$, for silicon when the unit oxygen is 8. Similarly, for water, hydrogen is 1·008 when oxygen is 8. Again, in hydrogen chloride when hydrogen is 1·008, chlorine is 35·45 ; in silver chloride, silver is 107·88 when chlorine is 35·45 ; when silver is 107·88, fluorine is 19·0 ; and when chlorine is 35·45, magnesium is 12·16. Collecting together the results of these calculations, we get

Oxygen.	Silicon.	Hydrogen.	Chlorine.	Silver.	Fluorine.	Magnesium.
8	7·07	1·008	34·45	107·88	19	12·16

We have previously obtained a number of results for some metals for the standard oxygen 8 by a different process, and the number for magnesium obtained by an indirect process : Oxygen → Hydrogen (water) → chlorine (hydrogen chloride) → magnesium (magnesium chloride) gives the same results within the limits of experimental error as was obtained by a totally different process. Similar results are obtained in all cases, subject, of course, to the greater risk of experimental error when a long chain of compounds is involved. As a rule, there is no need to follow such an extended series as we have done, for fluorine and for magnesium. Most of the elements unite directly with oxygen ; and with the other elements, one intermediate step usually suffices.

We are therefore able to deduce an important generalization : The combining weights of the elements are specific constants, *i.e.* they change from element to element, but for each element, the combining weight is fixed and invariable. Otherwise expressed: **A number can be assigned to each element ; this number—called the combining, reacting, or equivalent weight—represents the number of parts by weight of the given element which can enter into combination with 8 parts by weight of oxygen, or one part by weight of hydrogen.** All combining weights are relative numbers, and they are conventionally referred to oxygen 8, or hydrogen unity. When an element unites with another element in more than one proportion, the higher proportions will always be simple multiples of the combining weights—one for each element. This is the so-called **law of combining or reacting weights : when a substance enters into chemical combination it always does so in quantities which are proportional to its combining weight ;** and the law of multiple proportions becomes :[1] The quantities of the different elements in a compound are simple multiples of their equivalent weights. The term *equivalent weight* is generally attributed to W. H. Wollaston (1814), and *combining weight* to T. Young (1813).[2]

If the combining weights of the elements are fixed, as they undoubtedly are, and since the elements can combine to form compounds which, in turn, can form compounds with other elements and with one another, it follows that the compounds themselves also have combining weights if they also can enter into chemical combination. Hence the so-called **law of compound proportion—the combining weight of a compound body is the sum of the combining weights of its components.** This deduction from the law of combining weights is as firmly established experimentally as the law of combining weights itself. The neutralization of acids by bases, and numerous other chemical reactions, can be cited in illustration.

The experimental results, indicated in § 2, raise the suspicion that **there is a difference between chemical and gravimetric equality.** E. Divers (1902) has pointed out that in the latter, equal quantities of the different forms of matter are represented by equal weights; whereas, in a chemical sense, equal quantities of matter are the weights or masses of different forms of matter which unite with one another chemically. Consequently, chemical union may be regarded as a measure of the amounts of the different forms of matter which are chemically equivalent. Chemical equality is thus as clearly defined as gravimetric equality. The former is a measure of chemical and the latter a measure of physical phenomena; the latter is wholly independent of, and the former mainly dependent upon the nature of the substances compared.

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§ 13. The Perdurability of Matter

The annihilation of matter is unthinkable for the same reason that the creation of matter is unthinkable, the reason namely that nothing cannot be an object of thought.—H. SPENCER (1851).

I cannot see what warrant there is for assuming that when a weight A of one substance combines with another whose weight is B, the weight of the resulting compound is universally and necessarily $A+B$.—A. D. RISTEEN (1895).

In 1774, A. L. Lavoisier heated tin with air in a closed vessel and found that the weight of the whole system, before and after the calcination of the tin, was the same, thus showing that the whole system neither gained nor lost in weight during the oxidation of the metal. H. Follinus also noticed, in 1613, that mercury could be transformed into the sulphide and the product transformed back to the metal without a change in the weight of the mercury, and Jean Rey was very emphatic, for he said in 1630:

> I now give a flat denial to the erroneous maxim which has been current since the birth of philosophy—that the elements mutually undergoing change, one into the other, lose or gain weight according as in changing they become rarefied or condensed. With the arms of reason I boldly enter the lists to combat this error, and to sustain that weight is so closely united to the primary matter of the element that they can never be deprived of it. The weight with which each portion of matter was endowed at the cradle will be carried by it to the grave.

J. R. Glauber, in his *Furni novi philosophici* (Amsterdam, 1648), described the reaction between a solution of gold in *aqua regia* and a solution of silica in potash lye, by stating:

> The potash paralyses the action of the acid with the result that the gold and silica are respectively deprived of their solvents, and are accordingly precipitated. The weight of the precipitate so obtained is the sum of the weights of the silica and gold originally taken.

These experiments are here mentioned because they emphasize very well the fact that, in spite of the most painstaking care, every time all the substances taking part in a chemical reaction are weighed before and after the change, there is no sign of any alteration in the quantity of matter. The need for assuming the perdurability or constancy of matter emphasized in the so-called *law of the indestructibility of matter* has been recognized from the very beginning of the Ionian physics; for example, Democritus said twenty-four centuries ago: Nothing can ever become something, nor can something become nothing—*ex nihilo nihil fit, et in nihilum nihil potest reverti*. J. B. van Helmont's experiment on the transformation of water into vegetable substances, and the analytical work indicated in connection with the law of constant composition, all tacitly assume the principle of the indestructibility of matter. A. L. Lavoisier is generally supposed to have first demonstrated the law in 1774 by experiments like that cited above, but the law is very much older; it was definitely enunciated in 1756 by M. W. Lomonossoff; and the law must have been at the back of J. Black's mind when he worked on the alkaline earths in 1755. The alleged demonstrations that "in all changes of a corporeal nature, the total *quantity* of matter remains the same, being neither created nor destroyed," illustrate but do not prove the proposition, and they assume that no new substance can possibly come into or go out of existence.

The chemist's law of "indestructibility of matter" really means that, in all cases which have been examined, the total *weight* of the elements in any reacting system remains constant through all the physical and chemical changes it is made to undergo; although the observed facts are better generalized as **the law of persistence of weight: no measurable change in the total weight of all the substances taking part in any chemical process has ever been observed.** If A and B represent respectively the weights of two compounds which form two other compounds M and N; and if the symbol = be employed in place of "produces," and + for "together with," the law of persistence of weights can be symbolized algebraically $A + B = M + N$. If the weight of one of these four compounds be unknown, it can be computed by solving the equation. Chemists constantly use this principle in their work, for, as A. L. Lavoisier said in 1774:

> Experiments can be rectified by calculations, and calculations by experiments. I have often taken advantage of this method in order to correct the first results of my experiments, and to direct me in repeating them with all proper precautions.

When faith in magic was more prevalent than it is to-day, many believed that by some potent incantation or charm, matter could be called out of nothingness, or could be made non-existent.[1] Superficial observation might lead to the belief that a growing tree, the evaporation of water, and the burning of a candle prove the creation and the destruction of matter, but a careful study of these and innumerable other phenomena, has shown that the apparent destruction of matter is an illusion. Matter may change its state as when liquid water is vaporized, and when a candle is burnt. In the case of a growing tree, the nutrition the tree receives from the soil and from the air (carbon dioxide) is overlooked. There is an old demonstration experiment commonly used to illustrate the fact that the apparent destruction of matter in the burning of a candle is illusory:

> A candle is fixed on one pan of a balance below a cylinder fitted with wire gauze, quicklime, soda lime, and glass wool. Weights are added to the right scale-pan until the beam of the balance is horizontal. The candle is lighted. The gases rising from the flame pass through the cylinder where the products of combustion are absorbed by the soda lime. In 3 or 4 minutes the pan carrying the candle is depressed. The increase in weight is due to the fixation of the products of combustion by the soda lime. The products of combustion are formed by the combination of the carbon and hydrogen of the candle with oxygen from the air; this oxygen was not included in the first weighing. The fact illustrated by this experiment is undoubtedly true, but the experiment, though popular, is inconclusive because quicklime and soda lime both absorb moisture and carbon dioxide from the air. Hence, to make the experiment conclusive, it would be necessary to remove these compounds from the air used in the burning of the candle, or else to make due allowance for them. This would involve complicated operations; the test has been made, and the result is qualitatively the same as with the simpler experiment.

Every time a chemical reaction takes place in a closed vessel, which permits neither the egress nor the ingress of matter, the total weight remains unchanged within the limits of experimental error. The more carefully the experiments are made, the more nearly do the values approach identity. Both A. Heydweiller (1901) and J. J. Manley (1912) have tried to find if a loss in weight occurs during chemical action, taking the most extreme precautions known to man in order to secure the utmost accuracy.

The experiment may be illustrated by introducing a solution of silver nitrate into one limb of the λ-shaped tube by means of a suitable funnel and a solution of potassium chromate in the other limb. The opening of the tube is then sealed, the tube is weighed and tilted so as to mix the solutions and start the reaction. The tube is again weighed. When the reaction is over and the conditions of temperature, etc., are the same as when the first weighing was made (for illustrative work on the lecture table, the opening of the tube may be corked and the solutions mixed). Other pairs of solutions are: a solution of potassium iodate, slightly acidulated with hydrochloric acid, and potassium iodide; lead acetate and sodium sulphide; acidulated potassium chromate and sodium sulphite; etc.

No difference has been detailed in the weights of the initial and final products of the reaction within the limits of experimental error—0·000006 grm. After an examination of fifteen different reactions, H. Landolt (1909) [2] again failed to detect a variation in weight; and added, " since there seems no prospect of pushing the precision of the experiments further than the degree of exactness attained, the experimental proof of the law may be regarded as established."

The law of the persistence of weight or the so-called law of the indestructibility of matter means that a **variation in the total weight of the substance taking part in chemical reactions, greater than the limits of experimental error, has never been detected.** Hence it is inferred that **in chemical reactions, substance persists while matter changes its form.** It might also be added that the many and varied determinations of the atomic weights of the elements furnish valuable illustrations of the law in question. The law of persistence of weight is quite empirical like the law of excluded perpetual motion. It is shown later, that if a real difference of weight in the substances taking part in a reaction could be detected, perpetual motion would be possible.

If immeasurably small and trifling differences be taken into consideration, as is sometimes done in theoretical speculations, objection might be made to the statement that the weight of a compound must be equal to the weight of the separate constituent elements, for, as I. Todhunter [3] pointed out in 1876, the converse is the strict truth. The weight of a body depends upon the positions of the component particles, and, in general, by altering the *positions* of the particles, the resultant effect which we call weight is altered, though it may be to but an inappreciable extent. Moreover, even the *time* at which the weighing is performed is theoretically important, for the weight must change to a trifling extent with the changing position of the sun and moon in the sky. It is quite conceivable, too, that the weight of the iron in, say, magnetic oxide of iron might *appear* to be greater than the same amount of iron in, say, potassium ferrocyanide because of the effect of the *earth's magnetic field* upon the former. But if such an effect were observed, it would not interfere with our faith in the law as soon as the disturbing effect was recognized.

H. Spencer considers that all the so-called experimental proofs by weighing tacitly assume the object being proved, since weighing implies that the matter forming the weights remains unchanged in quantity; or as H. S. Redgrove puts it, " weight measures matter because matter is indestructible, and matter is indestructible because weight measures matter."

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§ 14. The Atomic Theory of John Dalton

> It seems probable to me, that God in the beginning formed matter in solid, massy, hard, impenetrable, movable particles, of such sizes and figures, and with such other properties, and in such proportion to space, as must conduce to the end for which He formed them ; and that these primitive particles, being solids, are incomparably harder than any porous body compounded of them, even so hard as never to wear or break in pieces ; no ordinary power being able to divide what God Himself made one in the first creation. . . . The changes of corporeal things are to be placed only in the various separations and new associations and motions of these permanent particles. . . . These principles I consider not as occult qualities, but as general laws of nature by which the things themselves are formed ; their truth appearing to us by phenomena, though their causes be not yet discovered.—ISAAC NEWTON.

The three laws of chemical combination : (1) the law of constant composition ; (2) the law of multiple proportions ; (3) the law of reciprocal proportions ; and the law of the persistence of weight, summarize observed facts. They exist quite independently of any hypothesis we might devise about their inner meaning ; but we have an intuitive feeling that there must be some peculiarity in the constitution of matter which will account for the facts.

An atom is the unit of chemical exchange.—Chemists in imagination have invested matter with a granular structure. Matter is supposed to be discrete, and built up of corporeal atoms. The imagination can subdivide matter indefinitely ; the chemist says that however true this may be, nothing less than an atom ever takes part in a chemical reaction. The atom is the limiting size so far as chemical combination is concerned. An atom cannot be subdivided by any known chemical process. What A. Kekulé wrote in 1867 applies equally well to-day, in spite of some interesting though abortive attempts to eliminate atoms from chemistry. Should the progress of chemistry lead to a different view of the constitution of matter, it will make little alteration to the chemist's atom. The chemical atom will always remain the chemist's unit. As a chemist, continued A. Kekulé,[1] the assumption of atoms appears to be not only advisable but absolutely necessary provided that the term be understood to denote those particles of matter which undergo no further division in chemical transformations.

Compare this hypothesis with observation. Fix the attention on the facts: Elements combine with one another either in amounts which correspond with their combining weights (law of constant composition), or with multiples of their combining weights (law of multiple proportions). Otherwise expressed, definite amounts of matter—the atoms—corresponding with the combining weights, act as chemical units. Reactions between different elements are reactions between these units. Atoms of the same element all have the same constant weight, and atoms of different elements have different weights. All this is in agreement with the law of constant combining weights. It is not the mass *per se* but the constituent particles of the elements which combine each to each.

Fractions of an atom do not take part in chemical changes.—The proportions in which one element combines with another can alter only by steps one atom at a time ; 1, 2, 3, . . . atoms of one element can combine with 1, 2, 3, . . . atoms of another element. This is but one way of stating the laws of multiple and reciprocal proportions. The weight of an atom of each element is a constant quantity, and therefore elements can only combine with each other in certain constant proportions or in multiples thereof. The atoms of the elements are the units from which nature has fashioned all the different varieties of matter in the universe. One atom of mercury unites with one atom of oxygen to form mercuric oxide. If two atoms of mercury united with one atom of oxygen, the result would not be mercuric oxide, but some other oxide of mercury—if otherwise, the law of constant composition would be false. As a matter of fact, such a compound is known, but it is mercurous oxide. Mercurous oxide has its own specific properties which are different from those of mercuric oxide.

The analyses of C. F. Wenzel (1777), J. B. Richter (1791) J. L. Proust (1800), J. Dalton (1801), J. J. Berzelius (1810), and a host of followers are summarized in the laws of chemical change, and these laws, in turn, are rendered luminous and coherent by the hypothesis which assumes that all the different forms of matter in the universe are aggregates of insensibly small homœomeric particles which all the powers of chemistry cannot further subdivide. We thus adopt the view of J. B. Dumas and of M. Faraday that whether matter be atomic or not, this much is certain, granting it be atomic, it would behave in chemical transformations as it does now; A. Kekulé expressed similar views in 1867:

> The question whether atoms exist or not has but little significance from a chemical point of view; its discussion belongs rather to philosophy. In chemistry we have only to decide whether the assumption of atoms is a hypothesis adapted to the explanation of chemical phenomena, . . . and to advance our knowledge of the mechanism of chemical phenomena.

It remains to find the canons by which chemists have been able to fix the relations between the weights of the atoms of different elements.

Atomic weights are relative.—The combining weights of the atoms can be expressed in any desired units; it is quite immaterial whether a grain or a ton be imagined. **In dealing with combining or atomic weights, the conception of absolute quantity is irrelevant.** Given sufficient oxygen, 100 tons, kilograms, pounds, grams, or grains of mercury will give respectively 108 tons, kilograms, pounds, grams, or grains of mercuric oxide—no more, no less. Several different lines of argument, given by O. E. Meyer in his *The Kinetic Theory of Gases* (London, 1899), indicate that there are about 1280,000000,000000,000000 or $12\cdot8 \times 10^{20}$ hydrogen atoms in a milligram, so that the weight of an atom of hydrogen is not far from $\frac{1}{1280,000000,000000,000000}$th or $12\cdot8 \times 10^{-20}$ of a milligram. This estimate may not be exact, and it is not here emphasized as a fact, although it is probably not far out. Suppose for the sake of illustration it is true, then, with the evidence so far adduced, an atom of mercury will weigh $100 \times 12\cdot8 \times 10^{-20}$th milligram, and an atom of oxygen $8 \times 12\cdot8 \times 10^{-20}$ mgrm. We do not know the absolute weights with any degree of precision, but the relative weights are known with a fair degree of accuracy. Given the relative weights, and the weight of an atom of one of the elements, the absolute weights of the atoms of all the other elements can be computed, for the masses of the other elements bear the same ratios to one another that are assigned to them in the table of atomic weights. The ratio of the weights of the different kinds of elements in a compound represents the relation between the weights of the several different kinds of atoms (or aggregates of atoms) which make up the compound.

J. Dalton's atomic hypothesis.—It is impossible to say who invented the atomic theory, because it has grown up with chemistry itself. It certainly did not arise by one effort of modern science, as W. Nernst supposes, "like a phœnix from the ashes of the old Greek philosophy." In the work of William Higgins and his predecessors, the hypothesis was little more than an inanimate doctrine. It remained for Dalton to quicken the dead dogma into a living hypothesis. John Dalton's atomic hypothesis explains the structure of matter and of chemical combination upon the following postulates, which may be regarded as a very brief statement of what is called Dalton's atomic theory:

> 1. Atoms are real discrete particles of matter which cannot be subdivided by any known chemical process. 2. Atoms of the same element are similar to one another, and equal in weight. 3. Atoms of different elements have different properties—weight, affinity, etc. 4. Compounds are formed by the

union of atoms of different elements in simple numerical proportions—1 : 1; 1 : 2; 2 : 1; 2 : 3; etc. This led Dalton to deduce the law of multiple proportions which was later confirmed by experiments. 5. The combining weights of the elements represent the combining weights of the atoms.

J. Dalton seems to have assumed that the atoms are in perfect repose, unless disturbed by mechanical or chemical forces.[2]

Some defects in Dalton's atomic theory.—The hypothesis of Dalton's respecting atoms, and more particularly atomic weights, is not quite that which prevails in modern chemistry. According to the atomic theory: **an atom is the smallest particle of an element which can enter into or be expelled from chemical combination.** The assumption that the combining weights of the elements represent the combining weights of the atoms has caused some difficulty. How is the smallest combining weight of an atom to be fixed? In carbon monoxide, for example, we have oxygen and carbon in the following proportions by weight: Oxygen : carbon 8 : 6, and in carbon dioxide: Oxygen : carbon 8 : 3 or as 16 : 6. What is the atomic weight of carbon if the atomic weight of oxygen is 8? Obviously, the evidence now before us would be consistent with many different views. Carbon monoxide may be a compound of one oxygen atom with two carbon atoms each with a combining weight of 3; or a compound of one oxygen atom with one carbon atom with a combining weight of 6. In the latter case, carbon dioxide is a compound of one carbon atom of combining weight 6 with two oxygen atoms, and the same combining weights would have been obtained if any number n of carbon atoms were combined with $2n$ oxygen atoms. Again in, order to ascertain the complexity of a combination of atoms, J. Dalton[3] stated that

> If only one combination of two elements exist, it must be presumed to be binary; if two combinations exist, one will be a binary compound and the other a ternary compound.

This hypothesis was also adopted by J. J. Berzelius,[4] but in the case of the so-called carbon dioxide or carbon monoxide, there is at present nothing to show which is the binary and which the ternary compound. Similar difficulties arise when the idea of atoms so far developed is applied to other combinations of the elements. There is therefore some confusion. The concept of the atom becomes more or less indistinct and vague when the attempt is made to develop a consistent system on the basis of the atomic hypothesis as propounded by Dalton. **Dalton's theory is defective because it lacks a standard for fixing the atomic weights of the different elements.** The difficulty was removed only when chemists had learned the value of Avogadro's hypothesis in fixing a definite standard for evaluating atomic weights. Chemists then conventionally came to an understanding as to the relation between the composition and specific gravity of a vapour or gas.

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§ 15. The Evolution of the Atomic Theory up to the time of Dalton

> Il est regrettable que les traitées modernes négligent l'histoire et présentent comme des monuments achevés des sciences en perpétuelle évolution.—F. OSMOND (1906).

The atomic theory seems to have been born in the twilight of history. The earliest philosophers of the Eastern fore-world made many quaint guesses at the constitution of matter. Among these guesses, there is one which appears to have been promulgated by Kanada as a doctrine among the ancient Hindus [1] long prior to the rise of Grecian philosophy. This doctrine assumed that the world of sensible matter is produced or constituted by the concourse of substantial or concrete monads or atoms moving more or less freely about one another. A similar guess was propounded by Leucippus about 450 B.C., and advocated as a doctrine about thirty years later—420 B.C.—by his disciple Democritus.[2] About 300 B.C. the same guess was elaborated by Epicurus into a definite system, and the same guess still lives, more or less modified, in modern chemistry.

From the imperfect fragments which have been transmitted to us, it is scarcely possible to dissociate the ideas of Leucippus from those of Democritus. Epicurus taught Democritus' views, which thence passed to Lucretius, and were summarized in an immortal poem *De rerum natura* (written about 80 B.C.). According to C. Daubeny,[3] a Phœnician named Mochus promulgated similar views before Leucippus time; and it has also been stated that the ideas of Pythagoras (*c.* 500 B.C.) about corpuscular monads, mentioned by Aristotle, in his *Metaphysics* (**12**. 6), were derived from the Egyptian priests. E. Zeller [4] has argued that the available evidence does not justify the assumption that Leucippus derived his hypothesis from Mochus, and he further considers that Democritus adopted nothing but mathematics from Pythagorean sources, since there is no affinity between the two philosophies. Democritus, however, travelled extensively on his own account; and it is probable that he visited the Egyptian priests, the Chaldeans, and the Persians. There are traces of atomistic views in the writings of Empedocles (*c.* 500 B.C.), Anaxagoras (*c.* 450 B.C.), and Heracleitus (*c.* 450 B.C.). P. Gomperz [5] has emphasized his belief that the atomic theory of Leucippus and Democritus was a resultant of the labours of their predecessors, and that it "was the ripe fruit on the tree of the old doctrine of matter which has been tended by the Ionian philosophers."

In the fifth century before Christ, Anaxagoras' attempt to compress an inflated bladder led him to recognize the impenetrability of matter. If matter be continuous it was not so easy to see how movement without appreciable hindrance could be possible in air, and yet be impassably resisted by a rock. The atomic theory of Leucippus provided a satisfactory explanation. Motion in a medium is easy or difficult according to the disposition of the constituent atoms which makes it easy or difficult for the atoms to be displaced. The Hellenic theory of atoms seems also to have been opposed as a counter-proposition to the idea of Zeno (*c.* 460 B.C.) that matter is infinitely divisible. Zeno argued that whatever be the dimensions of matter, it must be geometrically divisible, for however small a particle may be, it can be supposed to be halved, quartered, or split into a thousand parts. The atomicians, however, postulated that the monads or atoms could not be cut, bruised, broken, or frayed; otherwise they would wax old, crumble, and lose their shape. Consequently, substances formed by the aggregation of wearable atoms would gradually change their characteristics. Water and earth, said Isaac Newton, composed of old worn particles would not be the same in nature and texture as water and earth originally composed of unworn particles. There is no reason to suppose that there has been any change in the character of water and earth in past ages, and hence, in order that nature may be enduring and permanent, it was inferred that the atoms must be adamantine and perdurable. Zeno's concept is quite different from that of the atomicians'. The latter could have readily admitted with Zeno that atoms are capable of geometrical subdivision, but reserved the right to hypothecate that further subdivision does not occur. Consequently, with those apparently opposing tenets, said S. Brown, the disputants did not argue in answer to one another at all. They crossed swords without touching one another. Each fought his own shadow.

Among other names for atoms, Democritus employed ἄτομα, but Lucretius does not use this term. Lucretius' favourite expression is *primordia* or *rerum primordia*, which is translated "the first elements" or "the first beginnings of things." Lucretius also uses *figuræ*, *semina*, or *semina rerum*—the seeds of things; *materia corpora genitalia* or *prima*; *corpora* or *corpora rerum* or *corpora materia*; *elementa*; and *corpuscula*—but never atom. Cicero used Democritus' term *atomi* for these primitive corpuscles. The derivation of the term *atom*—ἀ, not; τέμνω, I cut—means something which cannot be subdivided. The present-day definition of an atom says nothing about its ultimate nature. John Dalton certainly considered the atom to be indivisible, and this is illustrated by his favourite aphorism: "Thou knowest no man can split an atom." Thomas Graham (1842) defined the atom, not as a thing which cannot be divided, but as one which has not been divided. The term atom was once used for a small interval of time—according to Ducange, the $\frac{15}{54}$th part of a second—a moment. Thus, in the Greek text of Paul's *First Epistle to the Corinthians* 15. 52), there is an expression: ἐν ἀτόμῳ, ἐν ῥίπῃ ὀφθαλμοῦ—in an atom or moment, in the twinkling of an eye.

Concrete indivisible atoms.—The more characteristic features of the Hellenic theory of the atomic constitution of matter, as expounded by Lucretius,[6] are best illustrated by quotations from H. A. J. Munro's translation of Lucretius' poem.

1. Matter is discrete, not a continuum.

> However long you may hold out by urging many objections, you must needs in the end admit that there is a void in things. . . . Wherever there is empty space which we call void, there body is not. . . . If there were no empty void, the universe would be solid . . . for without void, nothing seems to admit of being crushed in, broken up, or split in two.

2. All substances are formed of solid atoms which are separated from one another by void space. Each atom is a distinct individual.

> First beginnings are of solid singleness, massed together and cohering closely by means of least parts, not compounded out of a union of those parts, but, rather, strong in everlasting singleness. . . . First beginnings are strong in solid singleness, and by a denser combination of these all things can be closely packed and exhibit enduring strength.

3. The atoms are impenetrable, indivisible, and indestructible. They are as perfect and fresh to-day as when the world was new.

> There are therefore certain bodies which can neither be broken in pieces by the stroke of blows from without, nor have their texture undone by aught piercing to their core, nor give way to any other kind of assault. . . . Since by the laws of nature it stands decreed what these things can do and what they cannot do, and since nothing is changed, but all things are constant . . . they must sure enough have a body of unchangeable matter also. Therefore, if first bodies are as I have shown solid and without void, they must be everlasting. . . . For if the first beginnings or things could in any way be vanquished and changed it would then be uncertain too what could and what could not rise into being, in short on what each thing has its powers defined, its deepest boundary mark. . . . From these parts nature allows nothing to be torn, nothing further to be worn away, reserving them as the seeds of things.

4. The atoms differ from one another in shape, size, and weight.

> Next in order apprehended of what kind and how widely differing in form are the beginning of things, how varied by manifold diversities of shape. . . . The things which are able to affect the senses pleasantly consist of smooth round elements; while all those, on the other hand, which are found to be bitter and harsh, are held in connexion by particles that are more hooked and for this reason are wont to tear open passages in our senses, and on entering in to break through the body. . . . And quickly as we see wines flow through a strainer, sluggish oil on the other hand is slow to do so, because sure enough it consists of elements either larger in size or more hooked and tangled in one another. . . . Again things which look hard and dense must consist of particles more hooked together, and be held in union because compacted throughout with branch-like elements. . . . Those things which are liquid and of fluid body ought to consist more of smooth and round elements.

5. There is a finite number of different kinds of atoms, but an infinite number of homœomeric atoms of each kind.

> The first beginnings of things have different shapes, but the number of shapes is finite. If this were not so, then once more it would follow that some seeds must be of infinite bulk of body. . . . Wherefore you cannot possibly believe that seeds have an infinite variety of forms, lest you force some to be of monstrous hugeness. . . . The first beginnings of things which have a like shape one with another, are infinite in number. For since the difference of forms is finite, those which are like must be infinite or the sum of matter will be finite, which I proved not to be the case. . . . It is clear then that in any class you like the first beginnings of things are infinite, out of which all supplies are furnished.

6. The properties of all substances depend upon the nature of the constituent atoms, and the way the atoms are arranged. In his *Metaphysics*, Aristotle illustrated the effect of shape, arrangement, and position by examples borrowed from the Greek alphabet, and his illustration may be interpreted: The difference of *shape* is illustrated by the opposition of A and N; the difference of *arrangement* or contact, by AN and NA; and that of *position*, by the conversion of N to Z by turning the former on its side.

> It often makes a great difference with what things and in what position the same first beginnings are held in union and what motions they mutually impart and receive; for the same make up heaven, sea, lands, rivers, sun; the same make up corn, trees, living beings; but they are mixed up with different things and in different ways as they move. Nay, you see throughout even in these verses of ours many elements common to many words, though you must needs admit that the lines and words differ one from the other both in meaning and in the sound wherewith they sound. So much can elements effect by a mere change of order, but those elements are the first beginnings of things can bring with them more combinations out of which different things can severally be produced.

7. The atoms are in constant motion; motion is an inherent property of atoms.

> Solid bodies of matter fly for ever unvanquished through all time. . . . The first beginnings of things move of themselves. . . . No rest is given the first bodies through the unfathomable void, but driven on rather in ceaseless and varied motion they partly, after they have been pressed together, rebound leaving great spaces between, while in part they are so dashed away after the stroke as to leave but small spaces between. . . . Herein you need not wonder at this, that though the first beginnings of things are all in motion, yet the sun is seen to rest in supreme repose, unless where a thing exhibits motions with its individual body. For all the nature of first things lies far away from our senses beneath our ken; and therefore since they are themselves beyond what you can see, they must withdraw their motions from sight also; and the more so that the things which you can see, do yet often conceal their motions when a great distance off. For often the woolly flocks as they crop the glad pastures on a hill, creep on whither the grass jewelled with fresh dew summons and invites each, and the lambs, fed to the full, gambol and playfully butt; all which objects appear to us from a distance to be together and to rest like a white spot on a green hill.

8. Combination or aggregation is due to the coalescence of moving particles. Democritus supposed the particles to move in straight lines, and the collisions to be accidental. In order to better the account for the coalescence, Epicurus supposed that the atoms moved in paths which deviated slightly from the rectilineal.

> When bodies are borne downwards sheer through void, at quite uncertain times and uncertain points of space they swerve a little from their equal poise; you just and only just can call it a change of inclination. If they did not swerve, they all would fall down, like drops of rain, through the deep void, and no clashing would have been begotten, nor blow produced among the first beginnings; thus nature never would have produced aught.

A. A. Cournot[7] believes that none of the ideas bequeathed to us by the ancients has had a greater or even a similar success to the atomic doctrine of Leucippus and Democritus. So far as the experimental evidence available to the Grecian philosophers in support of this particular doctrine is concerned, its long life, in the form of the chemist's atomic theory, can be attributed to chance, for if a sufficient number of thinkers speculate about the structure of matter, without checking their conclusions with facts, it is but in accord with the laws of probability that some of them will approximate to the truth. As C. Daubeny has said:

> The earliest philosophers appear to have often lighted upon the most sublime truths, astonishing us with an intermixture of the noblest views of nature with the most crude and vulgar conceits, and often leaving to their successors little more than the task of selecting from the mass of error, the grains of truth which are disguised by and confounded with it.

The modern theory, unlike the older speculation, is based upon the observed laws of chemical change, and can scarcely stand apart from them.

There is almost an historical continuity in the treatment of the doctrine from Leucippus to John Dalton (1801)—with a break during the dark ages. The atomism of Democritus and Epicurus grew into the corpuscular mechanics of the seventeenth century, and into the atomic theory of the nineteenth century. Francis Bacon[8] was one of the first of the Renaissance philosophers of the seventeenth century to recognize the importance of Democritus' doctrine of atoms; but he later regarded the study as unprofitable:

> Men do not cease from dissecting nature until they arrive at the atom; a thing which if true, can do but little for the welfare of mankind.

The atomic hypothesis was accepted with minor modifications by Robert Boyle,[9] who said in his *Sceptical Chymist* (Oxford, 1661):

> There are clusters wherein the particles do not stick so close together, but they may meet with corpuscles of another denomination, disposed to be more closely united with them than they were among themselves; and in such case, two corpuscles thus combining, losing that shape, size, or motion upon whose account they exhibited such a determinate quality, each of them really ceases to be a corpuscle of the same denomination as it was before; and from the coalition of these, there may result a new body, as really one as either of the corpuscles before they were confounded.

If this were paraphrased into the language of to-day it would be taken to embody the idea of a chemical affinity uniting atoms into compounds. Robert Hooke (1665), John Mayow (1669), Nicolas Lemery (1675), and most of the philosophers of the Renaissance—R. Descartes (1644), Pierre Gassend (1647), C. Huygens (1690), G. Amontons (1702), N. de Malebranche (1712), and M. N. Lomonossoff (1741)—were atomicians.[10] René Descartes seems to have believed in the existence of atoms, but he substituted in place of an interatomic void, a subtle imponderable atomic fluid, the *materia cœlestis*, which occupied the space between the atoms of matter. Therefore, while a given space could be freed from ponderable matter, the *materia cœlestis* still remained. This is equivalent to the more modern statement that an æther-vacuum is impossible. N. de Malebranche (1712) dogmatically asserted that

> The *matière subtile* or *éthérée* is necessarily composed of *petits tourbillons*—small vortices—which are the natural cause of all material changes, and of the most general phenomena—*e.g.* hardness, fluidity, weight, buoyancy, the refraction and reflection of light, etc.

Isaac Newton (1675)[11] assumed that the atoms of a compound were held together by attractive forces so long as they did not approach within a certain limiting distance; within this limit repulsive forces were supposed to come into play which prevented absolute contact and gave rise to the resilience of the particles during impact. Newton also tried to explain Boyle's law on the assumption that gases were made up of mutually repulsive particles, which recede from one another as far as the pressure of the superincumbent atmosphere will let them; and he referred chemical changes to different associations of atoms.

R. Kirwan (1783), Bryan Higgins (1776), and William Higgins (1789),[12] with more or less confidence, explained the constant composition of salts in terms of atoms. Bryan Higgins recognized seven elements composed of "atoms homogeneal, impenetrable, immutable, in figure inconvertible, and globular;" and he appears to have held the view that two different atoms combine in the proportions of 1 : 1, and in that proportion only. William Higgins imagined a combination in multiple proportions, but believed that the binary combination 1 : 1 was the most stable. Thus, he said:

> In volatile vitriolic acid, a single ultimate particle of sulphur is united only to a single particle of dephlogisticated air; and in perfect vitriolic acid, every single particle of sulphur is united to two of dephlogisticated air, being the quantity necessary to saturation.

This idea appears to have arisen in Higgins' mind because it was assumed that atoms of the same kind are mutually repulsive and that a combination containing two similar atoms would have a greater tendency to disruption on account of the assumed mutual tendency of similar atoms to break apart. About this time, W. Nicholson [13] defined chemistry as a science of atoms, for he said :

> Chemistry, as a science, teaches the methods of accounting for the changes produced in bodies by the motions of their parts amongst each other which are too minute to affect the senses individually ; and, as an art, it consists in the application of bodies to each other in such situations as are best calculated to produce those changes.

Then followed John Dalton's announcement of the atomic theory and the law of multiple proportions at a lecture delivered at the Royal Institution, London, in 1803–4 ; the theory was described in T. Thomson's *System of Chemistry* (Edinburgh, 1807), and by Dalton himself in the following year, in the first part of his remarkable book, *A New System of Chemical Philosophy* (Manchester, 1808–10), where he says :

> It is one great object of this work to show the importance and advantage of ascertaining the relative weights of the ultimate particles, both of simple and compound bodies, the number of simple elementary particles which constitute one compound particle, and the number of less compound particles which enter into the formation of one or more compound particles.

Quite a number of different suggestions have been made to explain how Dalton came to give to the atomic hypothesis he had no doubt imbibed from Isaac Newton, the distinguishing features which led to its being called Dalton's atomic theory. Dalton's own accounts of the genesis of the hypothesis are not always consistent, so much so, that H. Debus [14] has breathed an improbable suspicion that J. Dalton deliberately made a mystery of the evolution of the theory. In his *System of Chemistry*, 1807, T. Thomson stated that the theory was suggested to J. Dalton by a comparison of the analyses of marsh gas and olefiant gas ; but J. Dalton's notebooks show that the experiments on these gases were made in the summer of 1804, nearly a year after the first table of atomic weights had been compiled. H. E. Roscoe and A. Harden,[15] in opposition to H. Debus,[16] attempted to prove that Dalton was influenced in the development of the theory by experiments on the diffusion and solubility of gases, which led him to try to find the relative sizes of the particles of different gases. This involved a determination of the relative weights of the particles of each gas, which, in turn, necessitated a determination of the chemical composition of the gas. The results so obtained led J. Dalton to deduce the atomic theory. In a series of important papers on *The Development of the Atomic Theory* (1909–11), A. N. Meldrum [17] showed that the facts admit of a somewhat different interpretation.

At the beginning of the nineteenth century, the diffusion of gases was supposed to be the work of chemical affinity, and the oxygen and nitrogen in the atmosphere were supposed to be chemically combined. In 1801, J. Dalton [18] argued that the phenomenon is physical and that the mixture of oxygen and nitrogen gases in atmospheric air is mechanical because the "nitric acid gas" formed by the union of these two elements is "an elastic fluid totally distinct in its properties from either of the ingredients." Dalton frequently quoted Newton's views on the attraction and repulsion of atoms, and, in a lecture in 1810, Dalton explained that he did not at first consider a possible difference in the sizes of the particles of the two elastic fluids, but he said that in 1805, he considered that the sizes must be different because no equilibrium can be established by particles of different sizes pressing against each other. In Dalton's notebooks, these views are dated Sept. 14th, 1804. According to H. E. Roscoe and A. Harden, these dates are wrong, for they assume that, having established a difference in the sizes of the particles of the elastic fluids,

> Dalton thence proceeded to determine the relative *sizes* and *weights*, together with the relative *numbers* of atoms in a given volume. This led the way to the combination of gases. . . . Thus a train of investigation was laid for determining the *number* and *weight* of all chemical elementary principles which enter into any sort of combination with one another.

Otherwise expressed, it is assumed that Dalton *first* satisfied himself that the atoms of different gases have different sizes, and *then* devised the chemical theory.

A. N. Meldrum (1911), however, has shown that J. Dalton did not conclude that the atoms of different gases were different in size until *after* the chemical theory had been formed. In J. Dalton's notebook, dated Sept. 6th, 1803, the first table of atomic weights appears in the annexed form :

Ult. at.	hydrogen	1	Ult. at.	nitrous oxide	13·66
,,	oxygen	5·66	,,	nitric acid	15·32
,,	azote	4	,,	sulphur	17
,,	carbon	4·5	,,	sulphurous acid	22·66
,,	water	6·66	,,	sulphuric acid	28·32
,,	ammonia	5	,,	carbonic acid	15·8
,,	nitrous gas	9·66	,,	oxide of carbon	10·2

A. N. Meldrum has also indicated that John Dalton probably arrived at the law of multiple proportions as a result of experiments on the combination of nitric oxide and oxygen whereby he was able to write in his notebook, Aug. 4th, 1803, that 100 measures of air could take 36 or 72 of nitric oxide. J. Dalton then probably framed the rule that atoms combine in the proportion 1 : 1, and on considering the more complex cases, he tested the possibility of combination in other proportions by the available analytical data, so that, in the following month, Sept. 6th, he was able to draw up the table of atomic weights.

Punctual atoms or centres of force.—The Lucretian school has never receded from the primary assumption that matter is composed of ultimate, solid particles—potentially divisible, but physically incapable of further subdivision ; but another school of atomicians has assumed that there is no limit to the divisibility of the particles of matter, and that the smallest conceivable particle still consists of an infinitude of smaller particles. René Descartes has said :[19]

> It is very easy to recognize that there can be in substance no atoms, that is to say parts of bodies or matter which are by nature indivisible, as some philosophers have imagined ; in as much as however small we may suppose these parts to be, yet, since they must be extended we see there is not one of them that cannot be further divided into two or more others, of smaller size, and is accordingly divisible ;

and I. Kant (1781), in his *Observations on the Second Antinomy*,[20] argued that those who object to the infinite sub-divisibility of matter do not recognize the clearest mathematical proofs as propositions relating to the constitution of space. Zeno (460 B.C.) previously argued that matter must be made up of indivisible and unextended points. Some such particles as these—*points de substance*—were imagined by G. W. von Leibniz (1695), and called **monads**—μονάς, a unit—a term which was employed by Pythagoras, and which is said to have been suggested to Leibniz by G. Bruno's *De monade* (Frankfurt, 1591), or during his intercourse with F. M. van Helmont. Leibniz's ideas were described in his posthumous *La monadologie* (Berlin, 1840) :[21]

> Material atoms, still composed of parts, are contrary to reason, for the inviolable attachment of one part to another—if we could reasonably conceive or suppose such a thing—would not destroy their diversity.

Newton himself seems to have had some misgivings about the indivisibility of atoms, for he said in his *Philosophiæ naturalis principia mathematica* (Londoni, 1687) :

> Whether these parts, distinct, and as yet undivided by material forces, are able to be divided and sundered in their turn is uncertain.

The main difficulty with Leibniz's animated points is to understand how a body can possess extension in space if it be made up of components which have no spatial dimensions, for, as J. C. Maxwell (1877) observes, that which has neither figure nor extent can have no existence. The Democritians—Newton, etc.—assumed that it is necessary to suppose that the ultimate particles must possess some bulk, otherwise they could not produce bulk by aggregation ; on the contrary, Zeno, Wolf, Schelling, etc., do not consider this assumption necessary, for a number of self-repulsive points in limited space can also communicate bulk to the body they compose. For instance, if a point were endowed with the irresistible power of repelling the hand from a radius of one inch, the result would be the same as if the hand were to grasp a 2-inch ball of adamant.

R. J. Boscovich,[22] in 1763, attempted to improve Leibniz's ideas by assuming that matter is made up of unextended points which mutually *attract* one another, but which never come into contact because, as soon as they approach within a certain limiting distance, they mutually *repel* one another; the repulsive forces increase more and more in intensity as the points approach closer and closer together, so that they never come into absolute contact. Extension in space is an effect of this repulsion, and the aggregation of matter is an effect of the attractive forces. He said:

> Matter is not mutually penetrable, but each atom-centre extends, so to say, throughout the whole of the solar system, yet always retaining its own centre of force.

R. J. Boscovich assumed that when attraction predominates, the body is a *solid*, and a *gas* when repulsion predominates, while if the two forces are more equally balanced, a *liquid* results.

A great deal has been written in favour of both hypotheses—Newton's that an atom is a solid nucleus surrounded by spheres of repulsive and attractive forces; and Boscovich's that an atom is a mathematical point with a sphere of a repulsive force surrounded by a sphere of an attractive force. In 1844, in *A speculation touching electrical conduction and the nature of matter*, M. Faraday [23] points out that in the ordinary atomic theory it is assumed that solids, liquids, and gases are composed of material atoms occupying a definite space, and are held together by cohesive forces; and further, in order to explain the contraction in volume which occurs on cooling or compressing solids, liquids, or gases, it is assumed that atoms cannot be in actual contact, but must be separated by an intervening space. These assumptions involve the following dilemma: If space is a non-conductor of electricity in non-conducting bodies, and a conductor in conducting bodies, we are compelled to assume that space possesses opposite and contradictory qualities, for if space be an insulator, it cannot exist in conducting bodies, and if it be a conductor, it cannot exist in insulating bodies. Hence, M. Faraday wrote:

> I feel a great difficulty in the conception of atoms of matter with intervening spaces not occupied by the atoms. . . . The atoms of Boscovich appear to me to have a great advantage over the more usual notion. His atoms are mere centres of forces or powers, not particles of matter in which the powers themselves reside.

There is a similar dilemma involved in connection with the transmission of light, and the physicists, A. M. Ampère (1835), A. L. Cauchy (1836), and M. Seguin (1853), have accordingly regarded atoms as centres of force infinitely small, without extension in space. Cauchy's punctual atoms were supposed to vibrate differently in different directions so that the elasticity varied accordingly. J. F. Redtenbacher (1857) [24] regarded this as an impossible assumption. The atoms, said Ampère, regarded as *les centres d'actions moléculaires, ne doivent pas être considérées seulement comme très petites relativement aux distances qui les séparent, mais comme rigoureusement nulles.*

The difference in the two sets of hypotheses turns on whether cohesive or other forces emanate from immaterial points of zero volume, or from material particles each occupying a definite volume. Which hypothesis is to be accepted? It must be remembered that we can persuade ourselves that matter itself can be spirited away by trying to conceive the residuum which remains when each property known to be a manifestation of energy is subtracted from matter. An extended nothing, said G. W. von Leibniz, is meaningless, an extended something must have quality, and to call that quality extension is to cover up the difficulty with a name. J. Locke (1690), and G. Berkeley (1713), M. Faraday (1844), W. Ostwald (1892), as well as earlier and later philosophers, have emphasized how impossible it is to conceive or imagine the existence of matter independent of energy; we have evidence of the existence of energy, and therefore, the supposition that a material world really exists apart from energy is undemonstrable and false. The chemist, however, progresses with his work on the assumption that he lives in a material world which it is his business to investigate.

The atomic theory is the only satisfactory hypothesis which has correlated the numerous facts relating to the transformations of matter. It may be perfectly true, Lord Kelvin (1874) has pointed out, that the assumption of atoms can explain no property of a body which has not previously been attributed to the atoms themselves. This, added H. von Helmholtz, is not evidence against the existence of atoms, but is rather against efforts to derive the foundations of theoretical physics from purely hypothetical assumptions as to the atomic structure of natural bodies. The assumption of atoms has none the less proved an invaluable aid in forming vivid mental pictures of the different phases of a chemical reaction; it has served as a wonderful stimulus to the chemical explorer, for it has enabled chemists to anticipate successfully the results of experimental research. The vitality of this time-honoured theory is remarkable; it is ever assimilating new facts, and ever enticing the chemist to fresh fields and pastures new. Innumerable prophecies based on the atomic hypothesis have been completely verified so that the atomic theory is now regarded as a pyramid of truth. Consequently, although no one has ever seen an atom, A. R. A. Smith (1884) could say: We believe in atoms because, so far as we can see, nature uses them. **The greater the number of facts consistently explained by one and the same theory, the greater the probability of its being true.** The overwhelming mass of circumstantial evidence, direct and indirect, which modern chemistry and physics offer, has justified the faith of Dalton; and almost, but not quite, demonstrated the real existence of tangible atoms.

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§ 16. The Language of Chemistry

However certain the facts of any science, however just the ideas derived from these facts, we can only communicate false or imperfect impressions to others, if we want words by which these may be properly expressed.—A. L. LAVOISIER.

Words are the footsteps of reason.—FRANCIS BACON.

The nomenclature of a science, that is, the group of technical terms peculiar to that science, is of vital importance. It is virtually impossible to separate the nomenclature from the science itself. Lavoisier emphasized the importance of this in his classical *Traité élémentaire de chimie* (Paris, 1789). Every science consists of three things: (1) the facts which form the subject-matter; (2) the ideas represented by those facts; and (3) the words in which those ideas are expressed. Like three impressions of the same seal, said Lavoisier, the word ought to produce the idea; and the idea ought to be a picture of the fact.

Special technical words have been invented to fix and describe the ideas and principles of chemistry—as of all other sciences. Technical terms should be precise and clear, and not tainted with ambiguity and vagueness. Such technical terms form part of the current language of chemistry, and they are of international value.

Technical terms are obtained in two ways: (1) Owing to the poverty of language, words in colloquial every-day use are commandeered, and are given, by a special definition, a specific meaning. Such words are a prolific source of error and confusion, and they ofttimes lead to needless controversies because they have a variety of different meanings—energy, force, atom, etc., are examples. (2) Terms are specially invented for a specific purpose—electron, and telegraph, are examples. These terms are much less liable to misapprehension than adaptations of every-day words which possess several meanings. However strange the special terms may appear at first, they soon grow familiar to the ear, and they can be used without effort. W. Whewell has pointed out, very aptly, that "technical terms carry the results of deep and laborious research. They convey the mental treasures of one period to the generations that follow; and laden with this, their precious freight, they sail safely across the gulfs of time in which empires have suffered shipwreck, and the language of common life has sunk into oblivion." Witness: some of the terms used in the chemistry of to-day were coined by the early Arabian chemists—*e.g.* alcohol, alkali, borax, elixir, lac, etc.

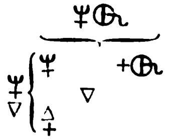
Naming the elements.—A great number of the elements have been endowed with names which refer to some salient property or characteristic, *e.g. iodine*—from its violet vapour; *chlorine*—from its green colour; *chromium*—from the colour of its compounds; *rhodium*—from the rose colour of its salts; *osmium*—

from its smell; *argon*—from its indifference to chemical reagents; similarly with platinum which refers to the silvery appearance of the metal—from the Spanish *plata*, silver. Likewise with the names phosphorus, radium, quicksilver, bromine, nitrogen, oxygen, hydrogen, argon, glucinum, iridium, praseodymium, thallium, indium, cæsium, and rubidium. Other elements have been named more or less capriciously; thus some elements are named after particular localities—*strontium*, from Strontian (in Scotland); *ruthenium*, from Ruthenia (Russia); *yttrium*, *ytterbium*, *erbium*, and *terbium* are all derived from Ytterby (in Sweden). Some elements have been named in honour of some country or from association with some other event at the time of their discovery—*e.g.* *helium*, from its occurrence in the sun; *gallium*, from Gallia (Gaul); *germanium*, from Germany; *lutecium*, from Leutéce, an old name for Paris; *palladium* was named after the planetoid Pallas discovered about the same time; *uranium* was likewise named in honour of the discovery of the planet Uranus; etc. Some names refer to the minerals in which they occur; *beryllium* is derived from the name of the mineral beryl; *zirconium*, from the mineral zircon; similarly with *molybdenum*, and many others. Some names refer to renowned personages—*e.g.* *victorium*, from Queen Victoria; similarly with *gadolinium*, from J. Gadolin; and *mosandrum*, after G. Mosander. Other names refer to mythological personages—*e.g.* *thorium*, from Thor, the son of Odin, a god in Scandinavian mythology; *vanadium*, from a Scandinavian goddess, Vanadus; *tantalum*, from Tantalus in Grecian mythology; *niobium*, from Niobe, daughter of Tantalus;[1] and similarly with cerium, titanium, palladium, and uranium. Some names are emblematic—*e.g.* selenium, cobalt, and nickel.

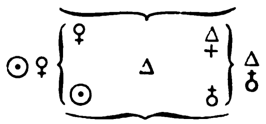
Unfortunately some elements have not yet been christened with a name recognized by all. *Niobium*—symbol Nb—and *columbium*—symbol Cb—are two different names for one element; *glucinum*—symbol Gl—and *beryllium*—symbol Be—are two different names for another element. There is at present a struggle for existence between these terms, no doubt the fittest will survive. The first terms here employed were recommended by the International Association of Chemical Societies, September, 1913; and F. W. Clarke wrote a strong protest, and claimed columbium in place of niobium for historical reasons.

Symbols.—The old alchemists used to represent different substances by quaint sometimes fantastic symbols—an example is given in Fig. 1, Cap. I. The hieroglyphs of the Hermetic priests in Egypt, and the fantastic symbols of the alchemists of the Middle Ages, were attempts to hide knowledge from the vulgar, and to surround the study of nature with difficulties and mysteries. The symbols of the modern chemist, on the contrary, are intended to facilitate the study of chemistry by abbreviating complicated expressions so that their meaning can be seen at a glance. Some of the older symbols did come under this category; for example, gold has been represented by the picture of a king on his throne; by the symbol ○ or ☼, for the sun, etc.; silver, by ☾, the moon; etc. Fantastic symbols, like that indicated in Fig. 1, Cap. I, could lead only to confusion. Symbols were employed by Raymond Lully somewhat frequently in the thirteenth century. Possibly the alchemists intended the symbols to convey some idea of the peculiarities of the metals they represented; indeed, it has been suggested that the circle which appears in certain of the symbols was intended to illustrate the perfection of the metallic state, and the half circle, an approximation thereto. In any case the alchemists were very fond of symbols, and of obscuring their meaning by using mystic triangles and special hieroglyphs so as to make their writings like cryptograms which required a key before the meaning could be deciphered.[2] Thus, Raymond Lully in his *Testamentum, duobus libris universam artem chimicam complectens* (Colon, 1568), used the symbol *A* to represent God the Creator, *B* stood for mercury, *C*, for saltpetre. . . . These symbols were not in general use, and each writer devised his own. The alchemists of the thirteenth century also represented Aristotle's four elements by triangles: △, fire; 🜁, air; ▽, water, and 🜃, earth. Other symbols gradually came into more or less general use; thus, about the fourteenth century the symbol △ for sulphur was fairly common in the writings of the alchemists.

At the beginning of the eighteenth century, symbols for chemical compounds began to be used more frequently, not with the idea of making the literature obscure and unintelligible to the uninitiated, but rather for conciseness, brevity, and clearness. St. F. Geoffroy, in his *Table de différents rapports observés en chimie entre différentes substances* (1718), used the ordinary alchemical symbols for the metals and introduced a number of others, *e.g.* ⊖ for salt; >⊖ for hydrochloric acid; >⏀ for nitric acid; >⏀⊣ for sulphuric acid, etc. In his *De attractionibus electiviis* (Upsala, 1775), T. Bergmann represented chemical reactions by symbols and signs. The two subjoined diagrams illustrate T. Bergmann's method. The symbols to the right and left, outside the brackets, represent the substances which react together; and those above and below, the products of the reaction, if any, which separate from the system. The symbols within the brackets represent the reacting components; and the disposition of the brackets is intended to indicate whether the products of the reaction are solid, or solution, or volatile. Thus,



Represents the action which occurs when an aqueous solution (▽) of calcium sulphide (♆) is treated with sulphuric acid (⏀). The lime (♆) and sulphuric acid (⏀) unite together to form calcium sulphate (♆⏀) which is precipitated (⏝) and the sulphur (🜍) also remains as a solid. (⏝).



Represents the action which occurs when an alloy of gold and copper (⊙♀) is fused (△) with antimony sulphide (🜍♁); The copper (♀) and gold (⊙) are separated; the copper (♀) and sulphur (🜍) unite together to form a solid (⏝), and the gold (⊙) and antimony (♁) also unite to form a solid (⏝).

A. F. de Fourcroy[3] employed a similar method in 1784. It must be added that, about 1756, W. Cullen is said to have been the first to employ diagrams to illustrate chemical reactions. A. L. Lavoisier used the symbol ▽ for water; ⊕ for oxygen; etc., and, like T. Bergmann (1775), he represented chemical reactions by combining these symbols in various ways.

John Dalton, in his *New System of Chemical Philosophy* (Manchester, 1808), made a step in advance by representing the atoms of the elements by symbols, and combining these symbols so as to show the elements present in a compound. Thus, ⊙ represented hydrogen; ○ oxygen; ● carbon, etc. Water was represented by ○⊙; carbon monoxide by ○●; carbon dioxide by ○●○; etc. These symbols have all been abandoned. They are too cumbrous. To-day, we follow J. J. Berzelius' method, suggested in various editions of his *Larbok i Kemien* (Upsala, 1811), and use one or two leading letters from the recognized name of the element to represent any particular element. The first letter is always a capital; the second, if present, is always a small letter.

Thus, O represents oxygen; H, hydrogen; C, carbon; N, nitrogen; Cl, chlorine; etc. The names of ten elements start with C, and to prevent the possibility of confusion, a second leading letter is selected either from the name, or from the alternative Latin name of the element. Thus C (carbon), Ca (calcium), Cb (columbium), Cd (cadmium), Ce (cerium), Cl (chlorine), Co (cobalt), Cr (chromium), Cs (cæsium), and Cu (*cuprum*), copper). The elements with alternative Latin names are symbolized: Sb for antimony (*stibium*); Cu for copper (*cuprum*); Au for gold (*aurum*); Fe for iron (ferrum); Ag for silver (*argentum*); Pb for lead (*plumbum*); Hg for mercury (*hydrargyrum*); K for potassium (*kalium*); Na for sodium (*natrium*); and Sn for tin (*stannum*).

Naming the compounds.—Each element forms with other elements a group of compounds which are said *to contain* the respective elements, because the elements in question can be obtained unchanged from the compounds. Consequently, **every compound has an elementary or ultimate composition.** Compounds are symbolized by joining together the letters corresponding to the different elements in the compound. Thus, HgO represents mercury oxide, a compound of mercury and oxygen. When only two elements are united to form a compound, the name of the second element is modified so that it ends in **ide.**

The symbol for the element also represents one of its atoms. If more than one atom is present in a compound, a small figure is appended to the bottom—in France, generally at the top right-hand—corner of the symbol of the element, to indicate the number of atoms present. Thus, H_2O represents a molecule of water, *i.e.* a compound containing two atoms of hydrogen and one of oxygen; CO represents a molecule of carbon monoxide—a compound containing one atom of carbon and one atom of oxygen; Na_2CO_3 represents a molecule of sodium carbonate a compound containing two atoms of sodium, one atom of carbon, and three atoms of oxygen. A letter affixed in front of a group of symbols represents the number of times that group is contained in the given compound. Thus, crystallized sodium carbonate is symbolized: $Na_2CO_3.10H_2O$, meaning that this compound contains one equivalent of Na_2CO_3, and ten equivalents of the group H_2O.

J. J. Berzelius (1814)[4] represented two atoms of an element in a compound by drawing a bar through the symbol of the element; for instance, $\cancel{\mathrm{H}}\mathrm{O}$ represented H_2O; $\cancel{\mathrm{Fe}}\mathrm{O}_3$: Fe_2O_3; $\cancel{\mathrm{Cu}}\mathrm{O}$ represented Cu_2O; etc. J. J. Berzelius also represented an atom of oxygen united with an element by placing a dot over the symbol of the element, and an atom of sulphur by a dash in a similar position; thus, $\dot{\mathrm{C}}\mathrm{u}$ represented CuO; $\ddot{\mathrm{P}}\mathrm{b}$, PbO_2; $\dot{\mathrm{C}}\mathrm{a}\ddot{\mathrm{C}}$, $CaOCO_2$; $\mathrm{CuS}+5\cancel{\mathrm{H}}$ represented CuO, SO_3+5H_2O; and Fe represented FeS_2. This system did not last long in chemical literature, although the mineralogists used it for a longer time.

Compounds of an element with oxygen are called **oxides,** and the process of combination is called **oxidation.** When an element forms more than one oxide, a Greek numerical suffix is often prefixed to the word oxide. Thus SO_2 is sulphur dioxide; SO_3, sulphur trioxide; CO, carbon monoxide; CO_2, carbon dioxide; PbO, lead monoxide; PbO_2, lead dioxide or lead peroxide. The Anglicized Latin and Greek numerical prefixes are indicated in Table I.

TABLE I.—LATIN AND GREEK NUMERICAL PREFIXES.

	Latin.	Greek.		Latin.	Greek.
1	Uni-	Mono-	17	Septemdeci-	Heptadeca-
2	Bi-	Di-	18	Duodeviginti-	Octodeca-
3	Ter-	Tri-	19	Undeviginti-	Enneadeca-
4	Quadri-	Tetra-	20	Viginti-	Icosi-
5	Quinqui-	Penta-	21	Unviginti-	Henicosi-
6	Sexa-	Hexa-	22	Duoviginti-	Docosi-
7	Septa-	Hepta-	23	Treviginti-	Tricosi-
8	Octo-	Octo-	24	Quattuorviginti-	Tetracosi-
9	Nova-	Ennea-	25	Quinviginti-	Pentacosi-
10	Deca-	Deca-	26	Seviginti-	Hexacosi-
11	Undeci-	Henadeca-	27	Septemviginti-	Heptacosi-
12	Duodeci-	Dodeca-	28	Duodetriginta-	Octocosi-
13	Terdeci-	Trideca-	29	Undetriginta-	Enneacosi-
14	Quattuordeci-	Tetradeca-	30	Triginta-	Triaconta-
15	Quindeci-	Pentadeca-	31	Untriginta-	Henitriconta-
16	Sedeci-	Hexadeca-	32	Duotriginta-	Dotriconta-

	Half	Whole	Equal	Many	One and a half	One third	Four thirds
Latin . .	Semi-	Omni-	Equi-	Multa-	Sesqui-	Tertia-	Quadritertia-
Greek .	Hemi-	Holo-	Homo-	Poly-	Hemitri-	Trita-	Tetratrita-

It is considered bad style to mix Latin and Greek root words and prefixes. Consequently we usually try to keep Greek with Greek, and Latin with Latin. Thus, we say "diatomic," not "biatomic"; "bimolecular," not "dimolecular"; "bivalent," not "divalent"; and "bivariant," not "divariant"; because "atomic" is derived from the Greek word, while "molecular," "variant," and "valent," are derived from Latin words. There are, however, many hybrids universally recognized. *E.g.* millimetre, centimetre, etc. Monovalent, divalent, etc., are also used in spite of their hybrid character. In the application of the Greek numerals in organic chemistry, some hybrids are used—*e.g.* in the methane series of hydrocarbons, Greek numerals are generally employed excepting for C_9H_{20}, $C_{19}H_{40}$, $C_{29}H_{60}$, . . . and for $C_{11}H_{24}$, $C_{21}H_{44}$, . . . where Latin numerals are used. The series thus runs pentane, C_5H_{12}; hexane, C_6H_{14}; heptane, C_7H_{16}; octane, C_8H_{18}; nonane, C_9H_{20}; decane, $C_{10}H_{22}$; undecane, $C_{11}H_{24}$; etc. For consistency nonane should be enneadecane, and undecane, hendecane, etc. The custom is so general, and so deeply rooted in the literature of organic chemistry, that, as F. Beilstein[5] says, the rectification *gegenwärtig nicht mehr empfehlenswert erscheint*. This state of crystallization has not yet been attained in the naming of inorganic compounds, and the Greek numerical prefixes can be consistently used if thought desirable; but "sesqui" is generally used whether Greek or Latin affixes are employed. However, we cannot always be purists without defying custom, which, as Horace has said, decides the language we must use.

Sometimes the termination **-ic** is affixed to the name of the metal for that oxide which contains the greater proportion of oxygen, and **-ous** for the oxide containing the lesser proportion of oxygen. For instance, SnO is either stannous oxide, or tin monoxide, and SnO_2 is either stannic oxide or tin dioxide; FeO is ferrous oxide; and Fe_2O_3 ferric oxide. For historical reasons, the names of some compounds do not conform to this system because the affix "ic" was assigned to the compound first discovered, and the compounds subsequently discovered were named accordingly. Consequently, when only one series of compounds is known, the use of either termination is now avoided—thus, potassium, sodium, and magnesium are preferred to potassic, sodic, and magnesic respectively. The method of naming the compounds now under discussion is not always satisfactory when the elements form more than two compounds. To get over the difficulty, a prefix **hypo-** (under, or lesser) is sometimes added to a compound less rich in oxygen than the **-ous** compound, and **per-, hyper-, or super-** (beyond, above) is added to the one with more oxygen. Thus,

Persulphuric acid	$H_2S_2O_8$	Perchloric acid	$HClO_4$
Sulphuric acid	H_2SO_4	Chloric acid	$HClO_3$
Sulphurous acid	H_2SO_3	Chlorous acid	$HClO_2$
Hyposulphurous acid	$H_2S_2O_4$	Hypochlorous acid	$HClO$

The six nitrogen oxides—nitrogen monoxide, dioxide, trioxide, tetroxide, pentoxide, and hexoxide—would be awkwardly named by this system.

It will be observed that *ous* from the Latin *osus* means "richness," so that *stannous* means *rich in* tin, and etymologically stannous oxide means an oxide *richer in* tin than stannic oxide, and by implication *poorer in oxygen*. In actual use, therefore, the etymological meaning is inverted, and the implied signification has been universally adopted. Etymologically the term *hypo* means *less rich*, so that hypochlorous means less rich in chlorine than chlorous—in practice the very opposite is the case, for hypochlorous acid has less oxygen than chlorous acid, and it contains a higher proportion of chlorine. Similar remarks apply to the prefixes *per*, *super*, and *hyper*.

Oxides like alumina—Al_2O_3; ferric oxide—Fe_2O_3, etc., are sometimes called **sesquioxides** (*sesqui*, one-half more). Compounds which have less oxygen than the normal are sometimes called **suboxides** (*sub*, below) instead of hypo-oxides, *e.g.* while CuO represents cupric oxide, Cu_2O represents cuprous oxide, and also copper suboxide; similarly, while AgCl represents the normal silver chloride, Ag_2Cl represents silver *sub*chloride. Custom has restricted the use of *hypo-* to the acids or acidic oxides, and *sub-* to the basic or indifferent oxides. The oxides can be roughly divided into two classes. Some oxides, with water, form acids, and others act as bases. It is not very easy to draw a sharp line of demarcation between the two. The *acidic oxides* have a sour taste, and turn a solution of blue litmus red; the *basic oxides* usually turn a solution of red litmus blue, and have a soapy feel.

The nomenclature of inorganic chemistry is thus based upon the principle that the different compounds of an element with other elements can be named by a simple change in the beginning or termination of the word—witness ferric and ferrous oxides; and also by the addition of a numerical suffix showing the relative number of atoms of the corresponding element in its compounds. The systematic name of a compound thus indicates its composition.[6] These little artifices, apparently trivial, are really important advances in the language of chemistry. The method has some defects, but when the necessity for a modification becomes acute, it will probably not be difficult to change. Language generally lags in the wake of progress.

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§ 17. The Evolution of the Chemist's Nomenclature

> For a language to be perfect, it is not sufficient that each substance, each idea, each modification of form, time, place, etc., should be represented by one word, or by one invariable symbol, it is necessary in addition, both to aid the memory and to facilitate the operations of the mind, that analogous words should designate analogous substances, analogous ideas, and modifications of ideas. It is thus that the words of our language represent to us by similar terminations or augments, similar modifications of ideas represented as when we say: *je vois, j'aperçois, je reçois; nous voyons, nous apercevons, nous recevons.* In like manner do chemists make use of the expressions sulphate, nitrate, chloride, etc.—A. LAURENT (1854).

In the British Association's *Report on Chemical Nomenclature*,[1] it is shown that the evolution of the chemist's nomenclature is largely conditioned by the history of chemistry itself. No attempt to name substances systematically appears to have been made before the time of Geber—about the thirteenth century. The names in vogue for chemical substances up to the middle of the eighteenth century were more or less arbitrary, for they were (i) relics of alchemists' terms—for instance, *aqua fortis* (nitric acid), *aqua regia*, etc.; or derived (ii) from the name of their discoverer—for instance, *Cadet's fuming liquid* (alkarsine); or (iii) from one who had made a special study of the substance—for example, *Glauber's salt* (sodium sulphate); or (iv) from the name of the locality where they occurred—for example, *Epsom salts* (magnesium sulphate); or (v) from some prominent property or quality they possessed—for instance, *tartar emetic* (potassium antimony tartrate); or (vi) the names were based upon some superficial resemblance, and thus what J. B. A. Dumas called *le langue des cuisinières*—the language of the kitchen—was applied; for instance, antimonious chloride was called *butter of antimony* because of its buttery appearance; zinc chloride for the same reason was called *butter of zinc*; and arsenic chloride, *butter of arsenic*. On account of this superficial resemblance, these substances for a time were classed along with butter from milk! Similarly, *oil of vitriol* (sulphuric acid), *oil of tartar* (deliquesced potassium carbonate), *olive oil*, and the fatty oils generally were classed together; so also were such unlike substances as *spirit of wine* (alcohol), *spirit of salt* (hydrochloric acid), *Libavius' fuming spirit* (stannic chloride), *Boyle's fuming spirit* (ammonium sulphide), *Glauber's fuming spirit of nitre* (nitric acid), and *spirits of hartshorn* (ammonia) were included in one class. This virtually means that the names of the compounds were the basis of the classification. The names were arbitrarily assigned, and hence the classification was almost as arbitrary and confusing as if the compounds had been classified according to the number of the letters in their names. Liquids were once called mercurys—mercury itself was *mercurius communis*, alcohol, *mercurius vegetabilis*, etc. Salts were distinguished by their taste—*salis acida*, *salis alcalina* —and by their volatility—*salis alcalina fixa*, *salis alcalina volatila*, etc. There are here, however, signs of a feeble attempt at a truer classification.

Towards the end of the seventeenth century, chemists began to assign similar names to salts having the same origin—more particularly in reference to the acidic component of the salts. Thus, salts derived from sulphuric acid were called *vitriols ;* and those from nitric acid were called *saltpetres.* A century later, P. J. Macquer and A. Baumé, in their *Plan d'un cours de chimie expérimentale et raisonnée* (Paris, 1757), emphasized the need for designating substances similar in composition by similar names so as to enable chemists to cope with a rapidly growing list of new compounds. The confused state of chemical nomenclature, even at the beginning of the nineteenth century, is shown by an illustration from Joseph Black's *Lectures on the Elements of Chemistry* (Edinburgh, 1803), where sometimes a dozen synonyms for a salt are listed.

About 1770, T. Bergmann advocated a new system of nomenclature which was described in his *Meditationes de systemate fossilium naturali ;* the system was based as far as possible on the terms then in use, and founded on the phlogiston theory. T. Bergmann also proposed to represent substances of analogous composition by similar symbols, and so compounded the symbols that each substance had its own special symbol. For instance, he called potassium sulphate, *alkali vegetabile vitriolatum ;* sodium chloride, *alkali fossile salitum ;* ammonium nitrate, *alkali volatile nitratum ;* and similarly for sodium nitrate, sulphate, etc. His system was excellent for its time, and shortly afterwards (1782), Guyton de Morveau [2] gave a consistent nomenclature for the salts which he described as compounds of acids and bases, and he illustrated the advantages of his system by applying it to 474 substances—*e.g. vitriol de barote* (barium sulphate) ; *nitre de mercure* (mercury nitrate) ; *muriate de calce* (calcium chloride) ; *fluor de calce* (calcium fluoride); etc. In the choice of names for chemical compounds, said G. de Morveau, the following five principles should be observed :

(1) A phrase like *liqueur alkaline saturée de la matière colorante de bleu de Prusse* is not a name and it should be replaced by *l'alkali prussien.* Both terms were then in vogue. (2) The name should correspond as nearly as possible with the object. When a name is made up of a noun and an adjective, the former should be applied to the least changeable and more essential constituent. The names of discoverers should be excluded from the system. (3) If the constitution of a body is not known, a term with no meaning is better than one which may ultimately prove to be a wrong one. Hence *l'alkali prussien* is preferable to *l'alkali phlogistique.* (4) New names are best derived from roots of the best known dead languages—Greek and Latin. (5) Names should be adapted to the peculiarities of the particular language in which they are to be used.

G. de Morveau's system, like Bergmann's, was founded on the phlogiston theory. These two schemes were probably the first attempts to devise a complete system of naming inorganic compounds so that each name indicates the qualitative composition of the substance for which it stands. These two systems are not very different, and are not much unlike the one in use to-day.

In 1787, A. L. Lavoisier and G. de Morveau, with the assistance of C. L. Bertholet and A. F. de Fourcroy, presented details of a new *Méthode de nomenclature chimique* to *l'Académie des Sciences* [3] in Paris. The proposed method was really an elaboration of T. Bergmann's and G. de Morveau's systems adapted to the dualistic hypothesis. Most chemists felt the need for a precise nomenclature independent of the phlogiston which the French chemists were rapidly driving out of chemical science. In the proposed system the names assigned to the various compounds were intended (i) to indicate the compound ; (ii) to define the compound ; (iii) to recall its constituent parts ; (iv) to classify it according to its composition ; and (v) to indicate the relative proportions of its constituents.

The French report laid the foundations of the chemical language of to-day—of course, after making due allowance for the development of the science which has necessitated many modifications. The terms *ic* (ique) and *ate, ous* (eux) and *ite,* for respectively distinguishing the higher and lower acidic oxides and their salts, are employed for the first time. In 1804, T. Thomson [4] introduced the plan of distinguishing the different oxides of an element by prefixing the Greek suffixes *proto*, first; *deuto*, second, . . . for the first, second, . . . compound of a series—*e.g.* CuCl would be the *proto*-chloride of copper; and $CuCl_2$ the *deuto*-chloride. In 1808, J. Dalton explained his notation in his *New System of Chemical Philosophy* (Manchester, 1808). J. J. Berzelius' modifications [5] followed in 1811 as indicated above. Berzelius introduced the term *ide*, or French *ure*, as a termination for simple compounds.

Various other systems of nomenclature have been proposed from time to time in which artificial words replace the arbitrary names applied to well-known substances—each vowel or consonant of the artificial word representing either a substance or a number.[1] These systems have been found to be unworkable. There are also systems based on M. Dewey's *Decimal Classification and Relativ Index* (Boston, 1885); for example, A. L. Voge, in his *The Inorganic Compounds* (Zurich, 1911), arranges 14,000 inorganic compounds on Dewey's system. He gives

	N_2O	NO	N_2O_3	NO_2	N_2O_4	N_2O_5
Symbols . .	133211	133311	133411	13351181	13351182	133611

These systems have possible uses in libraries and for card indexes.

The *Méthode de nomenclature* contained as appendices two *Mémoires sur de nouveaux caractères à employer en chimie* devised by J. H. Hassenfratz and P. A. Adet. In these, 54 straight and curved lines representing the combining units, were arranged in various ways to represent possible compounds. The appearance of the combined symbols, in many cases, recalls some of the modern systems of shorthand writing. The idea of using "shorthand systems" is revived every now and again, but has never come into general use.

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CHAPTER III

HYDROGEN AND THE COMPOSITION OF WATER

§ 1. The History of Pneumatic Chemistry

The history of human knowledge is a history of false inferences and erroneous interpretations of facts.—MAX NORDAU.

THE attention of the early workers in chemistry was mainly directed to visible and tangible liquids and solids, while the gases—spirits, fumes, vapours, and airs, as they were variously called—which escaped when different substances reacted together, were usually considered to be unwholesome effluvia, best avoided. Indeed, about the middle of the eighteenth century J. Black [1] could say :

> In their distillations, chemists have often observed that part of a body has vanished from their senses, notwithstanding the utmost care to retain it ; and upon further inquiry, they have always found that subtle part to be air, which, having been imprisoned in the body under a solid form, was set free and rendered fluid and elastic by the fire.

In the third century, Clement of Alexandria believed that the suffocating properties of some gases were manifestations of a diabolical nature, and J. B. van Helmont, who was the most advanced student of gases at the beginning of the seventeenth century, appears to have had a hazy belief that the gases he had discovered were in some senses living spirits—diabolic or divine. Even as late as the middle of the seventeenth century, G. Agricola [2] hinted that the gases in mines were manifestations of malignant imps ; and the idea had not been altogether exorcised at the beginning of the eighteenth century.

The old chemists used the term *spirit* or *air* where we use the term *gas* generically for aëriform elastic fluid. Thus, in the first century of our era, Pliny, in his *Historia natura* (2. 4), spoke of that *spiritus* which both the Greeks and the Romans called *aĕro*. The terms *spiritus*, *flatus*, *halitus*, *aura*, and *emanatio nubila* were also applied to aëriform fluids disengaged by heating other substances, and they are common in the writings of the alchemists of the Middle Ages. J. B. van Helmont, in speaking of the *spiritum sylvestrem* which he had obtained by the combustion of carbon, etc., said, " This spirit, unknown up to the present, I call by a new name *gas*," and he says elsewhere [3] that in order to distinguish the vapour given off by water at ordinary temperatures from the vapour which is derived from boiling water, " by the licence of a paradox, for want of a name, I call the vapour rising from water at ordinary temperatures, a *gas*, being not far severed from the *chaos* of the auntients (ancients)." Just as the " chaos of the auntients "—Hesiod's *χαος*—was a confused mixture of elements from which the Creator produced the universe ; so, to van Helmont, the vapour of water was a confused mass of elements from which all material substances could be produced. The word *chaos* was very frequently used by Paracelsus with a similar meaning. " Chaos," said he, " is an air like the wind. Air is nothing more than a chaos. What air is, that is chaos. The element air is named chaos." Stephen Hales (1727 also said that atmospheric air is a veritable Proteus and a chaos. It is an easy transition from *chaos* to *chas*, which has the sound of *gas*. According to M. Speter, the *ch* and *ao* of chaos when converted into Netherland speech become respectively *g* and *a*, so that van Helmont transformed Paracelsus' term to suit the language of his country. Some derive the word from the *geest*—spirit, volatile liquid, or refined fluid—of the Dutch ; or from the *gäscht*—yeast—of the Germans.[4]

Near the beginning of the seventeenth century, J. B. van Helmont, in his essay *De flatibus*, distinguished *gas sylvestre*—given off by fermenting liquids—from the inflammable gases which he named *gas pingue*, *gas sicum*, or *gas fuliginosum*. J. B. van Helmont seems to have adopted the common opinion that gases are different combinations of elastic air with various exhalations or impurities, for at that time chemists regarded the different gases as chaotic mixtures of various substances with atmospheric air. The term *sylvestre* was intended to imply that the artificial gases which he had prepared were untameable and uncondensable. In a letter to R. Boyle [5] in 1678, Isaac Newton stated that he considered that the ferrous gas (hydrogen) which R. Boyle had obtained by the action of acids on iron, and the cuprous gas (nitrogen oxide), which C. Huygens [6] had obtained by the action of nitric acid on copper, contained ultimate particles respectively of iron and copper brought to a state of aërial elasticity; but the idea of a *ferrous gas* from iron, and a *cuprous gas* from copper was disproved when H. Cavendish [7] demonstrated the identity of the gases obtained by the action of acids on iron and on zinc. According to J. Priestley, " Boyle [8] was the first who discovered that what we call fixed air, and also inflammable air, are really elastic fluids capable of being exhibited in a state unmixed with common air." R. Boyle extended his experiments on factitious (artificial) airs separable from fixed bodies to a variety of substances, and he noticed the condensability of hydrogen chloride (1676); the orange colour of nitrogen peroxide (1672); and the evolution of an air by heating red lead in the focus of a burning glass (1678). He also obtained an air from oyster shells and red coral (1661), and noted the inflammability of hydrogen obtained by the action of acids upon iron (1671). R. Boyle employed the term *air* generally (1676) in the same sense that the word gas is used to-day. *Tout corps invisible et impalpable,* said R. Descartes (1664), *se nomme air.* J. Mayow [9] examined the relative elasticities of the two gases obtained by R. Boyle by the action of nitric and sulphuric acids on iron, and decided that *there exist various elastic fluids other than air.* J. Mayow's conclusion was opposed by the elder Bernoulli,[10] who claimed that there are no other elastic fluids besides air; and, overlooking the constant diminution of volume which Mayow found to occur when air is breathed or burnt, J. Bernoulli further claimed that animals are suffocated and flames are extinguished in certain airs because the airs are charged with miasmata inimical to life and combustion.

It is sometimes said that S. Hales, in his *Vegetable Staticks* (London, 1727), confused the different gases which he prepared with atmospheric air. This erroneous idea has appeared because Hales focussed his attention on the generic physical properties of gases rather than on their specific chemical characteristics. Thus, W. V. Harcourt [11] has pointed out that when Hales states that " the airs generated by effervescences . . . resemble true permanent air " he really means that they are true elastic fluids with the same permanence of constitution, and the same elastic force as common air. Hales heated a number of substances in vessels arranged so that the gases evolved could be collected over water, and he measured the proportion of gas furnished by definite weights of different substances. He also collected airs furnished by fermentation processes, and airs generated by the action of acids on metals. S. Hales did not make any special experiments on the chemical properties of different gases—hydrocarbons, carbon dioxide, nitrogen oxides, oxygen, nitrogen, hydrogen, cyanogen, and chlorine—which he probably collected, nor on the aqueous solutions of the more soluble gases—hydrogen chloride, sulphur dioxide, and ammonia—which he must have prepared. In spite of the experimental facts which S. Hales thus accumulated, his attention was so preoccupied with their generic physical properties that he did not observe their specific chemical differences —*oculos habuit et non videbat*—and he was thus prevented from making many capital discoveries.

J. B. van Helmont seems to have believed that while gases could be prepared artificially in many ways, they could not be caught and held in vessels—*gas, vasis incoercible, foras in aerem prorumpit.* S. Hales is generally credited with the invention of the gas-collecting or **pneumatic trough.** J. B. van Helmont did not know how to isolate and preserve the *gas sylvestre* which he discovered near the beginning of the seventeenth century, and he distinctly stated that the gas cannot be confined in any vessel, since it overcomes all obstacles and mixes with atmospheric air.

R. Boyle (1661) and J. Mayow (1669) used a glass globe, Fig. 6, Cap. I, inverted in a basin of water for confining air: they filled the globe with water and inverted it in the basin of water so that the gas generated by the action of an acid on some scraps of iron in the basin displaced the water and collected in the globe. M. d'Elèment, in a brochure [12] published at Paris in 1719, had already shown that air could be manipulated and measured like other bodies by confining it in vessels over water; and in 1621, J. C. Drebbel had noticed the bubbling of gas from a retort heated with its beak dipping in water. S. Hales devised the apparatus indicated in Fig. 1, for collecting the gases evolved when different substances are heated in a retort—a glass vessel was used for generating the gases at low temperatures, and a bent gun barrel for high temperatures. The vessels used for collecting the gas were hung by strings mouth downwards below the surface of the water. H. Cavendish (1766) used a similar device. W. Brownrigg [13] used a shelf with two holes larger than the gas jar and above the level of the liquid in the trough; the latter were prevented sinking too deeply by means of wedges. J. Priestley introduced the use of a perforated shelf below the level of the liquid in the trough for supporting the vessel to be filled with gas. Modifications of S. Hales' and J. Priestley's pneumatic troughs were employed very effectively in chemical researches on gases by C. W. Scheele (1770) and A. L. Lavoisier (1772). Joseph Priestley also substituted mercury for water; and, by means of the **mercury pneumatic trough,** he collected and isolated gases—ammonia, hydrogen chloride, sulphur dioxide, silicon fluoride—which are so soluble in water that their existence had been overlooked when water was the confining liquid.

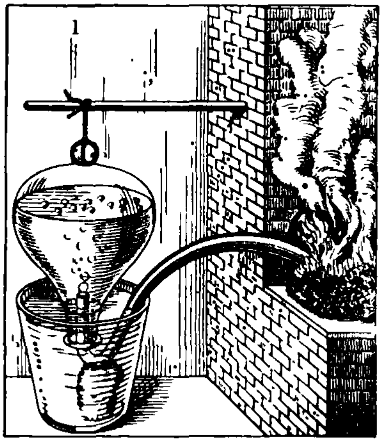

Fig. 1.—S. Hales' Pneumatic Trough.

The study of gases began to occupy serious attention towards the end of the eighteenth century, so that in 1779, although "only eight gases were certainly known with respect to their composition," yet chemists were so proud of their knowledge that T. Bergmann was able to write: "During the last ten years chemistry has not only soared into regions of invisible aerial substances, but it has dared to explore the nature of these substances, and to search into their constituent principles." The nineteenth-century chemists devoted a great deal of time and attention to the imperceptible, intangible gases ignored by the earlier workers. Indeed, chemistry could never have progressed very far if the gases and vapours had been ignored. The work of Joseph Priestley, between 1770 and 1780, gave such a stimulus to the study of gases that G. Cuvier, in his *Éloge historique de Priestley* (Paris, 1806), called him *un des pères de la chimie moderne.*

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§ 2. Hydrogen—Preparation and Properties

> It can scarcely be said that pneumatic chemistry was properly begun till Mr. Cavendish published his valuable paper on carbonic acid and hydrogen gas, in the year 1766 —T. THOMSON (1813).

The discovery of hydrogen.—It is inconceivable that the alchemists knew nothing about this gas, for they were perpetually operating with various metals in contact with acids. It must therefore have been known for a very long time that an inflammable air or gas is produced when iron is dissolved in dilute sulphuric acid. Paracelsus, in the sixteenth century, described the action somewhat quaintly. He said that when the acid acts on iron "an air arises which bursts forth like the wind." Near the beginning of the next century, J. B. van Helmont described this gas as a peculiar variety of air which was combustible and a non-supporter of combustion, but his ideas were somewhat hazy, for he confused it with other inflammable gases; indeed, up to about 1766, writers generally used **inflammable air** as a general term to include this gas, as well as the hydrocarbons, hydrogen sulphide, carbon monoxide, and other combustible gases. Hydrogen was sometimes specifically distinguished as the *inflammable air from the metals*. In 1650, T. Turquet de Mayerne [1] reported that the fumes evolved when dilute oil of vitriol acts on iron are inflammable, and in 1671 Boyle [2] observed that the flame was extinguished when placed under the receiver of an air-pump, but R. Boyle's chief concern was to show that the gas, which he called the *volatile sulphur of Mars*, was dilatable and compressible, and that it was really an air. Nearly a century later, J. Priestley also experimented with the gas, and S. Hales [3] found that iron filings and oil of vitriol gave scarcely any air, but on adding water, there was a copious evolution of the aëriform fluid. In 1766, H. Cavendish [4] showed that the combustible gas produced by the action of dilute sulphuric or hydrochloric acid on metals like iron, zinc, and tin is a distinct substance with definite properties peculiar to itself; hence, hydrogen was called *inflammable air*. Cavendish measured the amount of hydrogen obtained from a given weight of the different metals; he also measured the specific gravity of the gas, and found it to be seven times lighter than atmospheric air; he also showed that the specific gravity of the gas was the same whether zinc or iron were used in the preparation. F. de Lassone and C. W. Scheele discovered almost simultaneously that a solution of zinc in caustic lye furnishes the same gas. J. Watt (1783), R. Kirwan (1781), H. Cavendish (1766), and J. Priestley (1784) identified the gas with the evanescent phlogiston, and they called it *phlogiston*, or *phlogisticated air;* but neither this name nor *inflammable air* persisted very long, for both terms were ousted by the cognomen *hydrogen* which A. L. Lavoisier applied to the gas in 1783. In his *Considérations générales sur la dissolution des métaux dans les acides* (1784),[5] A. L. Lavoisier, following a suggestion of P. S. de Laplace, traced the source of the hydrogen which is evolved when a metal dissolves in a dilute acid, to the decomposition of the water. He assumed that the oxygen of the water united with the metal to form a calx, and the hydrogen escaped in the free state. The calx united with the acid to form water and a salt.

The preparation of hydrogen.—Hydrogen obtained by the action of dilute sulphuric or hydrochloric acid on metallic iron is not very pure, and it possesses a distinct smell owing to the presence of hydrocarbon gases, etc., formed by the action of the acid on the carbon compounds associated, as impurities, with commercial iron. The solution remaining after the action of sulphuric acid on the iron, when put aside in a cool place, soon forms beautiful pale green crystals of ferrous sulphate. Magnesium and aluminium furnish a fairly pure gas; with aluminium the acid should be warmed to start the reaction. In these cases, not only is hydrogen gas evolved but crystals of magnesium sulphate and of aluminium sulphate can be obtained from the liquids in which the respective metals have been dissolved. The action of the acid on tin is rather slow; granulated zinc is used for general laboratory work.

Hydrogen gas is made in small quantities in the laboratory by placing granulated zinc in a bottle fitted with a stopper with two holes—one to take a funnel tube, the other to take an L-shaped tube for conducting away the gas. Instead, the granulated zinc may be placed in a two-necked Woulfe's bottle—so named because these bottles were first described by Peter Woulfe (1784). The one tubulure is fitted with a one-hole stopper carrying a tube funnel, and the other, with the gas exit tube. The zinc is covered with water, and sulphuric acid is added a little at a time through the tube funnel until the gas begins to come off vigorously. For many purposes there is no need to use the pneumatic trough for collecting hydrogen, since by bringing the gas-jar mouth downwards over a jet of hydrogen the gas will collect in the upper part of the jar, and displace the air downwards—hence the term collecting gases by the downward displacement of air—many writers call this *collecting the gas by upward displacement.* Hydrogen gas so prepared is always tested before use by collecting a test-tube of the gas, and while holding the tube upside down, applying a lighted taper. If the gas burns quietly at the mouth of the test-tube, all is well.

Hundreds of different forms of apparatus[6] have been devised for supplying an intermittent stream of gas by the action of a liquid—*e.g.* hydrochloric or sulphuric acid—on a solid—*e.g.* zinc, ferrous sulphide, or marble. They are all based on the principle applied by J. W. Döbereiner in his hydrogen lamp. When the gas is no longer free to escape, the pressure generated by the gas drives the acid away from the solid; this stops the further generation of gas. When the pressure is relieved by allowing the gas to escape, the acid again comes in contact with the solid. In the better types of apparatus (i) the freshest acid is brought in contact with the solid; (ii) the emptying and recharging is simple; and (iii) a great over-pressure is avoided.

The properties of hydrogen.—Hydrogen gas is colourless and odourless—the impure gas may have a smell. The hydrogen gas streaming from the generating flask can be lighted, and a flame of burning hydrogen is obtained which was formerly called *lumen philosophicum*, or the *philosopher's flame.* To get the flame to burn steadily it is best to interpose between the exit tube and the jet, a wider tube loosely packed with granulated calcium chloride to arrest by absorption the water vapour carried along with the gas. The hydrogen flame is very hot and melts ordinary glass; a jet of hard glass, quartz glass, or platinum can be used. When a lighted taper is plunged into a jar of hydrogen held mouth downwards, the gas burns with a scarcely visible blue flame at the mouth of the jar, and the taper is extinguished showing that the gas is combustible and a non-supporter of combustion. When J. Black (1766) heard that H. Cavendish had found hydrogen to be much lighter than air, he thought that possibly a thin bag made from the allantois of a calf, when filled with hydrogen, would be buoyed up by air. Modifications of Black's idea are used as illustrative experiments on the lecture table, and not long afterwards the gas was used for filling balloons. The gas can be poured upwards from one jar to another, and it can be proved that the gas has actually been transferred from the one vessel to the other by testing the contents of each jar with a lighted taper before and after the pouring.

The extreme lightness of hydrogen and its combustibility enable many ingenious experiments to be performed with the gas. For instance, a cardboard box or a light glass vessel can be counterpoised bottom upwards, on a balance; the beam will ascend when hydrogen is poured upwards into the inverted vessel. Soap-bubbles blown with the gas, or collodion balloons filled with the gas, rise to the ceiling very quickly. The gas may be syphoned upwards from one vessel to another, or, the gas may be syphoned from, say a bell-jar and burnt at the long leg of the syphon. An explosive mixture with air is formed when the hydrogen has nearly all been syphoned away, and the flame at the top of the long leg of the syphon will then rush back and produce a loud but harmless explosion.

The explosive character of a mixture of hydrogen with oxygen of air can be illustrated by mixing two volumes of hydrogen gas with either one volume of oxygen or five volumes of air in a soda-water bottle. A lighted taper applied to the mouth of the bottle causes the gas to detonate. The combustion of the whole mass is almost instantaneous. The explosion is so violent that we can understand why N. Lemery, in his *Explication physique et chimique des éclairs et du tonnère* (1700), tried to show that thunder and lightning are produced by the fulminations of hydrogen.[7] The sound obtained when a long glass tube is placed about the flame of burning hydrogen led to W. Higgins (1777) calling the experiment the *chemical harmonicon*. The tones vary with the diameter, thickness, and length of the tube and on the nature of the jet. The sound appears to be the effect of an extremely rapid series of explosions. M. Faraday obtained a similar *musical flame* with inflammable gases and vapours other than hydrogen. M. Faraday's explanation is that a strong current of air is established; this lengthens the flame, and small portions of air are mixed with the hydrogen in such a manner as to form small quantities of detonating gas, which, when set on fire, produces slight explosions succeeding each other quickly and regularly. C. Wheatstone found that while producing sound within a glass tube, regular intermissions in the intensity of the flame are observed, and these present a chain-like appearance on a revolving mirror, indicating alternate contractions and dilations of the flame corresponding with the sonorous vibrations of the column of air.

Joseph Priestley[8] has told us that in 1776 his friend, J. Warltire, had noticed that when a flame of hydrogen is allowed to burn in air confined under a bell-jar, the whole of the receiver appears to be filled with "a fine powdery substance like a whitish cloud," when the flame was extinguished; and the air left in the glass was found to be "perfectly noxious." In the same year P. J. Macquer[9] inquired whether the flame of hydrogen evolved smoke or soot. He thus described his experiment:

> By placing a saucer of white porcelain in a jet of inflammable gas (hydrogen) burning tranquilly at an orifice, I found that the part of the saucer which the flame licked was moistened by small drops of liquid as clear as water, and which, in fact, appeared to be nothing but pure water.

It is probable that J. Warltire's white cloud was not produced by a finely powdered solid, but by minute drops of water. In 1779, J. R. Sigaud de la Fond also mentioned the formation of water during the combustion of inflammable air. P. J. Macquer did not stop to inquire: Whence came the water? He has been blamed because he felt no astonishment at that which is really astonishing, for he merely mentions, without comment, the appearance of the water. P. J. Macquer did not see before him a great discovery begging for recognition. Hence, asks F. J. Arago (1839),[10] is genius in the observational sciences to be reduced to the faculty of asking an appropriate Why? The inquiry can be made, (1) What happens to the surrounding air during the burning of a jet of hydrogen? and (2) Is the product of the action really water?

J. Warltire's 1776 experiment can be modified by making a jet of dried hydrogen burn under a bell-jar containing a measured volume of air standing over water. At first, there is a momentary expansion of the air due to the heating of the confined air by the flame; immediately afterwards, the water rises in the jar, and the hydrogen flame gradually expires. Immediately this occurs the stream of gas is stopped to prevent it passing into the air in the bell-jar. The gas remaining in the jar has quite similar properties to the nitrogen gas remaining after mercury is calcined in air. It is the "perfectly noxious air" alluded to by J. Warltire. In 1777, C. W. Scheele described an analogous experiment in his *Chemische Abhandlungen von der Luft und von dem Feuer* (Upsala, 1777), but with other combustible agents. The experiment shows that **when hydrogen burns in air, it unites with the oxygen and leaves nitrogen behind.** If the experiment be carefully made, nearly four-fifths of the original volume of air remains. The burning hydrogen removes nearly one-fifth of the original volume of air. Hydrogen does not burn in the residual nitrogen—although about 7 or 8 per cent. of oxygen is still present. A certain amount of dew collects on the inner walls of the bell-jar, but that, of course, may come from the water in the dish below. In fine, the facts give reasons for supposing that hydrogen, in burning, combines with oxygen to form an oxide of hydrogen in the same sense that mercury, when calcined in air, combines with oxygen to form mercuric oxide. It remains to try and isolate a sufficient quantity of the hydrogen oxide whose existence has just been inferred, but not proved, in order that its properties may be examined more closely.

The experiment of P. J. Macquer (1778) can be modified so that a jet of dried hydrogen is burned under a funnel, the stem of which is curved so that it passes into a two-necked globe; the other neck of the globe is connected with an aspirator so that the products of combustion from the hydrogen flame can be aspirated through the system. The glass bulb is kept cold and a clear colourless liquid collects therein. This liquid has all the properties of water; it is a clear, colourless, and tasteless liquid with no smell; it freezes at 0°, and boils at 100°. The water does not come from the condensation of the moisture already present in the gas as it rises from the generating vessel, because the gas is dried by the "scrubbing" it receives as it passes along the tower of calcium chloride; this statement can be tested by making a blank experiment with the un-ignited gas. It is therefore inferred that water is burnt hydrogen, or the *calx of hydrogen;* otherwise expressed, **water is hydrogen oxide formed when hydrogen burns in air.** Hydrogen and oxygen are both gases, and it is therefore more difficult to find the combining ratio Hydrogen : Oxygen in the formation of hydrogen calx, by direct weighing, than is the case with the metallic calces. It remains therefore to show how chemists have solved the problem.

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§ 3. Dumas' Experiment on the Composition of Water by Weight

After very careful examination of all the analytical researches made for the determination of atomic weights, I emphatically declare that the researches of Dumas are the most important of all, marking as they do the beginning of the analysis of precision, and offering also the first instance of a true series of determinations, such as is required to furnish the absolute values of the atomic weights.—G. D. HINRICHS.

Several determinations of the combining weights of hydrogen and oxygen in the formation of water have been made. Prior to J. B. A. Dumas' work, there were the pioneer attempts to find the combining ratio of hydrogen and oxygen by M. Monge, A. L. Lavoisier, and M. Meusnier[1] about 1786. They admitted measured volumes of hydrogen and oxygen into a globe, exploded the mixture, and after repeating the process 372 times, weighed the water produced, and calculated the weights of oxygen and hydrogen employed from the densities of the gases. It was found that in water the ratio of the weight of hydrogen to that of oxygen is as 1 : 6·61. In 1791, A. F. de Fourcroy, L. N. Vauquelin, and M. Séguin repeated M. Monge's work and found the ratio to be 1 : 6·17. In 1803, John Dalton estimated the ratio of hydrogen to that of oxygen to be 1 : 5·66, a result further removed from the truth than the ratios found by the French savants. J. Dalton corrected his first result in 1808, and gave the ratio 1 : 7. In 1814, from J. L. Gay Lussac and A. Humboldt's observation that two volumes of hydrogen and one volume of oxygen unite to form water, and J. B. Biot and F. J. Arago's observation of the relative densities of these two gases, W. H. Wollaston calculated the ratio of the weights of hydrogen and oxygen in water to be 1 : 7·545. This was followed by the work of P. L. Dulong and J. J. Berzelius in 1819, and of J. B. A. Dumas in 1842.

Hydrogen does not combine readily with many of the elements, but it readily combines with oxygen, chlorine, fluorine, lithium, and a number of others. So great is the attraction of hydrogen for oxygen that it will very often remove oxygen from its combinations with the other elements. For instance, on March 6th, 1783, J. Priestley[2] reported that he had confined lead oxide (minium or red lead) in a tall cylinder containing inflammable air standing over water; the red oxide of lead was heated in the focus of a burning glass. He observed:

> The minium became black, and then ran in the form of perfect lead; at the same time the air diminished at a great rate, and the water ascended within the cylinder. . . . Seeing that metal to be actually revived, and that in a considerable quantity, at the same time that the air was diminished, I could not doubt that the calx was actually imbibing something from the air; and from its effects in making the calx into a metal, it could be no other than that to which chemists had unanimously given the name phlogiston. . . . Consequently, phlogiston is the same thing as inflammable air.

The experiment was varied by confining the gases over mercury in place of water, and using other calces—*e.g.* the oxides of tin, bismuth, mercury, silver, iron, and copper. He further found that "1 oz. of lead was revived by 108 oz. measures of inflammable air, and 1 oz. of tin by 377 oz. measures." The 108 oz. and 377 oz. measures of inflammable air would weigh nearly 4·4 and 15·4 grains respectively. Priestley's measurements are good, because these numbers are close to their ideal values, 4·6 and 16·3 grains respectively. This remarkable experiment might have opened J. Priestley's eyes to the insufficiency of the phlogiston hypotheses. A. L. Lavoisier[3] has pointed out that J. Priestley did not notice that there was a decrease in the weight of the solid during the reduction, and that water was a product of the reaction. The true interpretation of the reduction observed by J. Priestley is due to A. L. Lavoisier.

In J. Priestley's experiment, the hydrogen is said to be oxidized; and the metallic oxide, *reduced* or *deoxidized*. The hydrogen is called a *reducing agent*, that is, a *reducer* or *deoxidizer*; and the copper oxide an *oxidizing agent* or *oxidizer*, because it oxidizes hydrogen to water. The reaction under consideration is both an oxidation and a reduction process. All depends upon whether the hydrogen or the copper be under consideration. In the fifteenth century, Paracelsus applied the term *reduction* to the preparation of the metals. During a reduction, the reducing agent is usually, not always, oxidized; and during an oxidation, the oxidizing agent, reduced. If a known amount of copper oxide be reduced by hydrogen, and the water formed be collected and weighed, the weight of the reduced copper oxide will show how much oxygen has been used in forming a definite amount of water. This was done by P. L. Dulong and J. J. Berzelius[4] in 1820, and by J. B. A. Dumas in his celebrated *Recherches sur la composition de l'eau* in 1843. J. B. A. Dumas' experiment is not the best of its kind, although it was the best of its time, and it has long and deservedly held an honoured place in chemical text-books. The experiment illustrates some important principles, and it is therefore here described in outline. The first stage of the work involved the purification of hydrogen.

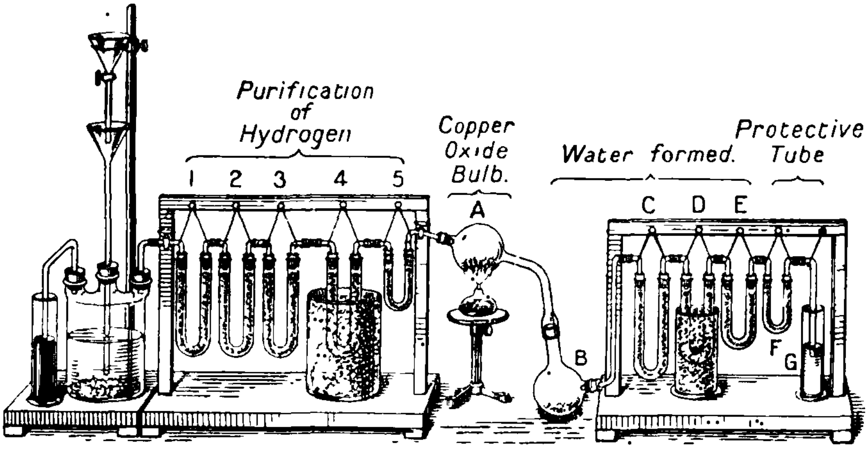

FIG. 2.—Dumas' Experiment (abbreviated).

The hydrogen was prepared by the action of zinc on sulphuric acid. It might be thought that pure zinc and pure sulphuric acid should be used. Experiment shows, curiously enough, that under these conditions the action is so very, very slow that some have jumped to the conclusion that "absolutely pure sulphuric acid, even when diluted with pure water, has no action on perfectly pure zinc." Moreover, it is exceedingly difficult to prepare pure zinc and pure sulphuric acid. Hence, pure reagents were not used for the preparation of the hydrogen. Accordingly, the gas may contain nitrogen and oxygen derived from the air; sulphur dioxide and hydrogen sulphide derived from the reduction of the sulphuric acid by the hydrogen; carbon dioxide; arsenic hydride (if the acid or the zinc contained arsenic); hydrogen phosphide (if the zinc or the acid contained phosphorus); nitrogen oxides (if the acid contained nitrogen oxides); and water vapour. Accordingly, J. B. A. Dumas (1842) used sulphuric acid, which had been well boiled, to get rid of dissolved air, and then passed the hydrogen through a series of U-tubes—Fig. 2—containing: (1) pieces of glass moistened with lead nitrate to remove hydrogen sulphide; (2) solution of silver sulphate to remove arsenic and phosphorus compounds; (3) solid potassium hydroxide to remove sulphur dioxide, carbon dioxide, and nitrogen oxides; and (4) phosphorus pentoxide to remove moisture not absorbed by the solid potassium hydroxide. J. B. A. Dumas used three potassium hydroxide tubes, and two phosphorus pentoxide tubes—like (4)—only one of each is in the diagram. The phosphorus pentoxide tubes were placed in a freezing mixture. The tube marked (5) in the diagram contained phosphorus pentoxide, and it was assumed that the hydrogen passing through was quite dry—this tube is accordingly called a *témoin tube* (*témoin*, a witness) because it can be employed as evidence that the hydrogen which passed through gave up no moisture to the desiccating agent.

J. B. A. Dumas passed the purified hydrogen over red-hot copper oxide, and determined the loss of weight (oxygen) which occurred. He then weighed the amount of water produced.

The purified hydrogen was passed through a weighed bulb, *A*, containing copper oxide, and heated by the spirit lamp underneath. Most of the water condensed in the bulb *B*, and the remainder was absorbed in the U-tube *C* containing solid potassium hydroxide, and in *D* and *E* containing phosphorus pentoxide. The phosphorus pentoxide tube *D* was kept cool by a freezing mixture. The three tubes *C*, *D*, *E*, and the bulb *B*, were weighed before and after the experiment. The last U-tube, *F*, containing phosphorus pentoxide was followed by a cylinder, *G*, of sulphuric acid through which hydrogen escaped. The vessels *F* and *G* were not weighed; they served to protect the other tubes from the external atmosphere.

The average of nineteen experiments by J. B. A. Dumas (1842) gave:

Copper oxide lost in weight	44·22 grams
Water produced	49·76 „
Hydrogen (by difference) . .	5·54 „

Hence, he inferred that 15·97 parts of oxygen united with two parts of hydrogen to form water, or 16 parts by weight of oxygen combined with 2·004 parts by weight of hydrogen to form water. His nineteen values ranged between 15·892 and 16·024, and his mean value for hydrogen is usually considered to be rather low, or the mean value for oxygen rather high. A later determination by E. W. Morley gave 16 : 2·016. In approximate work, we may take it that 2 parts by weight of hydrogen combine with 16 parts by weight of oxygen to form 18 parts of water; indeed, J. B. A. Dumas himself expressed his belief that the true value of the ratio Hydrogen : Oxygen is probably 2 : 16.

It is common to append to the arithmetical mean of a series of observations the so-called **probable error.** For example, the mean of Dumas' nineteen determinations of the relative weights of hydrogen and oxygen in water is given as: Oxygen, 15·96 ± 0·007, when hydrogen is 2; and O. L. Erdmann and R. F. Marchand's eight determinations by a similar method are represented by the average 15·973 ± 0·011. The probable error in the one place is ±00·07 and in the other ±0·011. This does not mean that J. B. A. Dumas' results were nearer the true value than O. L. Erdmann and R. F. Marchand's. The probable error does not tell how nearly the average of a given number of similarly conducted experiments would approach the average actually found. In J. B. A. Dumas' result, the chances are even that the true average of the determination by his method lies between (15·96 + 0·007 =) 15·967 and (15·96 − 0·007 =) 15·953. If an unrecognized constant error affected all the results, the average actually found would still differ from the true value by this amount. As a matter of fact, when J. B. A. Dumas had nearly finished his work, he did find that his numbers were affected by a curious error, previously unrecognized, so that the concordance of his individual determinations did not prove that his average was right. This error, if not corrected, makes the result appear a little low. The reduced copper retains some hydrogen very tenaciously;[5] similarly, when copper oxide is made, as is usually the case, by calcining the nitrate to redness in a current of air, it retains an appreciable amount of nitrogen. As a result, when the oxide is reduced in a current of hydrogen, the weight of the water formed is less than that which corresponds with the loss of weight which has occurred during the reduction of the copper oxide, assuming that water is really formed by the union of hydrogen and oxygen.

The main objections to J. B. A. Dumas' work turn on the following facts: (1) There is a great difficulty in thoroughly removing all the air from a large complicated apparatus; (2) The absorption of air by sulphuric acid which is slowly evolved along with the hydrogen when the acid acts on zinc; (3) M. Melsens showed that there is a retention or occlusion of hydrogen by the reduced copper; (4) T. W. Richards and E. F. Rogers showed that the copper oxide was probably contaminated with occluded nitrogen and other gases; (5) W. Dittmar and J. B. Henderson showed that there is a slight reduction of sulphuric acid by hydrogen to form gaseous sulphur dioxide (which is later absorbed by the potash); (6) The difficulty in drying the gas, etc., completely. The last is considered by T. W. Richards (1911) to be one of the most fertile sources of error in the determination of accurate equivalents. (7) Before the hydrogen reached the copper oxide, J. B. A. Dumas dried it with sulphuric acid and phosphorus pentoxide, and used calcium chloride to remove the aqueous vapour from the excess of hydrogen which left the copper oxide bulbs. Since phosphorus pentoxide removes more moisture from a gas than calcium chloride, it is possible that some aqueous vapour escaped. This would tend to give high results. (8) E. W. Morley has shown that hydrogen from sulphuric acid and zinc always contains carbon compounds which cannot be removed by absorption; (9) J. J. Berzelius emphasized the fact that the displacement of hydrogen by air at the end of J. B. A. Dumas' experiment, saturated the liquid water with air and made its weight too large; and (10) W. Dittmar has stated that J. B. A. Dumas did not correct his weighings for the buoyancy of air. This would make his weighing of the water produced appear too low.

In 1892 G. D. Hinrichs[6] argued that the combining ratio of oxygen in J. S. Stas' determinations is a function of the amount of potassium chlorate employed, such that with 30–35 grms. of chlorate the atomic weight is 16, and with 100 grms. of chlorate, 15·98. Similar results were obtained with the determinations of J. B. A. Dumas, J. S. Stas, and J. P. Cooke of the atomic weight of sulphur, chlorine, bromine, etc. Hence G. D. Hinrichs argues that the atomic weight should be calculated not from the mean, but from the limiting value corresponding with zero weight of the substance. P. A. Guye and E. Moles have shown that the relation observed by G. D. Hinrichs is confined to determinations in which the quantities of substances employed have been weighed in air and the reduction to vacuum effected by calculation; and the results are satisfactorily explained by assuming that the anomaly is due to the surface condensation of air and moisture, and should therefore disappear when the weighings are conducted in vacuo. The average deviation due to this cause is between 1 in 10,000 and 1 in 20,000. P. A. Guye and E. Moles found that with silver the error due to surface condensation is 2×10^{-5} gram per gram of metal.

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§ 4. E. W. Morley's Experiment on the Composition of Water by Weight

In the determination of atomic weights, a small number of values are to be regarded as fundamental. They are the standards of reference; and by comparison with them all the other atomic weights are established. The atomic weights of hydrogen and oxygen are primary; that is, one or other of them is the basis of the entire system of atomic weights.—F. W. CLARKE.

It will be observed that P. L. Dulong and J. J. Berzelius, and J. B. A. Dumas weighed the oxygen and the water, and estimated the hydrogen by difference. Then followed the work of J. Thomsen, J. P. Cooke and T. W. Richards, and E. H. Keiser, in which the hydrogen and water were weighed, and the oxygen estimated by difference. W. A. Noyes and Lord Rayleigh weighed the oxygen and hydrogen, and estimated the corresponding weight of water. In his memoir *On the Density of Hydrogen and Oxygen, and the Ratio of their Atomic Weights* (Washington, 1895), E. W. Morley first made what J. S. Stas called a *synthèse complète* by weighing all three quantities—oxygen, hydrogen, and water. He synthesized water by burning hydrogen in oxygen, and weighed both gases separately and afterwards in combination. In this way he was able to determine the combining ratio of hydrogen and oxygen. Since the combining ratio of oxygen with a number of metals has already been determined, the combining ratios of the same metals with respect to hydrogen can be computed when once the ratio Hydrogen : Oxygen is accurately known.

Known weights of pure dry hydrogen and pure dry oxygen were stored in two large glass globes. The vessels containing the hydrogen and oxygen were weighed separately. The hydrogen was prepared by heating palladium hydride, and the oxygen by heating potassium chlorate. The hydrogen was weighed as palladium hydride, and the oxygen was weighed in a compensated glass globe. The apparatus for storing and drying the hydrogen and oxygen is not shown in Fig. 3. The globe containing oxygen was connected with the apparatus, and the oxygen passed through a layer of phosphorus pentoxide, and thence into the glass chamber *M*, *viâ* one of the jets *A*; the globe containing hydrogen was similarly connected with the other tube containing phosphorus pentoxide, and the hydrogen led into the chamber *M viâ* one of the jets *A*. The phosphorus pentoxide was not intended to dry the *entering* gases—these had already been dried. The chamber *M* was previously evacuated and weighed. One of the gases, say oxygen, was allowed to enter *M*, and electric sparks were passed across the terminals *F* just over the jets *A*. Hydrogen was led into the apparatus and ignited by the sparks. The rates at which hydrogen and oxygen entered the chamber were regulated so that the formation of water was continuous. The water formed was condensed, and collected in the lower part of the chamber. To hasten the condensation the apparatus was placed in a vessel of cold water—dotted in the diagram. When a sufficient amount of water was formed, the apparatus was placed in a freezing mixture. The mixture of unconsumed oxygen and hydrogen remaining in the tube was pumped away, and analyzed. The weights of hydrogen and oxygen so obtained were added to the weights of unconsumed hydrogen and oxygen remaining in the globes. The phosphorus pentoxide tubes prevented the escape of water vapour. The amount of water formed was determined from the difference in the weights of the system *M* before and after experiment. The amounts of hydrogen and oxygen were determined from the weights of the corresponding globes before and after the experiment. The amount of water formed was determined from the increase in the weight of the above described vessel before and after the combustion.

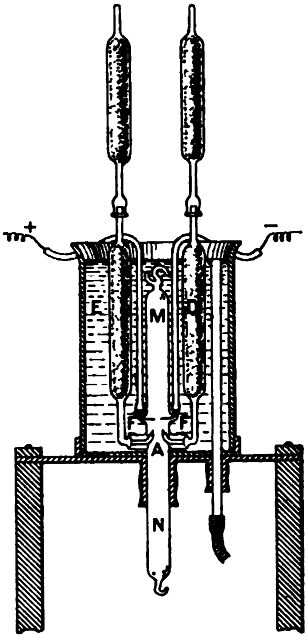

FIG. 3.—Morley's Experiment —Synthesis of Water.

E. W. Morley, as a mean of eleven experiments, found that:

Hydrogen used	3·7198 grams
Oxygen used	29·5335 ,,
Water formed	33·2630 ,,

Hence, taking oxygen = 16 as the unit for combining weight, it follows that **16 parts by weight of oxygen combine with 2·016 parts by weight of hydrogen**

to form 18·016 parts of water—within the limits of the small experimental error, and, adds E. W. Morley: "Until further light is obtained concerning the sources of error which doubtless affect all these experiments, this value is the most probable that can be derived from existing data." It might be added that the ratio Oxygen : Hydrogen = 16 : x for twenty-five sets of determinations by other workers, made since 1821, using different methods, has values of x ranging between 2·003 and 2·018.

§ 5. The Decomposition of Water by Metals

> If, as I have tried to demonstrate, water is really a compound of hydrogen with oxygen . . . in order to obtain hydrogen, it is only necessary to bring water in contact with a substance for which the oxygen has more affinity than it has for hydrogen, in order to liberate the hydrogen as a gas. Iron is commonly used for this purpose, and it is necessary to raise the temperature to a red heat in order to effect the separation. . . . There is *une véritable oxidation du fer par l'eau*. . . . The oxygen is fixed by unity with the iron, and the hydrogen is disengaged as an inflammable gas.—A. L. LAVOISIER (1789).

Water remains permanent and stable so long as the balance of the forces between its constituent elements is maintained, but in the presence of a metal which can unite with one of these elements, the water may be decomposed. One element—say hydrogen—is set free, while the other element—oxygen—unites with the agent of destruction to form a new compound—oxide of the metal. The application of this principle was suggested to A. L. Lavoisier by the illustrious P. S. de Laplace; and as a result, the first conscious analysis of water was made by A. L. Lavoisier, assisted by M. Meusnier, about 1784. This particular process has the disadvantage of isolating only one of the two elements of water. In their *Mémoire où l'on prouve par la décomposition de l'eau, que ce fluide n'est point une substance simple, et qu'il y a plusieurs moyens d'obtenir en grand l'air inflammable qui y entre comme principe constituant*, A. L. Lavoisier and M. Meusnier (1771)[1] passed steam over hot **iron,** and found that the metallic iron was converted into a "black oxide precisely similar to that produced by the combustion of iron in oxygen gas"; otherwise expressed, *the iron is oxidized by the water, and the water is reduced by the iron*, forming "a peculiar inflammable gas," which Lavoisier named hydrogen, because "no other term seemed more appropriate." The word signifies the generative principle of water, from the Greek ὕδωρ, water, and γεννάω, I generate or produce. The German word for hydrogen is *Wasserstoff*—the stuff from which water is made.

The following is a modernized form of M. Meusnier and A. L. Lavoisier's experiment:—Fill an iron, porcelain, or hard glass tube—60 cm. long and 1·5 cm. diameter—with bright **iron** turnings or bright iron nails. In Fig. 4 a hard glass tube is used. This is drawn out at one end as shown in the diagram. This end is fitted with a delivery tube dipping in a gas trough. A roll of previously ignited asbestos paper, 6 cm. long, is inserted in the opposite end. This end is closed with a red rubber stopper and the exit tube of the flask so arranged that it passes a short distance into the core of the asbestos paper. The asbestos roll, later on, prevents the liquid water from coming into contact with the hot glass and breaking the tube. Water is boiled in the flask, and the steam passing through the iron turnings is decomposed. When all the air has been driven out of the apparatus, hydrogen may be collected in the gas jar.

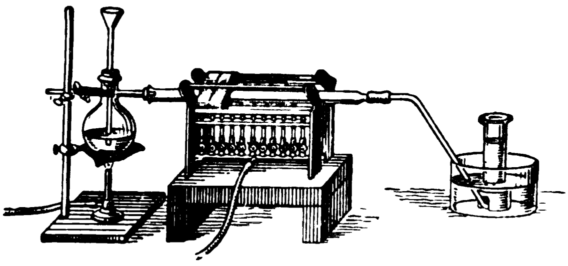

FIG. 4.—Decomposition of Steam by Hot Iron—A. L. Lavoisier and M. Meusnier's Experiment.

If **zinc** be used in place of iron, the temperature need not be much higher than the boiling point of water, since zinc reduces steam and forms zinc oxide at a comparatively low temperature. H. V. Regnault[2] found the zinc oxide is crystalline if the reaction occurs at red heat. If a strip of **magnesium** ribbon be placed in a bulb of a hard glass tube and heated, in a current of steam, at a red heat, the metal appears to burst into flame, forming magnesium oxide. The resulting hydrogen can be ignited if the jet of steam be not too vigorous. According to A. Ditte (1871), magnesium decomposes water slowly at 70°; and according to H. Fleck and H. Bassett (1895), magnesium amalgam decomposes cold water. In A. W. Knapp's experiment (1912) powdered magnesium is added to ten times its weight of water with a little palladious chloride in solution; metallic palladium is formed and this metal acts catalytically or electrolytically on the water. The decomposition is then so vigorous that the water appears to boil, and the escaping hydrogen ignites spontaneously. Metallic **calcium** decomposes cold water and gives off hydrogen, but the action slows down very soon, probably because the calcium hydroxide is not all dissolved by the water, and in consequence a protective crust of this substance forms over the surface of the metal. The calcium can be advantageously warmed with water in a flask which is connected directly with a delivery tube leading to the gas trough. If the water is not free from carbonates, a crust of calcium carbonate also forms over the surface of the metal. Calcium hydroxide is formed as well as hydrogen. The reaction with **strontium** is rather more vigorous than with calcium; and with **barium** more energetic than with strontium. The metal **sodium** decomposes cold water, giving off hydrogen, and forming sodium hydroxide. So much heat is generated during the reaction that the metal melts, showing that its temperature has risen over 95°. The experiment is liable to unpleasant explosions when the sodium is confined so as to enable the resulting hydrogen to be collected. The cause of the explosion has not been definitely established; it has been attributed to the formation of a dioxide or a hydride.[3] It is more likely to be due to the formation of a film or bubble of water superheated above its boiling point. **Potassium** alone reacts so violently with water that the temperature rises high enough to set fire to the hydrogen. The hydrogen burns with a violet-tinged flame, owing to the presence of the vapour of potassium; the hydrogen produced by the action of sodium on water burns with a yellow flame, owing to the contamination of the hydrogen with the vapour of sodium. According to J. J. Berzelius, a solution of metallic sodium in mercury—**sodium amalgam**—decomposes water much less turbulently than sodium alone; the result is similar when a small piece of **potassium amalgam**—3 or 4 mm. diameter—is placed on water. J. J. Berzelius says the gas obtained by the alkali amalgam is odourless, but if an acid or ammonium chloride is also present, the product smells like the gas derived from the dissolution of zinc in acids.

This set of experiments gives a series of metals which appear to react with water with increasing violence; the metals—iron, zinc, magnesium, calcium, sodium, potassium—seem to have an increasing avidity or affinity for oxygen so that they are able to tear the whole of the oxygen from the water, fix the oxygen, and thus liberate half or all the hydrogen as a gas. Under suitable conditions, by treatment with fluorine, chlorine, or bromine, the hydrogen is fixed and the oxygen liberated as a gas. Still further, by passing an electric current through water, both components are liberated in the gaseous state.

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§ 6. The Decomposition of Water by Electricity

Electricity is a key which will open a way into the innermost parts of nature.—J. W. Ritter (1798).

In 1758, G. B. Beccaria [1] exposed water to powerful electric sparks, and although he must have decomposed this substance, he does not seem to have been aware of it; in 1789, the Dutch chemists P. van Troostwijk and J. R. Deiman noticed that when an electric charge from a powerful electric machine was passed through water, bubbles of gas were obtained. They showed that the gases were not due to the expulsion of air dissolved by the water, since the same result was obtained by using distilled water, and water freed from dissolved air by a prolonged boiling. Hence, it can be inferred that **water is decomposed into its constituent gases by the electric discharge.** On May 2nd, 1800, W. Nicholson and A. Carlisle [2] happened to put a drop of water in contact with two wires from a voltaic battery, and noticed the formation of small bubbles of gas about the tips of the wires provided the wires were not in contact. They then immersed the two wires in a glass of water, and found that gases were formed about both wires; the gas collected about one wire was hydrogen, and about the other wire, oxygen. Hence, **hydrogen and oxygen are produced during the electrolysis of water.** The gases were mixed and exploded. The result was water. This is very interesting—chemical combinations can produce an electric current; here an electric current is used to produce chemical decomposition. H. Davy (1807) also showed that the hydrogen and oxygen liberated during the decomposition of water are in the proportions in which they combine to form water.

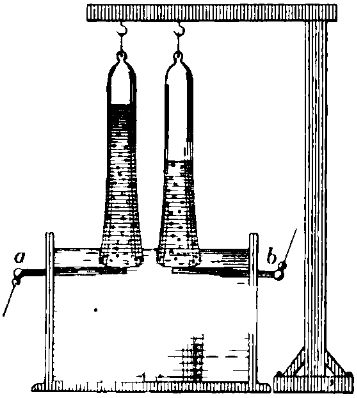

Fig. 5.—J. W. Ritter's Apparatus (1800) for the Electrolysis of Water—Gases separated.

The experiment of W. Nicholson and A. Carlisle appears to have excited a great deal of attention at the time, and many substances were treated in a similar manner. This culminated in the brilliant discovery of the alkali metals by H. Davy in 1807. J. W. Ritter's form of apparatus, shown in Fig. 5, is the prototype of the many ingenious forms of apparatus which have been devised for illustrating W. Nicholson and A. Carlisle's experiment. In place of J. W. Ritter's electrodes *a* and *b*, Fig. 5, adapted for the discharge from an electric machine, plates of gold or platinum, in communication with an accumulator or galvanic battery, are used. During the passing of the electric current, bubbles of gas accumulate on the metal plates and then rise into the test-tubes. More gas is given off at one plate than the other. In fact, the volume of the oxygen obtained approximates very closely to half the volume of the hydrogen. The gas in each tube can be identified by means of a lighted taper or otherwise. In the one tube, the taper burns with the "blinding brilliance" characteristic of oxygen; and the gas in the other tube burns with the blue flame characteristic of hydrogen.

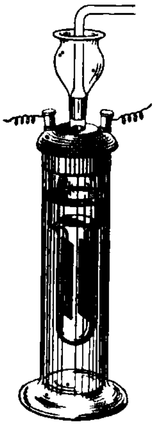

Fig. 6.—Electrolysis of Water—Gases mixed.

The water to be decomposed or electrolyzed is usually acidified with a few drops of, say, hydrochloric or sulphuric acid. Some of the water disappears during the electrolysis, but no change can be detected in the amount of acid mixed with the water. Hence it is inferred that the water, not the acid, has been decomposed. The experiment succeeds equally well if a solution of sodium or potassium hydroxide be used with nickel or iron electrodes. Here again the water, not the alkali, is decomposed. The acid or alkali is used because water alone does not conduct an electric current very well. In fact, pure water is said to be a non-conductor of electricity. Dilute solutions of acids or alkalies are good conductors. If iron electrodes are used in the acidulated liquid much of the oxygen formed during the decomposition of the water is used in oxidizing the metal.

A mixture of one volume of oxygen and two volumes of hydrogen, called **electrolytic gas** or **detonating gas**—A. Volta (1776) called it *aura tonante*—is often wanted in gas analysis, etc. This is easily provided by placing both electrodes under one receiver. The apparatus illustrated in Fig. 6 is often used for this work—it explains itself. The outer jacket keeps the electrolyte cool. Many forms of apparatus have been devised for the electrolytic preparation of small quantities of hydrogen and also of the mixed electrolytic gas.[3]

Are hydrogen and oxygen the sole products of the electrolysis of water?—Electrolytic oxygen often contains a little ozone and the electrolyte some hydrogen peroxide; both these compounds are formed by the electrolysis of acidulated water, but not if a solution of barium hydroxide be electrolysed. Besides oxygen and hydrogen, the early chemists noticed that an acid and an alkali are respectively formed about the positive and negative poles during the electrolysis of water. W. Cruickshank (1800) supposed the acid to be nitrous acid, and the alkali ammonia; J. B. Désormes (1801) considered that hydrochloric acid and ammonia were the products; while M. Brugnatelli (1802) explained the phenomenon by asserting that it is the nature of electricity to produce these substances, and he called the acid product *electric acid*. In 1807, Humphry Davy sought the origin of the acid and the alkali, and published an account of his experiments in a most important memoir entitled, *On Some Chemical Agencies of Electricity*. T. Thomson has styled this investigation "the finest and completest specimen of inductive reasoning which has appeared in the age in which Davy lived."

While accepting H. Cavendish's demonstration that water is a compound of oxygen and hydrogen, H. Davy considered the possibility that some product might result from the unexpected decomposition of oxygen and hydrogen, and he then divested the common experiment of every imaginable source of fallacy. It seemed to H. Davy that the acid and alkali are most likely produced: (1) from the water; or (2) by the decomposition of the glass; or (3) by the electrolysis of sodium chloride derived from the hands touching the instruments; or (4) from substances derived from the ambient air which are decomposed by contact with the electrical apparatus. Instead of conducting the electrolysis in glass vessels, Davy tried vessels of gold, and by taking precautions to eliminate disturbances produced by the contact of the vessels with the hands, and by the presence of impurities in the water, H. Davy found that while an acid still continued to be formed, no alkali appeared, and he showed that the alkali is derived from the solution of the glass vessels during the electrolysis. H. Davy next conducted the electrolysis in an atmosphere of hydrogen, and he then found that neither an acid nor an alkali was developed, and hence he inferred that the acid which appears in the electrolyte is derived from the nitrogen in the atmosphere. Consequently, **when precautions are taken to prevent the introduction of impurities from external sources, no acid or alkali is produced during the electrolysis of water.** It has since been found that the volume of oxygen obtained during the electrolysis of a solution of lithium, potassium, sodium, barium, or calcium hydroxide is sensibly less than half that of the corresponding hydrogen. The hydrogen obtained is rather more than double the volume of the oxygen when an electric current of low density is used for the electrolysis.

It must be emphasized that the decomposition of water by the electric current is not the same in kind as that produced by the disruptive discharge of an electric machine in P. van Troostwijk and J. R. Deiman's experiment. In the latter case, oxygen and hydrogen are evolved at both the poles dipping in the liquid, while in the former case, oxygen is evolved at the one pole, and hydrogen at the other. The electrolysis of water by the disruptive discharge is largely masked by the thermal decomposition of the water (A. L. Lavoisier and M. Meusnier's experiment). J. W. Ritter decomposed water the same year as W. Nicholson and A. Carlisle, but apparently in ignorance of their work. J. W. Ritter modified the experiment. He half-filled the two legs of a **V**-tube with concentrated sulphuric acid, *aa*, Fig. 7, so as not to wet the sides of the tube with acid; he then carefully poured distilled water, *ww*, into each leg of the tube so as not to disturb the acid, when he found the water in the upper part of the legs of the tube did not affect litmus paper. When gold wires, *gg*, connected with a battery were dipped in the water, hydrogen collected at one pole, oxygen at the other. J. W. Ritter said that the water in one leg of the tube is not in communication with the water in the other leg. He therefore inferred that water is an elementary body, and that about the one pole *water unites with negative electricity to form oxygen, and with positive electricity to form hydrogen*, about the other pole. This conclusion conflicts with the evidence obtained when water is decomposed by agents other than electricity, and it was explained by Faraday's experiment on electrolysis.

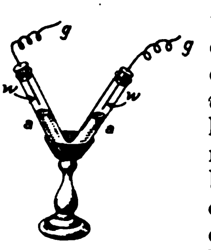

FIG. 7.—J. W. Ritter's Experiment.

The formula for water used to be written HO when the atomic weight of hydrogen was taken unity, and oxygen 8. This agrees quite well with the determinations of E. W. Morley and of J. B. A. Dumas. But we naturally ask for an explanation of the result of the electrolysis of water. Does an atom of hydrogen occupy twice the volume of an atom of oxygen ?

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§ 7. Cavendish's Experiments on the Synthesis of Water by Volume

> It is curious to note the changing fortunes of water in the history of chemistry. First the matrix of the whole universe; then only one of the four elements, though the chief of the quaternion; and at last discovered to be itself nothing but a liquid product of combustion, one oxide among many, the mere ash, rust, or calx of so much burnt hydrogen.—S. BROWN (1851).

From the earliest dawn of scientific speculation, water has been regarded by natural philosophers as one of the four primal elements, and they were quite right, so far as their knowledge went, because they did not know how to decompose it into simpler substances. The dogma had been reiterated so frequently that, down to the days of the first French revolution, no one appears to have entertained any doubts of the simple elementary nature of this liquid; Basil Valentine called it "the mother of the metals." At the beginning of the seventeenth century the sagacious J. B. van Helmont[1] planted a sprig of willow in a vessel suspended in air, and fed it on nothing but water; he found the plant to grow apace—new branches, leaves, and roots sprouted forth. He said:

I placed 200 livres of dried soil in an earthenware pot, and planted therein a sprig of willow weighing 5 livres. At the end of five years, the willow had increased to nearly 69 livres, 3 onces. The vase had never been watered with anything but rain water or distilled water.

Hence it was inferred that the constituents of plants—wood, foliage, acids, salts, and earths—are embodied within elemental water in some mysterious inscrutable way. The experiment seemed to him a crucial one, but J. Woodward's researches[2] showed the conclusion was fallacious because the parts played by the substances dissolved in the water, and by the atmospheric air surrounding the plant, were not recognized. The composite nature of water was not suspected until over a century after J. B. van Helmont's time. Even the shrewd Robert Boyle in his *Sceptical Chymist* (Oxford, 1661) lauded, beyond his predecessors, the importance of water:

It seems evident that water may be transmitted into all the other elements . . . not only plants, but animals and minerals may be produced out of water.

Near the end of the seventeenth century, Isaac Newton[3] noticed that while the refractive indices of various non-combustible substances increase proportionally with their densities, the increase with the refractive indices of combustibles—camphor, turpentine, oils—is greater than corresponds with their densities. "Water has a refractive index in a middle degree between those two sorts of substances, which consist as well of sulphureous, fat, and inflammable parts, as of earthy, lean and alcalizate ones." After the compound nature of water had been discovered, commentators read into Newton's statement a prediction that water would be found to contain an inflammable substance as one of its constituents, although it may be questioned if Newton intended to make any such assertion.

In 1782, J. Priestley[4] thought that he had proved that water is converted into "air of the same purity as the atmosphere" by heating it in porous earthenware vessels so long as there is free access of air to the outside of the retort, but he found the following year, in agreement with a hint he had received from Josiah Wedgwood, that the supposed conversion was a mal-observation, because the air was transmitted from the outside to the interior through the pores of the retort.

In 1776, P. J. Macquer[5] noticed the formation of a liquid resembling water when hydrogen burns in air, and the flame is allowed to impinge on a cold slab of porcelain. Soon after the discovery of oxygen, J. Priestley (1775) noticed that when hydrogen is mixed with certain proportions of oxygen, a violent detonation occurs when ignited by a flame. In the spring of 1781, J. Priestley[6] made what he called "a random experiment to entertain a few philosophical friends," in which a mixture of inflammable air with dephlogisticated air or oxygen was exploded in a closed vessel by means of an electric spark, as had been effected by A. Volta in 1777. The sides of the glass vessel were found to be bedewed with moisture after the explosion. Neither P. J. Macquer nor J. Priestley appears to have paid any particular attention, at the time, to the phenomena; they both seem to have thought that the dew "was nothing else than the mechanical deposit of the moisture dispersed in common air." According to J. Priestley, John Warltire repeated this experiment with a copper vessel, and obtained a slight loss of weight which he thought might be due to the escape of ponderable matter in the form of heat, through the pores of the vessel. In the light of subsequent events, *il est clair*, said A. L. Lavoisier (1781), *que M. Priestley a formé de l'eau sans s'en douter*. Meanwhile, H. C. Cavendish[7] looked upon the deposition of the dew as a fact "well worth examining more closely"; H. Cavendish also wished to find what became of "the air lost" during the combustion of hydrogen in common air. He tried (i) if the air had been changed into carbon dioxide; (ii) if it had been changed into nitric acid; and (iii) if it had been changed into sulphuric acid. He negatived these hypotheses one by one. In the summer of 1781, H. Cavendish followed up the subject by exploding mixtures of dephlogisticated air with inflammable air in closed vessels. A certain amount of the gaseous mixture lost its elastic form, and produced a certain amount of liquid water. In the fourth experiment on exploding gases—dated July 5th, 1781, in his laboratory notebook—H. Cavendish demonstrated the relations between the volumes of inflammable air and common air consumed in the formation of water, for he showed that by exploding a mixture of 7,344 volumes of inflammable air (from zinc and an acid) with 17,361 volumes of common air, there was a contraction of 10,630 volumes, and a gas $\frac{1}{62}$nd of the specific gravity of common air remained. Before the end of the month, H. Cavendish had proved the liquid product to be pure water, for his notebook says:

> The liquid was not at all acid, nor gave the least red colour to paper tinged with red flowers, it yielded no pungent fumes on evaporation, and yielded scarce any sediment on evaporation to dryness.

H. Cavendish stated his conclusion from these experiments when they were described in his paper *Experiments on Air* (London, 1784):

> When inflammable air (hydrogen) and common air are exploded in proper proportion, almost all the inflammable air, and near one-fifth of the common air, lose their elasticity, and are condensed into dew. And by this experiment it appears that this dew is plain water, and consequently that almost all the inflammable air and about one-fifth of the common air, are turned into pure water.

Cavendish repeated the experiment with a mixture of inflammable air (hydrogen) with nearly twice its volume of pure dephlogisticated air (oxygen), and found that almost the whole of the mixture in the globe formed pure water; a quantity of water was collected by repeatedly introducing more gas into the globe and exploding the mixture. The vessel and its contents underwent no change in weight or parted with anything ponderable during the explosion, while a certain volume of gas was replaced by a certain weight of water. Hence, as A. L. Lavoisier[8] has expressed it: *l'eau n'est point une substance simple, et qu'elle est composée poids pour poids d'air inflammable et d'air vital*—otherwise expressed, **water consists, weight for weight, of the hydrogen and oxygen gases lost in its production.** The results of H. Cavendish's experiments, 1781–2, were communicated to J. Priestley not later than March, 1783, and also to A. L. Lavoisier in June, 1783, and published in 1784; the delay in publication was occasioned by the need for investigating the puzzling appearance of nitric acid along with water when oxygen was substituted for atmospheric air. There appears to have been some extensive alterations in Lavoisier's paper before it was published, but there is no means of determining precisely the extent of the additions. J. Watt wrote a letter to J. Priestley, April 26th, 1783, containing an outline of a theory of the composition of water, and on June 19th, 1783, Joseph Priestley[9] read a paper before the Royal Society in which he stated in reference to the bedewed glass in his experiment:

> I carefully weighed a piece of filter paper, and then, having wiped with it all the inside of the glass, weighed it again, and always found, as nearly as I could judge, the weight of the decomposed air in the moisture acquired by the paper.

H. Cavendish's public statement that he had previously communicated to J. Priestley every experiment which was needed to determine the composition of water was publicly acknowledged by J. Priestley. These facts have never been impugned, and they are supported by the entry in the Minute Book of the Royal Society[10] which was confirmed at the meeting on the 26th June, 1783. J. Priestley said:

> These arguments received no small confirmation from an experiment of Mr. Cavendish, tending to prove that the reconversion of air into water, in which pure dephlogisticated air and inflammable air were decomposed by an electric explosion, and yielded a deposit of water equal in weight to the decomposed air.

The work of H. Cavendish was soon confirmed by M. Monge,[11] in a memoir *Sur le résultat de l'inflammation du gas inflammable et de l'air déphlogistiqué dans des* *vaisseaux clos*. M. Monge exploded measured volumes of hydrogen and oxygen in an exhausted glass globe, and by admitting fresh quantities of gas for explosion, he collected a relatively large amount of water. He calculated the weight of the original gases from their known densities, and weighed the liquid product. The results showed :

	Onces.	Gros.	Grains.
L'air inflammable	–	6	10·03
L'air déphlogistiqué . . .	3	0	58·53
Total weights of components . .	3	6	68·56
Total weight of product . . .	3	5	1·01
Deficit		1	67·55

Owing to the use of moist gas, M. Monge over-estimated the weight of the hydrogen which he had employed, and consequently there was a small deficiency between the observed weight of water and the estimated weights of gas required for the synthesis. The water produced was very slightly acid, and he assumed that the acidity is due to " the small quantity of vitriolic (sulphuric) acid which inflammable air carries when prepared by the dissolution of iron " in that acid ; H. Cavendish had already proved that nitric acid is a by-product of the reaction under certain conditions. M. Monge concluded (i) that the volume of hydrogen required for the formation of water is about twice as great as that of the oxygen ; and (ii) that " when inflammable air and dephlogisticated air, both pure, are exploded, there is no other product but pure water, heat, and light." Experiments similar in principle, but with highly purified materials, were made by A. Scott and E. W. Morley[12] over a century later.

J. Watt's claims to the first true conception of water.—In 1783, James Watt,[13] of engineering fame, expressed the opinion that " according to J. Priestley's experiments, dephlogisticated air unites completely with about twice its bulk of inflammable air . . . and therefore water is composed of dephlogisticated air and phlogiston." It is possible, though doubtful, that J. Watt had in mind inflammable air or hydrogen when he used the term phlogiston, and by dephlogisticated air, what is now called oxygen. In his *Thoughts on the constituent parts of water and of dephlogisticated air* communicated to the Royal Society, November, 1783, J. Watt said that he was convinced by the arguments of R. Kirwan and J. Priestley that inflammable air is either wholly pure phlogiston or at least that it contains no admixture of any other matter ; but he added that in his opinion inflammable air contains a small quantity of water and much elementary heat. He regarded heat as a material substance, and invested it with the capacity of combining with other substances like other material elements, and of becoming the basis of those sensible qualities by which bodies are permanently distinguished from each other. According to his theory, dephlogisticated air is composed of water deprived of its phlogiston and united to elementary heat. He believed that dephlogisticated air and phlogiston can unite in certain degrees to form, not water, but fixed air, while under other circumstances they can unite to form neither water nor fixed air, but rather phlogisticated air. In spite of this, it has been claimed that J. Watt was the first to form the conception that water is a compound of dephlogisticated and inflammable air, and that H. Cavendish made the proposition good by unassailable experiments. Naturally, J. Watt's claims have been disputed, and the so-called *water controversy* has been waged upon the rival claims of J. Watt, A. L. Lavoisier, and H. Cavendish.

The controversy is exceedingly involved. The three rival claimants almost simultaneously arrived at analogous conclusions by different paths. H. Cavendish was at work on the products of the combustion of hydrogen ; J. Watt was speculating on the latent heat of steam ; and A. L. Lavoisier was studying the production of acids by the oxidization of inflammable substances. All these paths ultimately converged into the one line of inquiry which culminated in the discovery that water is a compound of hydrogen and oxygen. The issue is confused by the fact that, while the date of publication or receipt by a scientific society is usually taken to be decisive in questions of priority, this is not always satisfactory. In the present case, the observed results of the one were communicated to others before they were published, and alterations were made in some of the original papers, after they had been read and before they were published. Lord Jeffrey has shown that the case cannot be decided by those narrow and jealous canons of evidence derived from the rigid maxims of law or the precedents in cases of patent:

> Courts of law must proceed on inflexible rules, and can make no distinction of persons; and are forced therefore peremptorily to reject all evidence proceeding from the parties concerned, or from those having any interest in the issue; though it is certain by so doing they must occasionally decide against the truth, and against the conviction of all unprofessional observers. The question in a court of law, in short, is never really what the truth of a case is, according to the actual and conscientious belief of the judges or jury, after considering every atom of producible evidence that is in existence, but merely what is the import of the *evidence that is legally admissible*. . . . In all questions before the public no evidence is inadmissible.

J. Priestley tried to repeat the experiment on the formation of water which he said had been described to him by H. Cavendish. In order to ensure the absence of moisture, Priestley prepared his dephlogisticated air from nitre; and his inflammable air, by heating what he called " perfectly made charcoal " in a retort. The gas from the charcoal would obviously be obtained by the diffusion of air and furnace gases through the walls of the retort and the reaction between these gases and the charcoal. J. Priestley failed because, through an extraordinary blunder, the wrong inflammable air was used. According to W. V. Harcourt (1846), " neither the phlogiston nor the inflammable air of Priestley and Watt were convertible terms for hydrogen, their notion of the change of air into water, and of water into air, had no reference to hydrogen, but first to nitrogen, and afterwards to a mixture of gases, the chief of which was carbon monoxide. J. Priestley's paper was communicated to the Royal Society on April 19th, 1783; H. Cavendish's communication to J. Priestley must therefore have been *anterior* to the speculation which J. Watt addressed to J. Priestley on the 26th of the same month, as well as to Lavoisier's experiments the following June." J. Priestley thus comes as an intermediate link, for through him an account of the experiments and conclusions of H. Cavendish were transferred to Watt.

Lavoisier's claims to the discovery of the composition of water.—For a time, some claimed A. L. Lavoisier to have discovered the composition of water independently of H. Cavendish. According to M. Berthelot, the laboratory journal shows that as early as March, 1774, the attention of A. L. Lavoisier was directed to the product of the combustion of hydrogen since he believed that every inflammation ought to be attended by an increase in weight, and in 1777, he burnt hydrogen in air, and, in 1781, oxygen in hydrogen; but A. L. Lavoisier's mind was preoccupied with the conviction that oxidation means acidification, and the production of water, which must have occurred, seems to have passed unheeded. Lavoisier said afterwards that he did not then know about Macquer's experiment. A. L. Lavoisier was always on the alert as to the nature of the products of the combustion of hydrogen, and in 1783 he was in such a position that the slightest hint would enable him to comprehend its true nature. This hint was furnished by the rumours of H. Cavendish's experiment which spread through the scientific world in the spring of 1783. C. Blagden communicated the result of H. Cavendish's experiment to A. L. Lavoisier, at Paris, on June 24th, 1783. A. L. Lavoisier confirmed the fact with a single hasty experiment made a few days after C. Blagden's communication, and described before the French Academy—partly in November and partly in December, 1783. Although the account of H. Cavendish's *Experiments on Air* was not read before the Royal Society until January 15th, 1784, Lavoisier[14] said that on

June 24th, 1783, "Mr. Blagden has informed us that Mr. Cavendish had burnt inflammable air in closed vessels, and that he had obtained a very sensible quantity of water." Consequently, H. Cavendish was undoubtedly first in the field, and he furnished his rivals with the grounds of their conclusions—J. Watt through J. Priestley, A. L. Lavoisier through C. Blagden.

H. Cavendish was certainly not clear about the character of the reaction involved in his synthesis because his mind was unconsciously mystified by the phlogiston hypothesis. He seems to have rather inclined to the opinion that the indifference of hydrogen to oxygen at ordinary temperatures implied the presence of some substance in the former which lessened the intensity of its affinity for oxygen, and he conceived that this substance could be water alone, because water is the sole residue of the combustion of hydrogen and oxygen. Thus, H. Cavendish remarked:

> From what has been said, there seems the utmost reason to think that dephlogisticated air is only water deprived of its phlogiston, and that inflammable air, as was before said, is either phlogisticated water, or else pure phlogiston, but in all probability the former.

The indifference of free hydrogen and oxygen to one another at ordinary temperatures was a source of perplexity to others besides H. Cavendish. Thus, J. Watt[15] said:

> Priestley accounts for the facts by supposing that the two kinds of air, when formed at the same time and in the same vessel, can unite in their *nascent state*; but that, when fully formed they are incapable of acting upon one another, unless they are first set in motion by external heat.

It certainly required Lavoisier's system to give a significance to Cavendish's capital discovery, by showing that water is a definite oxide or calx of hydrogen formed whenever hydrogen is burnt in air or oxygen.

The synthesis of liquid water.—The following is a modernized form of H. Cavendish's elegant experiment, although it is not any more demonstrative. In Cavendish's original experiment, the explosion vessel was weighed before and after the gases were exploded:

A stout glass vessel, *A*, Fig. 8, is fitted with a stopcock, *C*, at one end, and with a piece of strong pressure tubing, *D*, connected with a reservoir, at the other end. A pair of platinum wires, *T*, are sealed into the stout glass measuring vessel just below the stopcock. These wires are put in communication with an induction coil, which in turn is connected with an accumulator. The tube *A* is called the *eudiometer*, or the explosion tube. This is filled with mercury by adjusting the levelling tube *B* and the stopcock *C*. A mixture containing one volume of oxygen and two volumes of hydrogen is introduced into the explosion tube *viâ* the stopcock *C* and by depressing the levelling tube. When the explosion tube is about half or three-fourths filled, read the volume of its contents by bringing the mercury to the same level in both levelling tube and explosion tube. Then depress the levelling tube so that the mercury falls nearly to the bottom of the explosion tube. Pass a spark from the induction coil through the wire terminals of the explosion tube. The gases explode, and the level of the mercury is again adjusted after the apparatus has stood for a few minutes in order to regain the temperature of the room. The mercury rises nearly to the level of the stopcock. The mixed gas probably

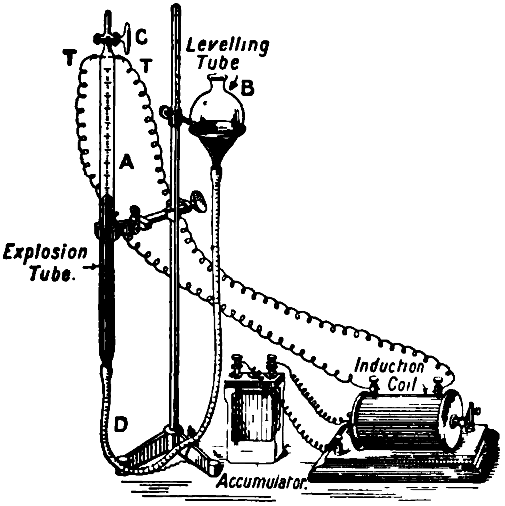

FIG. 8.—Modern Form of Synthesis of Liquid Water by Volume—Cavendish's Experiment.

contained a trace of air, and probably also a slight excess of either oxygen or hydrogen. The advantage of this form of explosion vessel lies in the fact that the explosion takes place under diminished pressure, and is not so liable to fracture the apparatus because it is less violent.

The result shows that two volumes of hydrogen unite with one volume of oxygen to form water. Suppose the experiment be repeated a number of times with, say, one volume of oxygen and three volumes of hydrogen—one volume of hydrogen remains after the explosion; again try the experiment with two volumes of oxygen and two volumes of hydrogen—one volume will remain uncombined after the explosion. It is inferred from this experiment, that **two volumes of hydrogen and one volume of oxygen combine to form water, and if an excess of either oxygen or hydrogen be present, the excess will remain uncombined after the reaction.**

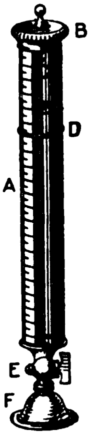

Fig. 9.—Volta's Eudiometer.

Gas analysis.—If a known volume of gas containing hydrogen be mixed with an excess of air or oxygen; or if a known volume of a gas containing oxygen be mixed with an excess of hydrogen and exploded in a eudiometer, the contraction represents the volume of water formed, and the corresponding amount of the gas under investigation can be computed. A. Volta [16] utilized these facts in devising a process to estimate the two gases. A metal cap, *B*, was fitted to the upper part of a graduated tube, *A*, Fig. 9, which constituted J. Priestley's eudiometer. The metal cap carries an insulated wire, *C*, which enabled a spark to be passed in the interior of the tube. A rubber ring, *D*, was used in reading the level of the liquid in the tube. The funnel, *F*, connected with the stopcock. *E*, was used in filling the eudiometer with gas in the pneumatic trough. The limits of explosibility of mixtures of hydrogen and oxygen are approximately Hydrogen : Oxygen=5·4 : 94·6; and 94·7 : 5·3. No explosion occurs if the proportions of these two gases are outside these limits.

Example.—20 c.c. of air were mixed with 20 c.c. of hydrogen and exploded. The mixed gases, after the explosion, occupied 28 c.c. Hence, the contraction shows that 12 c.c. of the mixture combined to form water. Of this two-thirds must have been hydrogen, and one-third oxygen. Hence, the original 20 c.c. of air contained 4 c.c. (*i.e.* one-third of 12 c.c. of oxygen). This illustrates an important principle used in gas analysis.

J. Priestley was led astray by the presence of nitric acid in the water formed by the union of hydrogen with oxygen. According to H. Cavendish's notebooks,[17] he found in September, 1781, that the liquid formed by exploding oxygen with twice its volume of hydrogen contained some nitric acid. H. Cavendish also found that this acid was obtained whether the oxygen was prepared from mercury nitrate, from mercuric oxide, or from plants under the action of solar light; and consequently he inferred that the nitric acid was not present as an impurity in the oxygen. In January, 1783, he showed that, if hydrogen is burnt in the presence of an excess of oxygen slightly contaminated with nitrogen, the excess of oxygen unites with the nitrogen forming nitric acid; but if the hydrogen is burnt with oxygen mixed with a large proportion of nitrogen, "the heat of the explosion is so much diminished that though the affinities of hydrogen and oxygen are sufficient to determine at that temperature the formation of water, the affinities of nitrogen and oxygen are not sufficient to determine the production of nitric acid." H. Cavendish thus demonstrated that the only product of the explosion of hydrogen and oxygen is water.

R. Bunsen (1857) [18] noticed that when electrolytic gas is exploded with air, some nitric oxide is formed, and if an excess of oxygen be present, some nitrogen peroxide is also formed. According to K. Finckh (1905), the amount of nitric oxide so formed depends upon the temperature and pressure of the admixed gases. For instance,

Initial pressure of mercury . . .	450	460	455	750 mm.
Electrolytic gas per 100 vols. air .	88	124	220	210 vols.
Nitric oxide formed	0·22	1·02	2·45	3·01 per cent.

To reduce the proportion of nitrogen oxides formed during the explosion of hydrogen (or hydrocarbons) with air, R. Bunsen found it best to keep the amount of pure hydrogen between 3·81 and 1·55 per cent., for the resulting error is then negligibly small If wider eudiometer tubes than those employed by R. Bunsen are used, these limits must be raised. According to A. Schuller (1882), when hydrogen is exploded with an excess of oxygen, some hydrogen peroxide is formed at the same time.

The volumetric synthesis of steam.—When hydrogen unites with oxygen to form water, is the product equal to the joint volume of the constituents when measured in the same state of aggregation, without allowing the gaseous water to condense to the liquid state? Water is a gas—often called *steam*—when its temperature is a little above 100° at ordinary atmospheric pressures. In 1865 A. W. Hofmann modified an old experiment of J. L. Gay Lussac (1808) by placing a hot vapour jacket about the explosion tube so that the water remains in the gaseous condition and does not condense to a liquid after the explosion. A. W. Hofmann's experiment was described in his *Introduction to Modern Chemistry* (London, 1865), and a modification is illustrated in Fig. 10.

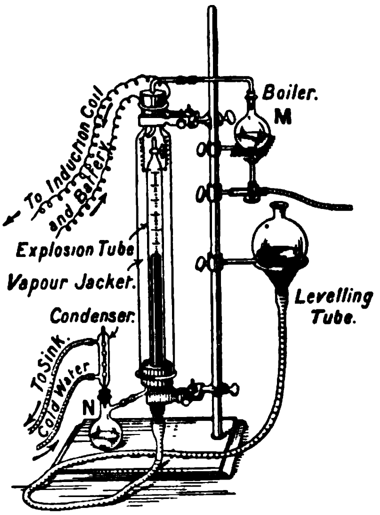

FIG. 10.—Synthesis of Steam by Volume.

The upper end of the glass jacket surrounding the explosion tube, Fig. 10, is connected with a flask, *M*, containing toluene, boiling at about 110°, or amyl alcohol, boiling at about 130°. The lower end of the jacket is connected with a flask and condenser, *N*, so that the amyl alcohol can be recovered. When the amyl alcohol is steadily boiling, and the explosion tube has been filled as described in the preceding experiment, the gases are sparked. In a few minutes, when the temperature has had time to adjust itself, bring the levelling tube in position for a reading.

The result of this experiment is to demonstrate that two volumes of hydrogen unite with one volume of oxygen to form two volumes of steam, for the steam occupies just two-thirds the original volume of the mixed gases. Hence, A. W. Hofmann's form of J. L. Gay Lussac's experiment demonstrates that **when water is synthesized at a temperature above its point of condensation—100°—two volumes of hydrogen react with one volume of oxygen to form two volumes of steam.** Several types of chemical problems are based on this fact. It is necessary to correlate the different results obtained when water is synthesized by volume and by weight.

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CHAPTER IV

THE PHYSICAL PROPERTIES OF GASES

§ 1. The Atmosphere

> The atmosphere in which we live and breathe is really a part of the globe on which we stand. We are not surrounded by mere empty space. On the contrary, we live and move at the bottom of a vast ocean of air, which is just as material as the water which surrounds the flat-fish living at the bottom of the sea (1914).

Air was once considered to be a thin, pellucid, evanescent, inscrutable, and imponderable spirit—the spirit of life. Even to-day, air is still used as a symbol for what is spiritual and divine; but to early man the analogy between the impalpable breath of the physical heavens and the inscrutable spirit of God, was very real. It was quite a long time before air was recognized to be a gravic material essentially ponderable like earth and sea.[1]

The physical properties of air were studied long before its chemical properties were investigated. Anaxagoras, who lived about the sixth century B.C., cited two experiments to show that air is material: (i) A blown bladder resists compression, and (ii) the inside of an inverted drinking glass when plunged beneath the surface of water remained dry showing that the presence of air prevented the ingress of the water. These are among the earliest experiments on record. Aristotle (B.C. 384), in spite of some confused ideas on the nature of gases, considered air to be a material substance which possessed weight, because he found that a blown bladder weighed less when empty than when inflated with air. Simplicius, a writer of the sixth century, commenting on Aristotle, said that Ptolemy showed that air has no weight when weighed in air, and that Aristotle's conclusion was vitiated by the condensation of moisture in the bladder derived from the air blown from the lungs during the inflation of the bladder. About a century before Christ, Hero of Alexandria, in an important work on *Pneumatics*, described some experiments to prove that air is a material substance. For instance, he said:

> Let a vessel which seems to be empty be inverted, and, being carefully kept upright, pressed down into the water; the water will not enter it even though it be entirely immersed; so that it is manifest that the air, being matter, and having itself filled all the space in the vessel, does not allow the water to enter. Now if we bore the bottom of the vessel, the water will enter through the mouth, but the air will escape through the hole. Again, if before perforating the bottom, we raise the vessel vertically, and turn it up, we shall find the inner surface of the vessel entirely free from moisture, exactly as it was before immersion. Hence, it must be assumed that the air is matter.

A similar experiment was mentioned by Empedocles[2] (*circa* 430 B.C.), and a correct explanation given. The same experiment was also described in the essay, *De ingeniis spiritualibus*, by Philo of Byzantium, about 300 B.C.

The weight of air.—In his *Book of the balance of wisdom*, written in the fifteenth century, the Arabian Al-Khazoni recognized clearly that air has weight. He said:

> When a heavy body of whatever substance is transferred from a rarer to a denser air, it becomes lighter in weight; and when transferred from a denser to a rarer air, it becomes heavier. . . . Although the weight of a substance in air does not appear to vary, there is an actual variation, owing to a difference of atmospheres at different times.

However, Galileo dei Galilei, in 1632, is usually credited with having first demonstrated satisfactorily that air possesses weight; and he made a rough determination of the specific gravity of air by comparing the relative weights of equal volumes of air and water. G. Galilei found water to be 400 times heavier than air; and twenty or thirty years later, R. Boyle (1661) found water to be 938 times heavier than air. Both measurements were very crude, and are quite unreliable; G. Galilei's result is too low, R. Boyle's too high. Refined experiments show that 1000 c.c. of dry air weigh 1·293 grms. under standard conditions—760 mm. pressure, 0°, and at sea level in latitude 45°. Hence the specific gravity of air is 0·001293 if water be unity. This means that **a normal litre of dry air freed from carbon dioxide and at 0° and 760 mm. weighs 1·2930 grams at sea-level and a latitude of 45°.** The actual numbers are: 1·29276 (H. V. Regnault, 1847); 1·293085 (P. von Jolley, 1879); 1·29284 (Lord Rayleigh, 1888–93); 1·29273 (A. Leduc, 1898); 1·2930 (P. A. Guye, J. Kovacs, and E. Wourtsel, 1912)—*vide* Cap. on atmospheric air.

The accidental or experimental errors affecting the number 1·2930 amount to less than one in ten thousand. The variations which have been observed show that the density of air is not constant but variable both with respect to place and time. This conclusion is in harmony with the variations which have been observed on the relative proportions of oxygen and nitrogen in air. Thus, P. A. Guye, J. Kovacs, and E. Wourtsel found the weight of a normal litre of air, collected during a rising barometric pressure, to be 1·2927 grm., and 1·2932 grm. when collected during a falling barometric pressure. The former number is taken to mean that the air has a slight deficit in the proportion of oxygen, and the latter, a slight deficit in the proportion of nitrogen—when the normal litre is taken as 1·2930 grms. The specific gravity of air, referred to the standard hydrogen 2, is taken to be 28·75; or it oxygen 32 be the standard, 28·95.

The terms **atmosphere** and **air** are sometimes taken to be synonymous and interchangeable, but the word air is often used when reference is made to a limited portion of the atmosphere. The word *air* was formerly used in the same general sense that the word *gas* is to-day. Later, the meaning of the word air was narrowed to connote the *atmosphere*. The word atmosphere is derived from the Greek ἀτμός, vapour; σφαίρα, the sphere. The term atmosphere is also applied to the gaseous envelope or medium surrounding any body, whatever be the nature of the gas—air, oxygen, carbon dioxide, etc. Hence the term *atmospheric air* is often used to emphasize the fact that *air* is the enveloping medium.

Both Anaxagoras and Aristotle believed that *there is no vacuum* and this belief crystallized into the phrase: Nature abhors a vacuum. For instance, when a glass cylinder, closed at one end, is filled with water; then closed at the open end with the hand; turned upside down; and the hand removed while the open end of the cylinder is under water, the water remains in the cylinder. The rise of water in pump barrels was explained by the same hypothesis. When it was found that water could not be pumped higher than about 34 ft., it followed that the hypothesis required modification, for nature's horror of a vacuum obviously could extend only to the equivalent of 34 ft. of water.

The pressure of the air.—In 1644, E. Torricelli,[3] a pupil of G. Galilei, published an account of an experiment which puzzled the philosophers of the time because they were obsessed by the hypothesis that nature abhorred a vacuum.

In E. Torricelli's experiment, a glass tube—about four feet long, and closed at one end—was filled with mercury, the open end was closed with the thumb, and the tube inverted so that, when the thumb was removed, the open end was immersed in mercury. No air was allowed to enter the tube during the operation. Instead of the mercury remaining suspended in the tube, the column of mercury fell to such an extent that its height above the surface of the mercury in the dish was nearly 30 inches, or 760 mm. The vacuous space in the tube above the mercury is called Torricelli's vacuum.

Nature's horror of the vacuum at the top of the tube extended only to the equivalent of 30 inches of mercury. It did not appear probable that nature should have a particular whim of this character, and E. Torricelli suggested the alternative hypothesis that *the column of mercury was maintained by the air pressing on the surface of the mercury in the outer vessel.* B. Pascal, in his *New experiments concerning the vacuum* (1647), argued that since mercury is nearly 13½ times as heavy as water, 30 inches of mercury will be equivalent to 34 ft. of water, and he accordingly repeated E. Torricelli's experiment with a tube 46 ft. long, using water instead of mercury. He obtained a column of water 34 ft. long. When the experiment was repeated with other liquids, he found, in every case, that the height of the column was inversely as the density of the liquid. Hence, it was inferred that **the height of the column of mercury is a measure of the pressure of the atmosphere,** and that fluctuations in the pressure of the air are accompanied by a corresponding rise or fall in the column of mercury. R. Boyle (1665) applied the term *barometer* to Torricelli's instrument—from the Greek βάρος, weight ; and μέτρον, a measure.

In 1647, B. Pascal persuaded M. Perier to repeat Torricelli's experiment at the bottom and at the summit of the mountain Puy-de-Dôme. On September 23rd, 1648, M. Perier wrote that the result *nous ravit tous d'admiration et d'étonnement,* for the mercury sank lower in the tube the higher up the mountain the vessel was carried. This confirmation of what was anticipated by Torricelli's hypothesis was taken to prove that the pressure of the air per sq. cm. is greater at the bottom than on the top of the mountain, and not as Aristotle and his followers would teach that Nature has a greater horror of a vacuum at sea-level than at higher altitudes. In a posthumous work, *On the weight of the mass of air,* published in 1663, B. Pascal summarized arguments which proved conclusively that *all those effects, previously attributed to Nature's horror of a vacuum, are really produced by the pressure, that is, by the weight of the air.*

After the discovery of Torricelli's vacuum a group of philosophers—Thomas Hobbes, Franciscus Linus,[4] etc.—refused to abandon a favourite hypothesis they had formed that the world is everywhere full and a vacuum is impossible. They were called *plenists* in contradistinction to the *vacuuists*—O. von Guericke, B. Pascal, Robert Boyle,[5] etc.—who believed that a vacuum was possible, and capable of being obtained by certain physical processes. A controversy followed, not always in the choicest of language; thus, Thomas Hobbes, addressing Drs. Ward and Wallis, said :

> But I here dismiss you both together. So go your ways, you uncivil Ecclesiastics, inhumane Divines, Dedoctors of morality, unasinous Collegues, egregious pair of Issachars, most wretched Vindices and Indices Academiarum, and remember Vespasian's law (*maledici senatoribus non opportere ; remaledicere fas et civile esse*) that it is uncivil to give ill language first, but civil and lawful to return it.

The facts finally conquered an erroneous hypothesis.

Units of pressure.—The pressure of the air in any given locality varies within comparatively narrow limits. **The normal or standard pressure of the atmosphere** is equal to the weight of a column of mercury of unit area, and 760 mm. high. This pressure is sometimes called " one atmosphere." It is merely necessary to know the height of the barometric column to know the weight or pressure of the air per unit sectional area. The standard corresponds with a weight of (76 × 13·596 =) 1033·3 grms. per sq. cm., or 14·7 lbs. per sq. in. The word *pressure* is generally used in preference to *weight,* because air, like all other fluids, not only presses downwards, but also equally in all other directions.

The selection of the atmosphere as the unit of pressure is quite arbitrary, and other units are used—*e.g.* the kilogram per sq. cm., and the pound per sq. in. The pressure of a dyne per sq. cm. was recommended by the International Physics Congress at Paris in 1900, because it is consistent with the C.G.S. system of units. This unit was called a *barie ;* a similar unit, the *barad,* was proposed by a committee of the British Association in 1888, and there has been some controversy as to whether the unit had better be referred to a dyne per sq. cm. or to a pressure a million times greater. The density of mercury is 13·596, and in latitude 45° the force of gravity is equivalent to 980·6 dynes. Hence, a barometer column 76 cm. high will be maintained by a pressure equivalent to $76 \times 13{\cdot}596 = 1033{\cdot}3$ grms., or $1033{\cdot}3 \times 980{\cdot}6 = 1{,}013{,}300$ dynes per sq. cm., or in round numbers, 10^6 dynes per sq. cm. This number—called a **megabar**—may be inconveniently large, and a ten-thousandth part of 10^6 is called a **bar**, hence, a bar is equivalent to 100 dynes per sq. cm. ; a

centibar to one dyne per sq. cm.; and a **millibar** to 0·1 dyne per sq. cm. This unit, the millibar, has been recommended for recording barometer readings. One megabar is equivalent to 750 mm. of mercury, under standard conditions. The approximation is correct to one part in 5000. Since $13·596 \times 980·6 = 13332$; and one ten-thousandth of this is 1·3332, it follows that **to convert centimetres into bars, multiply by 133·33**; and, **to convert bars into centimetres, multiply by 0·0075.** Since there are nearly 2·54 cms. in an inch, $133·33 \times 2·54 = 338·63$, therefore *to convert inches into bars, multiply by* 338·63. A pressure of one megabar is almost 2 per cent. greater than a kilogram per sq. cm.; and 1·3 per cent. less than the atmosphere unit.

The extent of the atmosphere.—The air gets less and less dense at higher and higher altitudes, and I. Newton (1704) estimated air to be four times rarer at an elevation of about 7½ miles than at sea level; 1,000,000 times rarer at a height of 76 miles; and 1,000,000,000,000,000,000 times rarer at an altitude of 228 miles; and so on. If p_0 be the pressure and D_0 the density of air at sea level, E. Halley's formula [6] becomes

$$\text{Pressure of air at an altitude } h = p_0 e^{-\frac{D_0 h}{p_0}}$$

Variations in the value of the gravitation constant, g, and the rotation of the planet are neglected. Under actual conditions, the earth's atmosphere is incessantly agitated by convection currents—winds and storms—so that there is a continual transfer of air from one part to another. The limiting height at which the atmosphere is in convective equilibrium is about 29 kilometres, and the temperature falls roughly about 10° per kilometre as we ascend. Above this region, the temperature of the air is constant. It is indeed impossible to place a limit to the height the atmosphere extends. G. J. Stoney showed that, because the molecules of some gases attain certain high velocities, these gases are able to escape from the atmosphere of the earth and the other planets. At a height of 100 to 125 miles, there is sufficient air to offer enough resistance to the passage of meteorites to raise their temperature to incandescence. Whatever be the height, the weight of the normal barometric column (per square centimetre of mercury) measures the normal weight of a column of air of the same sectional area and extending from sea level upwards. B. Pascal (1663) appears to have been the first to calculate the total weight of all air about the globe. His estimate is 8,283889,440000,000000 livres—where a *livre* is equivalent to 1 lb. 1 oz. 10¾ dr. avoirdupois.

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§ 2. The Influence of Pressure on the Volume of Gases—Boyle's Law

> At the bottom of all cosmic order lies the order of mathematics, the law that twice two is always four.—P. CARUS.

The quantity of matter in a gas is most frequently determined by the measurement of its volume. The volume of a gas is very sensitive to changes of pressure, and it is therefore very pertinent to inquire: What is the effect of variations of pressure on the volume of a gas? About the time Pascal and Torricelli demonstrated the weight and pressure of the atmosphere, O. von Guericke (1650) invented the air pump. The new instrument attracted much attention, and the effect of the "vacuum" (reduced pressure) was tried on all kinds of animate and inanimate objects. In his memoir, *Nova experimenta physico-mechanica de vi aeris elasticæ* (London, 1660), Robert Boyle says that he placed a partially inflated lamb's bladder in the vacuum produced by the air pump, and noticed that the bladder became fully distended to its former size. Boyle thus established the important fact that the less the pressure exerted upon a given mass of air, the greater its volume. In 1661, Boyle continued his work on the elasticity or spring of air, as he called it, and stated that R. Townley,[1] after reading about Boyle's experiments on the determination of the density of air from the height of a column of mercury which it supports, propounded the view that "the pressures and expansions are in reciprocal proportions." On August 2nd, 1661, R. Hooke made some experiments which confirmed Townley's hypothesis, and W. Croone and R. Boyle, at a meeting of the Royal Society on September 11th, 1661, gave an account of some experiments on the same subject. In his *Defense against Linus* (London, 1662), Robert Boyle published an account of the experiments which clearly established R. Townley's hypothesis. Accurate experiments of this nature, said Boyle, "have not been previously made (that I know) by any man." Boyle's result can be expressed in words: **the volume of a gas kept at one uniform temperature varies inversely as the pressure.** This is **Boyle's Law.** Some years afterwards, E. Mariotte, in his *Discours de la nature de l'air* (Paris, 1679), reported analogous results which he and M. Hubin obtained in 1676 by means of an apparatus similar to that employed by Robert Boyle, which led him to take it *pour une régle certaine ou loi de la nature, que l'air se condense à proportion des poids dont il est chargé*, and thus to confirm R. Boyle's deduction made fourteen years earlier. On the Continent, ignoring a priority of at least fourteen years, the law is sometimes improperly designated *la loi de Mariotte*, or *Mariottesches Gesetz.* At the time of the discovery of the law, air was the only gaseous body known, and therefore the accuracy of the law was established by Boyle and Mariotte for one body only. The law of Boyle may therefore be expressed: **The product of the pressure and the volume of a gas kept at one uniform temperature is always the same.** Or, for a given mass of air, $pv =$ **constant.** The numerical value of the constant, of course, depends upon what units are selected for representing the pressures and volumes. Pressures may be expressed in atmospheres, millimetres of mercury, pounds per square inch, etc.; and the volume in litres, cubic centimetres, cubic feet, etc. Boyle's law assumes yet another guise. If p_1 be the pressure of a gas occupying a volume v_1; and p, the pressure when the volume is v, then, since the products pv and p_1v_1 are equal to the same constant, they are equal to one another. Consequently $pv=p_1v_1$. If any three of these magnitudes be known, the fourth can be calculated directly. A large number of measurements are summarized in these formulæ, any one of which, indeed, contains the essence of all Boyle's observations condensed into a simple equation.

EXAMPLE.—A eudiometer holds 4·5 litres of gas when the barometer reads 755 mm. What will be the volume of the same body of gas when the barometer stands at 760 mm.? Here, $p_1=755$, $v_1=4{\cdot}5$, $p=760$, hence, $v=4{\cdot}47$ litres. The most common problem is to calculate—reduce—the volume of a gas at any observed pressure, to the corresponding volume at normal pressure, 760 mm. Given 4·5 litres of gas at 755 mm. pressure, there is no need for any formula to calculate the corresponding volume at 760 mm. The pressure 760 mm. is greater than 755 mm., hence the volume will be less, hence multiply 4·5 by the fraction $\frac{755}{760}$ and the result is 4·47 litres.

When the volume of gas, collected over mercury, is to be measured when the pressure of the atmosphere is 760 mm., and the difference in the levels of the mercury in the gas jar and in the pneumatic trough is 56 cm., it follows that the pressure of the gas in the narrow tube is 760 mm. less 560 mm.=200 mm. Whenever practicable, of course, the mercury inside and outside is brought to the same level before the gas is measured.

Suppose that the confining liquid is water, not mercury. Water is frequently used when the gases are not appreciably soluble in that liquid. Suppose that the external pressure is 760 mm. (barometer), and there is a difference of 10 cm. between the level of the water exposed to the gas, and the level of the water exposed to the air. The weight of 10 cm. of water is not the same as the weight of 10 cm. of mercury. Mercury is 13·596 times as heavy as water, hence, a 10 cm. column of water is equivalent to the weight of a column of mercury 10÷13·596 or 0·74 cm. or 7·4 mm. high. The pressure of the gas is therefore 760 — 7·4 = 752·6 mm. But water vapour exerts a definite pressure at any given temperature, and a still further reduction must be made if we want the pressure actually due to the gas and not to the mixture of vapour and gas. This will be investigated later.

Test for the equilibrium of gases.—If the gas be confined under such conditions that the product pv at any fixed temperature is not constant, the system will not be in a state of equilibrium. If a gas were confined in a cylinder with a sliding piston moving without friction and if the constant in Boyle's equation be p (in atm.) v (in litres)=12, then, if the piston supports a weight of 6 atms., the gas will expand or contract until the product pv satisfies the test. Consequently, **Boyle's law describes the necessary condition for the volume and pressure of a gas to be in a state of equilibrium when the temperature is invariable.** In practice there is no such thing as a frictionless piston, and if Boyle's law were to be tested in a real cylinder an allowance would have to be made for the friction of the piston by putting an extra weight α on the descending piston and a less weight β on the ascending piston; Boyle's law would then be $(p+\alpha)v$ or $(p+\beta)v$ is equal to a constant.

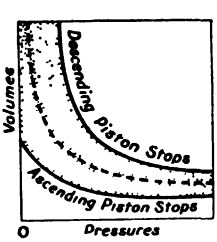

FIG. 1.—Duhem's Experiment.

P. Duhem (1902)[2] has used an interesting illustration. The dotted curve, Fig. 1, represents the relation between pressure and volume as defined by Boyle's law. If the volume corresponding with any given pressure be observed when the rising piston has come to rest, the observed volume will appear to be less than that corresponding with the pressure as defined by Boyle's law, because friction will prevent the piston rising to the point corresponding with the equilibrium position on the dotted curve. Similarly, on a descending piston, friction prevents the volume attaining that indicated on the equilibrium curve.

The friction thus corresponds to what J. W. Gibbs (1876) called the **passive resistance** of a system to assume a state of equilibrium. The nature of the passive resistance can here be recognized, but in some cases we feel sure that something analogous retards the movement of a system to the condition called stable equilibrium, although we know nothing of the character of the passive resistance or **hysteresis**—from ὑστερέω, I lag behind—which opposes the change.

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§ 3. Deviations from Boyle's Law

Experimentally we do not know of any gas behaving in strict conformity to the law of Boyle; but in the case of many gases, and of nearly all gases at very high temperatures, the deviation from uniformity is very slight.—J. B. STALLO.

The pressures used by Boyle extended over a range varying from 3 cm. to 300 cm. of mercury. It is hazardous to infer that because the product pv is constant over a limited range of pressures, it will remain constant for pressures widely different from those actually measured. The method of measurement used by R. Boyle, though excellent for its time, is now considered somewhat crude. In the middle of the eighteenth century, P. van Musschenbroeck (1729), J. H. Sulzer, and J. Robinson tried to find if Boyle's result could be extended to all pressures, but with no very definite results. In 1799, M. van Marum[1] called attention to the deviation of ammonia from Boyle's law at high pressures. H. C. Oersted and C. Suensson (1826), and C. Despretz (1827) extended the observations to other gases, and it was found that the easily condensable gases like ammonia, hydrogen sulphide, and cyanogen began to deviate appreciably from Boyle's law at pressures exceeding two atmospheres, and with air, the constancy of the product began to fail at pressures exceeding 20 atm., for it diminished with increasing pressures. Similar conclusions were established for other gases by F. J. D. Arago and P. L. Dulong (1831) and by C. S. M. Pouillet (1844).

Later on, many careful investigations were made by H. V. Regnault (1847), J. O. Natterer (1850–4), L. Cailletet (1870–9), E. H. Amagat (1869–93), and others, to find if the simple law of R. Boyle correctly describes the behaviour of gases at pressures far removed from the normal pressure of the atmosphere—76 cm. of mercury. The general results show that *no two gases behave precisely in the same way*. The deviations for many gases are significant. By differentiating the relation pv = constant, k, or rather $v = k/p$, $dv/dp = -k/p^2$, and if k be taken unity, and $p = 2, 3, 4, \ldots$ be substituted,

$$-\frac{dv}{dp}=\frac{1}{p^2}; \quad \therefore \quad -\frac{dv}{dp}=\frac{1}{4}, \frac{1}{9}, \frac{1}{16}, \ldots$$

meaning that the greater the pressure to which a gas is subjected the less the corresponding decrease in volume, $-dv$, for any subsequent increase of pressure. With most gases, the concentration increases more, that is, the volume increases less than Boyle's law describes; and at high pressures, the concentration increases less, that is, the volume is greater than Boyle's law indicates. This is illustrated by plotting Boyle's law. Boyle's law, when graphed, furnishes the continuous curve shown in Fig. 2. This curve is a rectangular hyperbola. The deviations with nitrogen from this ideal condition are indicated by the dotted line in the same Fig. 2. If it were not for this phenomenon, the density of the gas would increase so that while oxygen at one atm. pressure weighs about 0·0014 grm. per c.c., at a pressure of 3000 atm. the gas would be four times as heavy as water, and at 10,000 atm. pressure over 13 times as heavy as water.

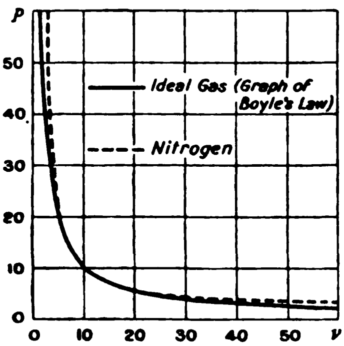

FIG. 2.—Volume : Pressure Curves.

According to Boyle's law, the volume of a gas should diminish indefinitely as the pressure is increased, and in time the volume would approach zero, or become indefinitely small. This is absurd. Pressure can diminish only the space between the molecules and not the actual substance of the molecules. Hence, if b denotes the volume occupied by the molecules the changes in the volume of the gas with variations of pressure will be represented by $p(v-b)$=constant, not by pv=constant. It does not follow that b represents the actual volume of the space occupied by the matter in the molecules. The effect of the volume of the molecule on the compressibility of a gas was dimly recognized by D. Bernoulli, 1738; and by M. W. Lomanossoff, 1750; it was studied by A. Dupré, in 1865; and by J. D. van der Waals in 1872.

In his important *Mémoires sur l'élasticité et la dilatabilité des fluides jusqu'aux* *très hautes pressions*, embodying the results of work extending from 1878 to 1893, E. H. Amagat showed that while the product pv remains fairly constant at low pressures for many gases, the numerical value of pv changes in a remarkable manner as the pressures increase in magnitude. E. H. Amagat's measurements for carbon dioxide show that the product pv is not constant, for when

p . .	1	50	100	125	150	200	500	1000 atms.
pv . .	1	0·92	0·49	0·31	0·31	0·50	1·02	1·81

Notice how the product pv at first diminishes in magnitude and then steadily increases. This is brought out very clearly on plotting the numbers. If the products pv were constant for all values of p, we should get the straight line, dotted and marked *ideal gas line* in Fig. 3; with carbon dioxide, however, the curve descends below the line for an ideal gas, and then steadily rises, passing above the ideal gas line when the pressure is nearly 500 atmospheres.

The curves for hydrogen, helium, argon, and neon, at ordinary temperatures, do not descend below the ideal gas line, but take a path resembling the hydrogen line shown in Fig. 3. However, even these gases exhibit the same peculiar behaviour at lower temperatures. Thus, according to H. K. Onnes and C. Braak (1907), with hydrogen at —140°, the product pv reaches a minimum when the pressure is about 25 atmospheres; at —195°, 45 atmospheres; and at —213°, 51 atmospheres. In 1886, C. Bohr reported that oxygen behaved in a peculiarly abnormal manner at a pressure of about 0·7 mm. of mercury. The pressure-volume curve gave an abrupt change of direction which was ascribed to the transformation of oxygen into another variety; but some careful measurements by Lord Rayleigh (1907) and M. Thiesen (1901) indicate that the statement is probably based upon a mal-observation. To summarize these results at a constant temperature:

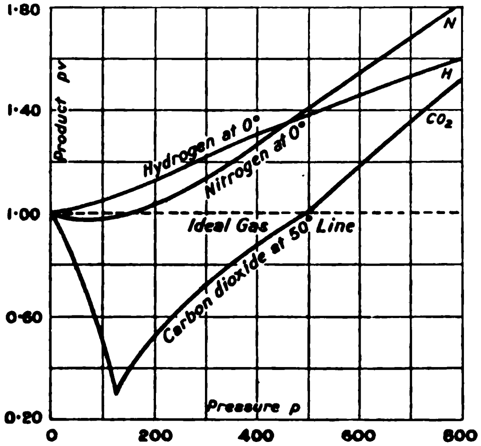

Fig. 3.—pv-Pressure Curves (Amagat).

(1) With small pressures, the product pv decreases with increasing pressure showing that the volume of gas, at relatively small pressures, is less than is described by Boyle's law. At very low pressures, the gas will follow Boyle's law $pv = p_1v_1$. Lord Rayleigh (1901–2) found no appreciable variation with oxygen, hydrogen, and nitrogen between 0·01 and 1·5 mm., showing that between these pressures the deviations from Boyle's law are too small to be detected.

(2) With large pressures the product pv increases with increasing pressure, showing that the volume of the gas, at relatively great pressures, is greater than is described by Boyle's law.

(3) All gases, in consequence, show a minimum value for the product pv. At 0°, for example, the minimum value of pv for air and nitrogen occurs at 100 atm. pressure; for oxygen at about 200 atm.; for carbon dioxide, at about 35 atm.; and for ethylene at about 42 atm. The pressure corresponding with the minimum depends on the nature of the gas and on the temperature. The minimum is less prominent with the more permanent gases than with the more condensable gases.

Gases which obey Boyle's and Charles' laws under ordinary atmospheric conditions usually remain gaseous at comparatively low temperatures and are accordingly called *permanent gases.*

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§ 4. Dalton's Law of Partial Pressures

> Accurate and systematic investigation has brought to light the infinite complexity of nature; the fineness of the dovetailing of every event into many others; the never-ending response of all things to changes in the conditions that encompass them; the universal orderliness of natural occurrences; and the absolute interdependence of cause and effect. —M. M. P. MUIR (1894).

When two gases, which do not act chemically on one another under the conditions of the experiment, are brought together, the gases mix intimately, by diffusion, so as to form a homogeneous mixture. Furthermore,[1] John Dalton (1802) found that each gas seemed to exert the same pressure as if it occupied the space alone, and the total pressure of the mixture of gases was the sum of the several pressures due to each gaseous component of the mixture. If P be employed to denote the total pressure of a mixture of gases, and p_1 the partial pressure exerted by one of the gases, p_2 the partial pressure exerted by another gas, p_3 the partial pressure of a third gas, Dalton's discovery means that: $P = p_1 + p_2 + p_3 + \ldots$ In words, **in a mixture of gases which exert no physical or chemical action on one another, each gas exerts the same pressure as if it alone occupied the entire vessel, and the total pressure is the sum of the partial pressures due to each of the gases.** This is Dalton's law of partial pressures. If the four volumes of nitrogen and one volume of oxygen in the atmosphere be under normal pressure, the nitrogen gas will sustain a pressure approximately 608 mm. and the oxygen gas 152 mm. of mercury. J. Dalton added:

> Since two gaseous fluids which exert neither attraction nor repulsion on one another, distribute themselves so that their united pressure is equal to the pressure of the atmosphere, all the components of the atmosphere are arranged together at a given pressure and temperature, and by a paradoxical though true disposition, each of them occupies all the space destined for the aggregate.

It might be added that Dalton's partial pressure law is quite independent of Boyle's law, and can be extended to mixtures of any number of gases.

Examples.—(1) Moist hydrogen gas is confined over water under a pressure of 747·2 mm. of mercury at 15·3°, the partial pressure of water vapour at that temperature is 12·9 mm. of mercury. Then, from Dalton's law of partial pressures, it follows that the hydrogen gas itself is under a partial pressure equivalent to 747·2 less 12·9, or 734·3 mm. of mercury.

(2) If atmospheric air contains a mixture of four volumes of nitrogen and one volume of oxygen, show that if the manometer records a pressure p, the partial pressure of the oxygen gas will be $\frac{1}{5}p$, and of the nitrogen gas $\frac{4}{5}p$.

(3) If a moist gas of volume v_1 be confined in a vessel at a pressure p_1, show that the volume v of dry gas at normal pressure, 760 mm., and the volume v_2 of the water vapour at normal pressure, are respectively $v=v_1(p_1-f)/760$, and $v_2=v_1f/760$, where f denotes the vapour pressure of the water at the temperature of observation.

There are many reasons for supposing that the molecules of a substance exert some kind of attraction on one another. This intermolecular attraction gives rise to phenomena of cohesion, viscosity, capillarity, surface tension, etc. The intermolecular attraction is probably very powerful in solids, weaker in liquids, and very small with gases; but it is highly probable that the molecules of nearly all gases do exert some attractive influence on one another, and the gases, in consequence of this *physical* action, "deviate" from Dalton's law to an extent dependent upon the magnitude of the intermolecular attraction. Many mixtures of gases show slight, but not marked deviations from the law, *e.g.* carbon dioxide and sulphur dioxide; hydrogen with air, and with nitrogen; etc.

P. Fuchs[2] has investigated the change in volume which occurs on mixing chemically indifferent gases—nitrogen with nitrous oxide, carbon dioxide, or oxygen; nitrous oxide with carbon dioxide or oxygen; and oxygen with carbon dioxide. In every case there is an expansion which is greater the more the two components differ in physical properties. The change in volume does not correspond with the ratio of the two gases, but reaches a maximum which is beyond the 1 : 1 ratio, so that the maximum change occurs with mixtures containing more than 50 per cent. of the gas with the lower critical temperature; and the maximum lies nearer to the 1 : 1 ratio, the more the components resemble one another. The change in volume δv is qualitatively but not strictly quantitatively represented by J. D. van der Waals' equation

$$\delta v = x(1-x)\left(\frac{a_1+a_2-2a_{12}}{MRT}-(b_1+b_2-b_{12})\right)$$

where x denotes the number of gram-molecules of the one gas, and $(1-x)$, of the other; a_1 represents the attraction constants of the molecules of the one component; a_2, of the other component; and a_{12}, of the molecules of the different components for one another; b_1, b_2, and b_{12} represent the corresponding volume constants. Accordingly, the theoretical results agree more closely with the observed results when an allowance is made for the effect of the attraction of the molecules for one another.

J. Dalton's law is thus a limiting law for ideal gases. A. Leduc[3] prefers to state the law for actual gases in the form: *The volume occupied by a mixture of gases is equal to the sum of the volumes which the component gases would separately occupy at the same temperature and pressure as the mixture.* If two gases, originally at the same pressure, are mixed so that the temperature and total pressure remain unaltered, the pressure of the mixture can be calculated if the coefficients of deviation from Boyle's law, A, be known between the common pressures p and p_1 for the mixture and for each of the two gases, where

$$A_1^2=\left(\frac{p_1v_1}{p_2v_2}-1\right)\left(\frac{1}{p_2-p_1}\right)$$

There is usually found to be a slight increase of pressure on admixture which is scarcely measurable with the less condensable gases. The value of A at 16° between

1 and 2 atm. is 0·000143 for a mixture of nearly equal volumes of carbon and sulphur dioxides; 0·000005 for air; −0·000002 for equal volumes of hydrogen and oxygen.

The law had been applied to test if chemical action occurs on mixing certain gases, *e.g.* to find if any sign of chemical action occurs when nitric oxide (NO) is mixed with nitrogen peroxide (NO_2) resulting in the formation of nitrogen trioxide (N_2O_3). It is assumed that if no chemical combination takes place, the mixture will obey Dalton's law, and conversely.[4] The conclusion can be valid when it has been shown that the molecules of the two gases exert neither attraction nor repulsion upon one another. If they did, the test might lead to wrong conclusions with respect to chemical action. A slight contraction, for instance, might be evidence of molecular attraction, not of chemical combination.

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§ 5. The Laws of Nature

We must confess that physical laws have greatly fallen off in dignity. No long time ago they were commonly described as the Fixed Laws of Nature, and were supposed sufficient in themselves to govern the universe. Now we can only assign to them the humble rank of mere descriptions, often erroneous, of similarities which we believe we have discovered. —J. H. Poynting (1899).

Nature, always working by law, is always consistent, always inexorable; her laws are invariable.—A. Simmons.

This is a convenient place to further emphasize the meaning of the term "law" in chemistry. The laws of a country may be the enactments of a ruling power, the ukases of a czar, or the regulations of the police superposed upon a people compelling them to act in particular ways, but it is of course absurd to say that Dalton's law and Boyle's law *must* be obeyed, implying that these laws are commands imposed upon gases which they are compelled to obey. The laws of nature describe, they do not compel. A substance does not act in a particular way because there is a law, but the law originated when it was found that substances acted in that particular way. Consequently, law is a useful term which the careless sometimes personify; it is a figure of speech, and is employed by scientific men purely in a metaphorical sense. The term has led to some confusion, for it has led to the belief that the uniformity described by the law has been imposed on nature by the will of a rational being—God himself. As previously indicated, a law in science is a kind of summary of the present state of our knowledge of the phenomena described by the law, and it is always subject to revision with the growth of knowledge. **Laws do not necessarily establish facts.** Consequently, the term would be replaced by another word, if we could think of a better. *Rule* would perhaps lead to less misunderstanding. The German equivalent—*Gesetz*, statute—is perhaps worse. A law of nature can have authority only in so far as it is based on facts. As indicated previously, the term "law of nature" is applied to a comprehensive generalization which "methodically and systematically describes certain natural phenomena." The laws of chemical combination describe what the elements do under definite conditions; and generally, **the laws of chemical and physical phenomena are collocations of those circumstances**

which have been found by experiment and observation to accompany all chemical and physical changes included in the statement of the law. The test of the "law" is that the statement holds good without exception. A broken law, said J. H. Poynting, is a false description.

It is sometimes said that a law of nature has never been disproved; this can only mean that if a law of nature is disproved, it ceases to be a law. The common meaning attached to the saying, "The exception proves the rule," is wrong, and it is an instance of confusion arising from the double meaning of words. In the old Latin form, *Exceptio probat regulam*, the word *probat* means tests, just as to-day proving wines means testing them. The proverb therefore meant that the apparent exception furnishes a means of trying, testing, or proving the rule, and if the exception cannot be explained, then the rule breaks down, for the **exception disproves the rule.** The exception annihilates the rule, for, said J. W. Ritter in 1798, a law must be abandoned immediately a real exception is discovered—it is no longer a law.

When the exact conditions are set up, the law describes the phenomenon without variableness or shadow of turning. The law is then regarded as an objective power. This power is called a force, and further, the force is said to be the cause of the phenomenon. Thus gravitation is regarded as an attractive force causing one particle to attract every other particle in the universe; chemical affinity is regarded, in this sense, as a selective chemical change. If therefore we find a gas deviating from Boyle's law, or a mixture of gases "disobeying" Dalton's law, the alleged laws may be false, incomplete, or imperfect descriptions, or some perturbing influence is at work which masks the simple phenomena described by these laws.

§ 6. The Influence of Temperature on the Volume of Gases—Charles' Law

> According to the schools of philosophy, it has been proved that the effect of cold is to make bodies contract while heat makes them expand.—G. GALILEI (1615).

The expansion of air by heat has long attracted the attention of chemists. Hero of Alexandria (*c.* 117 B.C.), G. B. Porta (1616), C. Drebbel (1608), and G. Galilei (1615) experimented on the subject. H. Boerhaave considered the effect of temperature on the volume of gases, and, in his *Elementa chemiæ* (Lugduni Batavorum, 1732), he stated that when air is heated, it becomes so rare that neither the measure nor the limit of its dilation has been yet discovered; and added:

> Air of unequal masses but of the same density, is always expanded in the same measure by the same degree of fire; so that these expansions in the same density of air, by a constant law of nature, are always proportional to the augmentations of heat.

Influence of temperature on the volume of gases—pressure constant.—In 1790, Joseph Priestley concluded "from a very coarse experiment" that "fixed and common air expanded alike with the same degree of heat;" J. Dalton, in 1801, inferred from his experiments: "Upon the whole, I see no sufficient reason why we may not conclude that all elastic fluids, under the same pressure, expand equally by heat;" and J. L. Gay Lussac,[1] in 1802, quoted some experiments in support of the generalization: **The same rise of temperature produces in all gases the same increase in volume, provided the pressure and mass be kept constant.** This law is generally designated **Charles' law,** in honour of J. A. C. Charles, who, according to Gay Lussac, made some crude experiments on the subject fifteen years before Gay Lussac's publication. Some call this relation *Gay Lussac's law.* It might, perhaps, with more propriety be called **Volta's law,** because A. Volta,[2] described it in his *Memoria sulla uniforme dilatazione dell'aria,* in 1793. G. Amontons had an inkling of this law in 1702.

The increase in volume which occurs when one litre of nitrogen at 0° is heated in a suitable vessel is shown in the following table (R. Chappius, 1888):

TABLE I.—THERMAL EXPANSION OF NITROGEN.

Temperature $\theta°$.	Volume v litres.	Expansion per litre per degree.
0	1·0000000	0·0036778
10	1·0367781	0·0036770
20	1·0735396	0·0036763
30	1·1102875	0·0036761
40	1·1470244	

The numbers in the last column—called **the coefficients of thermal expansion**—mean that the volume v of a litre of nitrogen, when heated through $\theta°$ can be represented very closely by the expression : $v=(1+0·003676\theta)$ litres. In other words, nitrogen increases 0·003676, or very nearly $\frac{1}{273}$rd part of its volume at 0° for every degree rise of temperature. More generally, if v_0 be used to denote the volume of gas at 0°, we have, instead of the preceding expression, $v=v_0(1+\frac{1}{273}\theta)$, or $v=v_0(1+\alpha\theta)$. This is very nearly true for most of the common gases, and it therefore represents a condition which must be satisfied by the temperature and volume of a gas, under constant pressure, in order that the system may be in stable equilibrium.

While solids and liquids have their own characteristic coefficient of expansion, gases have nearly the same coefficient of thermal expansion. This is the meaning of Charles' law. The coefficients of thermal expansion (pressure constant) for the gases run something like this for one atmosphere pressure and variations of temperature between 0° and 100° :

Air	0·003671
Hydrogen	0·003661
Carbon dioxide	0·003728
Carbon monoxide	0·003669
Sulphur dioxide	0·003903
Nitrous oxide	0·003719

These numbers are close enough to $\frac{1}{273}$ for most practical purposes. In general, the more easily a gas is liquefied and the greater its molecular weight, the greater the deviation from the constant 0·003665 found for air—witness carbon dioxide, 0·003728 ; hydrogen bromide, 0·00386 ; etc.

For every degree centigrade the temperature falls, the volume of the gas decreases by $\frac{1}{273}$rd. If $\frac{1}{273}$rd part of a gas be taken away 273 times, no more gas remains. This is illustrated by plotting the above equation.

If the temperature be less than $-273°$, the gas would have a negative volume, that is, a volume less than nothing ! If the temperature be $-273°$, the gas would occupy no volume ! It is impossible to imagine a substance occupying no space, but such is a logical conclusion from Charles' law. Where is the fallacy ? Whenever a natural process is represented by mathematical symbols, it is well to remember that the artificial statement often expresses more than actually obtains in nature, because, in the physical world, only changes of a certain kind occur. We must therefore limit the generality of the mathematical expression. Charles' law includes a simplifying assumption. The apparent volume of a gas may be resolved into at least two parts . (1) *the volume occupied by the molecules of the gas ;* and (2) *the space between the molecules.* If b denotes the space occupied by the molecules, and v the observed volume of the gas, the space between the molecules will be represented by $v-b$. Although for the sake of simplicity, we assume v to represent the *total volume* occupied by the gas, Charles' law refers to $v-b$, that is, to the space between the molecules, and in that case, the conclusion that $v=0$ when the temperature is $-273°$ involves no absurdity. Moreover, the gas would liquefy before the temperature $-273°$ was attained, and the simple gas law of Charles would not then be applicable.

It has been urged that J. L. Gay Lussac's statement of Charles' law means that the increase in the volume of a gas at any temperature, for a rise of 1°, is a constant fraction of its initial volume at 0°—in symbols, $v=v_0(1+\alpha\theta)$; while J. Dalton's statement of the law means that the increase in the volume of a gas at any temperature, for a rise of 1°, is a constant fraction of its volume at that temperature—in symbols $dv/d\theta=\alpha v$; hence by integration, $v=v_0e^{\alpha\theta}$. If the latter expression be expanded, $v=v_0(1+\alpha\theta+\frac{1}{2}\alpha^2\theta^2+\ .\ .\ .)$, and if the second and higher powers be outside the range of measurement, the two statements amount to the same thing. R. Mewes and L. Neumann[3] proposed to replace $v=v_0(1+\alpha\theta)$ by $v=x+(v_0-x)(1+\alpha^\theta)$, or approximately $v=v_0(1+\alpha)^\theta$. The results at ordinary temperatures are good, but they become less accurate with decreasing temperatures. The discrepancies are in fact attributed to errors in the measurements at low temperatures which are introduced by surface condensations, etc.

Influence of temperature on the pressure of a gas—volume constant.—About 1682, R. Boyle made some experiments on the influence of " cold and heat " on the pressure, or the spring of air, as he called it, and found that the effect of the greatest degree of cold he could produce did not " weaken the spring by anything near so considerable as one would expect." The subject did not attract much attention until G. Amontons (1702–3)[4] published two memoirs in which he demonstrated that equal masses of air, measured at the same initial pressure, acquire equal increments of pressure when heated to the boiling-point of water provided the volumes are maintained at their initial value; and if the pressure of the air before heating be doubled or tripled, the additional pressure produced when the air is heated to the boiling-point of water is likewise doubled or tripled. Otherwise expressed, the ratio of the total pressures (p and p_1) of air at two definite temperatures (T and T_1), and kept at a constant volume, has always the same value R and is independent of the initial pressure. In symbols, $p/T=p_1/T_1$; which can be written $p=RT$, where R is the constant of proportion. In words, **the same rise of temperature produces the same increase of pressure provided the volume and mass of the gas be maintained constant.** This relation might be called **Amontons' law.** It can be very simply deduced from Charles' and Boyle's laws, expressed in an analogous form, $p=p_0(1+\frac{1}{273}\theta)$, or $p=p_0(1+\beta\theta)$, where β denotes the coefficient of increase of pressure (volume constant). J. L. Gay Lussac thought that all gases had the same values of α and β; and it was thought that $\alpha=\beta$. More exact measurements have shown that neither statement is true. The coefficient β for the above-named gases between 0° and 100° are:

Air	0·003665
Hydrogen	0·003663
Carbon dioxide	0·003688
Carbon monoxide	0·003845
Nitrous oxide	0·003676

Absolute zero.—J. Amontons (1703)[5] argued that air would exert no pressure at all if it were cooled below freezing-point of water to about 2½ times the range of temperature between the freezing- and boiling-points of water. In 1779, J. H. Lambert[6] repeated Amontons' experiment and estimated that air would occupy no volume at all, if cooled to −270°; more accurate measurements make this temperature −273°. This temperature, −273°, is supposed to be a *non ultra plus*, or limiting temperature —the nadir or lowest possible temperature—a kind of *primum frigidum*. Hence, −273° is sometimes called the **absolute zero**; and temperatures reckoned from this zero are called **absolute temperatures.** *L'Association Internationale de Froid*[7] recommended that the letter K—from Lord Kelvin—be employed to denote absolute temperatures so that 0° C.=32° F.=273° K. On the absolute scale of temperatures, 0° C. will be 273° K. If T be employed to denote the temperature on the absolute scale, and θ the temperature on the centigrade scale, we have $T=273+\theta$. Hence, if v be the volume of a gas when the absolute temperature is T, and v_1 the volume when the temperature is T_1, from the preceding equation (3) $v:v_1=T:T_1$, which is but another way of stating Charles' law. The volume of a gas varies directly as the temperature, so that $v=RT$, where R is the constant of proportion. The arbitrary nature of the absolute zero deduced from the coefficient of thermal expansion of air, will appear when it is remembered that a similar train of reasoning would furnish −5000° as the absolute zero, if the coefficient of expansion of mercury were made the standard. It must be remembered, however, that the coefficient of thermal expansion of all gases, unlike liquids and solids, has nearly the same value; and further, the gaseous state probably represents the simplest form in which matter can exist. There are, however, other reasons for selecting −273° as the absolute zero which are discussed in works on thermodynamics.

The combined influence of temperature and pressure on the volume of a gas.—According to Boyle's law, the volume of a gas varies inversely as the pressure, so that if a pressure p_1 and volume v_1 change to a volume x at a pressure p_2, then, from the relation $p_1v_1=p_2x$ (Boyle's law). Again, according to Charles' law, the volume of a gas varies directly as the absolute temperature, so that if a gas whose volume is x at a temperature T_1 changes to a volume v_2 when the temperature rises to T_2, we have from the above relation, $xT_2=v_2T_1$. On substituting the value of x from the preceding relation

$$\frac{p_1v_1}{T_1}=\frac{p_2v_2}{T_2}$$

If p_2, v_2, T_2 represent the volume of the gas under standard conditions of temperature and pressure, p_2v_2/T_2 will have a constant numerical value, say R; and it follows at once that when both temperatures and pressure vary, the effect on the volume will be given by the equation **pv=RT**, where R is the constant of proportion—generally called the **gas constant.** An equation which attempts to express the relation between the pressure, temperature, and volume of a gas is sometimes called the **equation of state**—*Zustandsgleichung*, or *équation caractéristique*—or the *characteristic equation* or the *gas equation*. The equation of state is applicable to ideal gases. If an arbitrary value be assigned to the constant R, and corresponding values of p and v be plotted for a series of values of T, say $T=1,2,3,\ldots$, a series of curves, Fig. 4, are obtained. These curves may be supposed to have been drawn on a surface *abcd*. While a *plane* suffices for showing the relation between *two* variables, a *surface* in three dimensions is needed for *three* variables. These formulæ are used a great deal in calculations involving the variations in the volumes of gases owing to variations in temperature and pressure. For instance, in reducing the volume of a gas at any observed temperature and pressure to the corresponding volume at **the standard or normal pressure and temperature**—0° C. and 760 mm. pressure—often represented by n.p.t., or N.P.T., or S.T.P., or S.T., S.P.

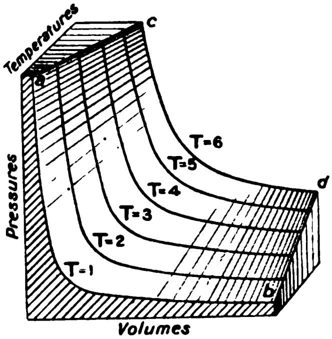

FIG. 4.—Surface showing the Relation between the three variables: Temperature, Pressure, and Volume of Gases.

EXAMPLE.—(1) If a gas measures 170 c.c. at a pressure of 735 mm. mercury, and a temperature of 15°, what is the volume of the gas at normal temperature and pressure? Here it is required to find v in the preceding formula where $p=760$; $T=273$; $T_1=288$; $v_1=170$; and $p_1=735$; hence, $v=\frac{273}{288}\times\frac{735}{760}\times170=155{\cdot}8$ c.c.

(2) Show that 13·8 c.c. of a gas at 747·6 mm. pressure at 19° reduce to 12·4 c.c. at 760 mm. and 0°.

Approximations can be used for general calculations,[8] and books on gas analysis have tables for converting unit volume at $\theta°$ and pressure p to its volume under standard conditions. It will be observed that the fraction T/T_0 for θ and θ_0 is $(273+\theta)/(273+\theta_0)$, and if θ_0 be 0°, the fraction reduces to $1+\frac{1}{273}\theta$, or $1+0{\cdot}003367\theta$.

The numerical value of the gas constant R.—The numerical value of R depends upon the units of pressure and volume; if unit mass of gas be taken, the value of R will depend upon the molecular weight of the gas. If one gram-molecule be taken, $pv=RT$, and if n gram-molecules be taken, $pv=nRT$. *If the litre be taken as the unit of volume and the atmosphere as unit of pressure,* and since a gram-molecule of gas occupies nearly 22·4 litres at 0° and under one atmosphere pressure, $1\times22{\cdot}4=1\times R\times273$; or $R=0{\cdot}082$ litre-atmosphere. *If the gram and cubic centimetre* be taken as unit, it follows that if v_1 represents the volume of a gram-molecule of any gas at n.p.t., $v_1=22{,}400$ c.c.; p_1 is 1033·3 grms. per sq. cm.; and $T_1=273$. Hence, $R=pv/T=(1033{\cdot}3\times22{,}400)/273=84{,}760$ gram-centimetres of energy. From measurements of the mechanical equivalent of thermal energy, it is known that one gram-centimetre of mechanical energy is equivalent to 42,650 calories. Hence, $R=pv/T=1{\cdot}9$ cals., or 2 cals. nearly.

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§ 7. Deviations from Charles' Law

Nature abhors the straight line.—R. Ross (1914).

We have already seen that the coefficients of thermal expansion of all gases are only approximately the same. The coefficients for the individual gases differ a little among themselves as indicated above. The variation in the coefficient of thermal expansion at temperatures and pressures not far removed from normal atmospheric temperatures and pressures, is not very marked, and for regular gas calculations can be ignored. It remains to indicate the variation, if any, in the coefficient of thermal expansion with large variations of temperature and pressure. H. Fläugergues (1825) showed that the coefficient of expansion of moist air is rather larger than that of dry air. Charles' law was also tested by P. L. Dulong and A. T. Petit (1815), F. Rudberg (1837), H. V. Regnault (1841), G. Magnus (1842), E. H. Amagat (1873), P. Jolly (1874), P. Chappius (1888), H. K. Onnes and M. Boudin (1900), etc.[1] The more important results are as follows:

(1) **The exact coefficient depends on the nature of the gas.**—H. V. Regnault, about 1850, proved that different gases have not the same coefficients of thermal expansion, as Charles' law assumes, but that each gas has its own specific constant. For ordinary calculations, particularly with gases which cannot be liquefied in the neighbourhood of atmospheric temperatures, the coefficient is taken to be $\alpha=\beta=\frac{1}{273}$.

(2) **The influence of pressure.**—The coefficient of expansion of most gases is increased by augmenting the pressure of a gas until a maximum value is attained, after that, the coefficient diminishes with increased pressure. For instance, E. H. Amagat (1893) found that the coefficients of expansion of carbon dioxide at temperatures between 50° and 60° assumed the following values when the pressure changed from 30 to 1000 metres of mercury:

Pressures .	30	60	125	200	500	1000 metres
Coefficients .	0·0069	0·0085	0·0410	0·0085	0·0033	0·0018

Carbon dioxide thus shows a marked variation in the coefficient of thermal expansion at high pressure. In agreement with these facts, the coefficient also diminishes as the pressure is reduced, even as low as 0·077 mm. of mercury. The variation is not so marked with gases like nitrogen, oxygen, and hydrogen which are not easily condensed to the liquid condition. The general result of H. V. Regnault's and Amagat's work is to show that if a gas is more compressible than is represented by Boyle's law, the coefficient of thermal expansion is increased by pressure; and conversely for gas less compressible than is indicated by Boyle's law, the coefficient of thermal expansion decreases with an increase of pressure. The value p which furnishes the greatest coefficient of thermal expansion is that same value of p which gives the minimum product pv. At ordinary temperatures, therefore, hydrogen and helium do not exhibit this variation in the value of their coefficients of expansion. With these gases, the coefficient of expansion steadily diminishes with increasing pressure; although even these resemble other gases if the temperature be low enough. Consequently, *at high enough pressures, when the minimum pv is reached, the coefficient of thermal expansion of all gases decreases with an increase of pressure.*

(3) **The influence of temperature.**—The general effect of raising the temperature is to lower the coefficient of expansion. For instance, Hirn (1862) found that for water vapour from 0° to

	118·5°	162°	200°	246·5°
Coefficient of expansion .	0·004187	0·004071	0·003938	0·003799

Similarly, L. Troost and P. Hautefeuille (1876) found the coefficient for silicon tetrachloride fell from 0·00449 between 100° and 125° to 0·00399 between 125° and 180°; while between the same temperatures the coefficient for carbon tetrachloride fell from 0·00470 to 0·00414; and for phosphorus trichloride, from 0·00489 to 0·00417.

The changes in the coefficient of expansion with increasing pressure become less and less as the temperature is raised, and finally disappear. So does the minimum value of the product pv become less and less marked as the temperature is raised. The gradual flattening of the carbon dioxide curves as the temperature rises from 40° to 100° is brought out very clearly in Fig. 5. All gases exhibit a minimum value for pv. The pressure required for a minimum depends on the temperature as well as on the nature of the gas. The minimum is most marked when the gas is near its temperature of liquefaction. If the temperature is much above this critical point, the minimum is very small—with hydrogen the minimum is inappreciable at 0°—Fig. 3. All other gases show a minimum at ordinary temperatures. Hence, H. V. Regnault, who discovered this peculiarity of hydrogen, was led to say ironically that hydrogen is a gas *plus que parfait*—a gas more than perfect; but hydrogen also shows a minimum at reduced temperatures. Similar remarks apply to helium and neon.

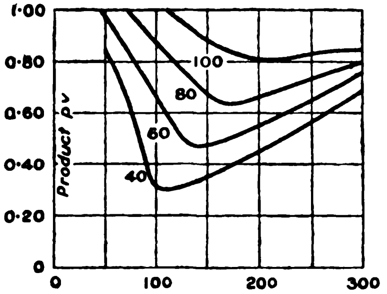

Fig. 5.—Amagat's pv-T—Curves for Carbon Dioxide.

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§ 8. The Critical State of Gases

> The ordinary gaseous and liquid states are only widely separated forms of the same condition of matter, and may be made to pass into one another by a series of gradations so gentle, that the passage shall nowhere present any interruption or break of continuity. Gas and liquid are only distinct stages of a long series of continuous physical changes.—T. ANDREWS (1869).

The fact that some elements occur as gases, others as liquids, and yet others as solids is a mere accident of temperature or pressure. Similar remarks apply to chemical compounds which do not decompose when the temperature is augmented. If the prevailing atmospheric temperature were 100° higher than it is, water would be a gas; and if 100° lower, water would be a solid. Similarly, if the atmospheric pressure were ten times as great as it is, chemistry books would describe sulphur dioxide and many other so-called gases either as liquids or solids; while if the pressure were much less than it is, many so-called liquids would be styled gases. **Every substance is potentially solid, liquid, and gas.** The solid, liquid, and gaseous states of matter are merely phases assumed by virtually all kinds of matter as the temperature rises from absolute zero upwards. The three forms which the elements and their compounds can assume are called the **three states of aggregation.** The three states of water are: *Gas* above 100°; *liquid* between 100° and 0°; and *solid* below 0° under ordinary atmospheric pressure. These facts are symbolized:

$$\text{Water}_{\text{ice}} \overset{0°}{\rightleftharpoons} \text{Water}_{\text{liquid}} \overset{100°}{\rightleftharpoons} \text{Water}_{\text{steam}} \quad (760 \text{ mm.})$$

Investigators who have special facilities for working at high temperatures, report that gold has a melting point, 1062°, and a boiling point, 2530°, or:

$$\text{Gold}_{\text{solid}} \overset{1062°}{\rightleftharpoons} \text{Gold}_{\text{liquid}} \overset{2530°}{\rightleftharpoons} \text{Gold}_{\text{gas}} \quad (760 \text{ mm.})$$

Similarly, those working in laboratories specially equipped for measurements at low temperatures, report that oxygen has a melting point, —227°, and a boiling point, —182·5°, or

$$\text{Oxygen}_{\text{solid}} \overset{-227°}{\rightleftharpoons} \text{Oxygen}_{\text{liquid}} \overset{-182·5°}{\rightleftharpoons} \text{Oxygen}_{\text{gas}} \quad (760 \text{ mm.})$$

M. Faraday (1819) [1] emphasized the fact that when any form of matter passes from the solid to the liquid state, or from the liquid to the gaseous state, its physical properties diminish in number and variety. Thus, solids in becoming liquids lose their hardness, crystalline form, etc.; and in passing to the gaseous state, the phenomena are still more marked, thus, all gases have nearly the same coefficient of thermal expansion. "The varieties of density, hardness, opacity, colour, elasticity, and form which render the number of solids and fluids almost infinite, are in gases supplied by a few slight variations in weight, and some unimportant shades of colour."

The critical state.—T. Andrews demonstrated in his paper *On the continuity of the gaseous and liquid states of matter*,[2] in 1869, that if gaseous carbon dioxide be gradually compressed in a vessel suitable for the observation, the volume diminishes more rapidly than would occur if Boyle's law correctly described the behaviour of the gas; and when the pressure attains a certain value, the gas begins to liquefy. A further decrease in the volume does not change the pressure, but only increases the quantity of gas liquefied. At length, when all the gas has liquefied, a large increase of pressure only causes a minute decrease in the volume of the liquid, since liquids in general undergo but a small change of volume on compression.

If the experiment be made with carbon dioxide at 0°, the gas commences to liquefy when the pressure has attained 35·4 atmospheres; if at 13·1°, liquefaction commences at 49·8 atmospheres pressure; if at 30°, 70 atmospheres pressure; while if the temperature exceeds 31°, or, more accurately, 31·35°, no pressure, however great, will liquefy the gas. Other gases exhibit analogous phenomena. This is in agreement with M. Berthelot's conclusion[3] in 1850 that pressure will not liquefy gases under all conditions of temperature. **For each gas there is a particular temperature above which liquefaction is impossible however great be the applied pressure.** Andrews called this the **critical temperature of the gas**; the corresponding pressure, or the **critical pressure,** is the least pressure which will liquefy the gas at the critical temperatures; the volume of unit mass of the substance at the critical temperature and pressure is the **critical volume**; and the reciprocal of the volume is the **critical density.** Consequently, a substance at the critical temperature and pressure is at its critical density, and is said to be in its **critical state.** The critical constants of a few substances are indicated in Table II., where the atmosphere is the unit of pressure; and the volume refers to one gram of the gaseous substance in litres at 0°, and 760 mm. is the unit of volume; and the density is referred to water at 4°.

TABLE II.—CRITICAL CONSTANTS OF SOME GASES.

Substance.	Critical pressure.	Critical temperature.	Critical density.	Critical volume.
Hydrogen	14·0	−240·8°	0·043	0·00264
Nitrogen	35·0	−146·0°	0·400	0·00517
Oxygen	50·8	−118·8°	0·650	0·00426
Carbon dioxide	77·0	31·35°	0·450	0·00660
Nitrous oxide	74·5	38·8°	0·454	0·00436
Sulphur dioxide	78·9	155·4°	0·520	0·00249
Water	194·6	364·3°	0·208	0·00386
Carbon disulphide	75·0	273·0°	0·377	0·00900
Air	35·9	−140·7°	0·344	0·00468
Helium	2·3	−267·8°	0·066	0·00299
Argon	52·9	−117·4°	0·509	0·00404
Ammonia	110·3	131·0°	0·239	0·00481
Methane	45·6	−82·85°	0·1623	0·00488
Acetylene	64·5	35·25°	0·2346	0·00690
Ethylene	54·0	11·0°	0·210	0·00752
Tin tetrachloride	32·9	318·7°	0·7414	0·00060
Hydrogen chloride	83·0	52·3°	0·462	0·00520
Nitric oxide	71·2	−93·5°	0·524	0·00347
Chlorine	93·5	146·0°	0·547	0·00615

In 1883, J. Dewar[4] showed that the ratio of the critical temperature to the critical pressure of many gases is nearly proportional to the molecular volume, and that the quotient T_c/p_c for the common gases generally lies between 3½ and 5. Other dependent relations have been indicated by E. Ariès and W. R. Fielding.

T. Andrews' critical temperature was forshadowed by D. I. Mendeléeff in 1861 in a paper on the expansion of liquids above their boiling points,[5] when he said:

> The absolute boiling point of a liquid is the temperature at which the cohesion and heat of vaporization become zero. At this temperature, the liquid changes to vapour regardless of pressure and volume.

D. I. Mendeléeff's **absolute boiling point** thus corresponds with T. Andrews' critical temperature. D. I. Mendeléeff estimated the absolute boiling point of water to be 580°, and of ethyl alcohol, 250°. It is interesting to notice the influence of temperature on carbon dioxide, partly liquid, partly gaseous. Observe the upper surface of the gas confined in a glass tube containing partly liquefied carbon dioxide over mercury at 18°. The surface of the liquefied gas has a sharply defined meniscus. On raising the temperature, the meniscus of the liquid becomes flatter and flatter, until, at 31·35°, the surface of the liquid seems to disappear. The sharp line of demarcation between the liquid and gas vanishes at the critical temperature. In the words of T. Andrews, as the temperature of the liquefied gas approaches 31°:

> The surface of demarcation between the liquid and the gas became fainter, lost its

curvature, and at last disappeared. The space was then occupied by a homogeneous fluid, which exhibited when the pressure was suddenly diminished, or the temperature slightly lowered, a peculiar appearance of moving or flickering striæ throughout the entire mass.

At 40°, the tube contains a homogeneous gas. Liquid carbon dioxide cannot exist at this temperature, however great the pressure. Small tubes of liquid carbon dioxide for illustrating the phenomena by lantern can be obtained. Thin sections of quartz found in many granites contain cavities with liquid carbon dioxide which can be seen to pass through the critical point when the sections are warmed on the stage of a microscope.

A blue opalescent mist appears in the tube before the meniscus of the liquid can be detected when the temperature of the gas is gradually lowered. The converse series of changes occur on heating. According to D. Konowaloff (1902),[6] the **critical opalescence** is due to the scattering of light by fine particles of liquid spontaneously formed about dust particles ; or, according to M. von Smoluchowsky (1908), to accidental aggregations of molecules produced by molecular collisions. The appearance of the blue mist is connected with slight disturbances which have been observed in the equation of state when applied to observations in the neighbourhood of the critical temperatures. P. de Heen (1888) argues that there are two kinds of molecules—*molécules liquidogéniques*, and *molécules gasogéniques*—and that the former can persist in the vapour phase. I. Traube (1892) and P. Villard favoured this view. If P. de Heen means that the pressure of a saturated vapour of a pure substance, like that of a mixture, depends upon the relative masses of liquid and vapour phases, the hypothesis is contrary to all experience. This was emphasized by G. G. Stokes and M. Prud'homme. According to M. von Smoluchowsky, the ceaseless to-and-fro agitation of the molecular particles of a gas will produce, spontaneously and continuously, minute inequalities in the density of different parts. A given cube of dimensions μ, for example, will contain sometimes more and sometimes less molecules. Usually these differences are inaccessible to measurement. The case is different when the fluid is not rarefied such as occurs when it is near the critical state. There is then a permanent condition of fine-grained heterogeneity where contiguous regions of notably different density are almost in equilibrium. Owing to molecular agitation, the denser swarms of molecules break up slowly, and, at the same time, others are forming elsewhere. The opalescence is produced by the molecular swarms causing a lateral diffraction of the light. The fluctuations of density increase as the compression increases and are very much more accentuated with a compressed gas than with a gas of normal density. The smaller the aggregates, the shorter the wave length of the light undergoing diffraction. Hence the opalescence may appear blue. M. von Smoluchowsky's theory has been extended by A. Einstein and confirmed by the work of H. K. Onnes and W. H. Keesom. It has also been applied to explain the opalescence of liquid mixtures in the neighbourhood of the point of critical miscibility, and the blueness of the sky.

The relation between the pressure and the volume of, say, carbon dioxide, at different temperatures—T, T_0, T_1, T_2—is represented diagrammatically in Fig. 6. The portion of the curve K_2T_2, or K_1T_1, represents the behaviour of the gas when liquid is present ; the portion K_2M_2, or K_1M_1, the behaviour of the gas in the presence of its own liquid and M_2p_2, or M_1p_1, the behaviour of the liquid when no gas is present. It will be observed that K_2M_2 or K_1M_1 is the **line of constant vapour pressure** which is horizontal with the v-axis. It illustrates in a graphic manner the well-known law : At any fixed temperature, the pressure of a gas in the presence of its own liquid is always the same. The curve $T_0K_0p_0$ represents the relation between pressure and volume at the critical temperature ; and the curve T, the relation between p and v at a temperature when the gas does not liquefy. The line $K_0K_1K_2B$ represents the condition under which the gas, compressed at the stated temperatures T_0, T_1, and T_2, begins to liquefy, and hence it is the curve for saturated vapour, and also the curve for the liquid at its vaporization temperature ; it is not quite accurately called the **dew curve,** or *ligne de rosée*, because a gas under a gradually increasing pressure, first shows signs of liquefaction under conditions represented by a point on this line; similarly, the line $K_0M_1M_2A$ is called the **boiling curve,** or *ligne d'ébullition,* because a liquid under a gradually diminishing pressure first shows signs of vaporization under conditions represented by a point on this line. Note also that the lines K_0A, K_0B, and K_0p_0 divide the plane of the paper into three regions Every point to the right of BK_0p_0 represents a homogeneous gas; every point in the region AK_0B represents a heterogeneous mixture of gas and liquid; and every point to the left of AK_0p_0, a homogeneous liquid. The gas in the region K_0BVT_0 is below its critical temperature, and, in consequence, is sometimes called a *vapour* as distinct from a *gas.* The diagram, Fig. 6, thus represents the conditions of equilibrium of a liquid or gas under different conditions of temperature, pressure, and volume.

The continuity of the liquid and gaseous states.—It is interesting to note historically that C. Caignard de la Tour (1822),[7] long before Andrews' experiment, noticed that when a liquid is heated in a sealed tube there is a definite temperature at which the surface of separation between the gas and liquid disappeared and the whole contents of the tube become homogeneous. C. Caignard de la Tour's experiments thus demonstrate that the critical temperature is the upper limit of the liquid state; and Andrews' experiments prove that the critical temperature is the lower limit to the homogeneous gaseous state. The passage from the one state to the other proceeds in a continuous manner. **The liquid and gaseous states are continuous, not abrupt.** The properties—density, surface tension, viscosity, refractive power, heat of vaporization, compressibility, etc.—of a liquid gradually lose their distinctive character as the temperature is raised, until, at the critical temperature, the properties of liquid and gas are the same.

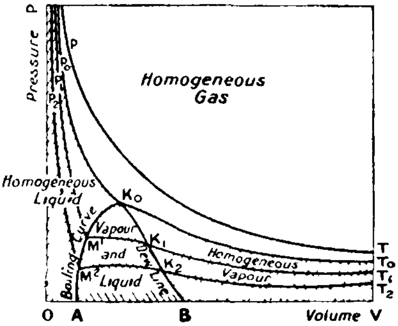

FIG. 6.—Pressure · Volume Curves for Carbon Dioxide.

There is no evidence of a change in molecular structure when, say, carbon dioxide passes from one state of aggregation to another; nor is there any evidence of a polymerization of the molecules when the common gases condense to liquids. Nitrogen peroxide, water, and some other substances, however, do appear to polymerize and form compound molecules on passing from the gaseous to the liquid state of aggression. The properties of the condensing gases do not then exhibit that continuity shown by carbon dioxide and other gases which do not polymerize or dissociate.

The difference between liquids and gases *below* the critical temperature seems to be a question of molecular attraction. If the molecules of a substance in the liquid state have essentially the same motions as in the gaseous state, the specific heat of a vapour should be nearly the same as that of the corresponding liquid. This is by no means the case. For example, the specific heat of liquid mercury is twice as large as that of the vapour; and the specific heat of liquid water is three times that of steam. There is, however, usually less difference between the specific heats, densities, and coefficients of thermal expansion of solids and the corresponding liquids.

The condensation of binary mixtures of gases.—In a posthumous memoir presented to the Royal Society in 1886, T. Andrews[8] showed that some extraordinary phenomena occur when certain binary mixtures of gases are subjected to a gradually increasing pressure. A mixture of 6 parts of carbon dioxide and one of nitrogen commences to liquefy at 3·5° under a pressure of 48·3 atm. Here nitrogen condenses to a liquid at a temperature nearly 150° higher than its critical temperature, and at 102 atm. pressure, the whole of the nitrogen liquefies along with the carbon dioxide. The individual properties of the gases are thus profoundly modified in the presence of other gases which are supposed to be chemically indifferent. The conception which has crystallized from Dalton's law of partial pressures, namely, that the two components of a mixture of gases are perfectly independent of one another, each preserving its own individuality, and each behaving as if it were an isolated individual, is quite erroneous. The explanation turns on the existence of a definite relation between the composition of a condensed liquid and of the vapour during, say, the distillation of a binary mixture of two volatile liquids which exert no chemical action on one another. L. P. Cailletet discovered this remarkable phenomenon during his *Expériences sur la compression des mélanges gazeux* in 1880. If a mixture of one volume of air and nine volumes of carbon dioxide be subjected to a gradually increasing pressure at about 2°, the gas begins to liquefy at a pressure of about 72 atm.; and on increasing the pressure, still keeping the temperature constant, the liquid again passes into the gaseous state when the pressure reaches 149 atm. ; and the liquid does not reappear again however great the pressure. If the pressure at which the liquid appears and disappears be plotted with the corresponding temperature, we get the dew curve *BKC*, Fig. 7. For the same abscissa T_1, there are two ordinates, p_1 and p_2, between which the mixture is in a heterogeneous condition. At temperatures above T_0, no condensation will occur at all ; below T_1, only normal condensation takes place ; at temperatures between T_1 and T_0, both normal and **retrograde condensation** as P. Kuenen (1893) named the phenomenon, will occur. The dotted line *AC* represents the boiling curve ; above *AC*, the system will be in the liquid state. *K* corresponds with the critical temperature of the mixture ; *C* is called a **plait-point.** For mixtures of two gases, therefore, (1) there is a critical zone of temperature above which complete or partial liquefaction is impossible. (2) Within the temperature of the critical zone itself a part of the mixture can be brought by pressure to the liquid state, and in the region of retrograde condensation, condensation is produced by diminution of pressure, and evaporation by an increase of pressure. The phenomena with mixtures thus appears quite different from what obtains with single gases. (3) Below the temperature of the critical zone, the whole of the mixture can be liquefied by pressure.

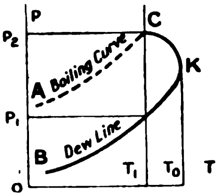

Fig. 7.—Diagrammatic.

The phenomenon occurs only with mixtures of a certain composition ; above and below these limits, the dew curves are quite normal. The curves can be taken in three dimensions with the three variables—pressure, volume, and temperature. The two dew points of a given mixture approach one another as the temperature rises. Thus, F. Caubet (1901) found with a mixture of 74·58 per cent. of carbon dioxide and 25·42 per cent. of sulphur dioxide gases :

TABLE III.—RETROGRADE CONDENSATION OF MIXTURES OF CARBON DIOXIDE AND SULPHUR DIOXIDE.

70°		72°		74·2°	
Pressure.	Volume of liquid.	Pressure.	Volume of liquid.	Pressure.	Volume of liquid.
61·0	0	60·0	0	75·0	0
66·2	*	70·0	*	78·2	*
69·4	0·066	74·5	0·066	80·6	0·066
77·0	0·164	84·8	0·164	83·4	0·099
83·4	0·250	87·8	0·184	86·2	0·066
87·8	0·428	89·6	0·099	88·0	**
89·6	0·263	89·8	**	93·0	0
90·0	**	95·6	0	105·0	0
91·0	0	105·0	0		
105·0	0				

One asterisk * represents the first dew point—1er *point de rosée ;* and two asterisks ** the second dew point—2^{e} *point de rosée.*

L. P. Cailletet and E. Mathias (1866) [9] found empirically that the mean values of the densities of a liquid, D_l, and of its saturated vapour, D_v, at a constant pressure, vary with the temperature in a very simple manner. If the densities be plotted with the temperature, a closed curve *AKB*, Fig. 8, is obtained. The mean values of the densities of the co-existing liquid and vapour, plotted against the temperatures, fall on a straight line, *KC*, Fig. 8. The density of the liquid decreases while that of the vapour increases as the temperature rises, until, at the critical point, *K*, the two densities are equal to the critical density. Hence, the rule was called the *loi du diamètre rectiligne*, or Cailletet and Mathias' **law of rectilinear diameters.** According to this empirical rule, **the mean values of the densities of a liquid and of its saturated vapour is a linear function of the temperature**; so that if D represents the mean value of the two densities, $D=a+b\theta$, where a and b are constants, and θ denotes the temperature on the centigrade scale. For argon, the equation of the mean density curve is $D=0{\cdot}20956-0{\cdot}0026235\theta$; and in cases where the curve has a slight curvature, the equation $D=a+b\theta+c\theta^2$ usually represents the observed results. The law has been tested with carbon dioxide, sulphur dioxide, nitrous oxide, hydrocarbons, alcohols, carbon tetrachloride, tin tetrachloride, oxygen, helium, xenon, etc. In all cases the empirical law was found to be remarkably exact, except in the case of those substances—*e.g.* the alcohols, fatty acids, etc.—which are known to exhibit molecular aggregation. The curvature of the line is taken to indicate molecular association, although the absence of curvature does not necessarily mean that molecular association is absent. E. Mathias and H. K. Onnes' results for oxygen are indicated in Fig. 8; the curve is plotted from the following observations:

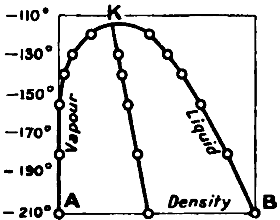

FIG. 8.—Variations in the Densities of Co-existing Liquid and Gaseous Oxygen.

Temperature . .	−210·4°	−182·0°	−154·5°	−140·2°	−129·9°	−123·3°	−120·4°
Density of liquid, D_l .	1·2746	1·1415	0·9758	0·8742	0·7781	0·6779	0·6032
Density of vapour, D_v .	0·0001	0·0051	0·0385	0·0805	0·1320	0·2022	0·2701
Mean density, D . .	0·6373	0·5733	0·5072	0·4773	0·4550	0·4400	0·4366

The mean densities calculated from the linear expression, $D=0{\cdot}1608-0{\cdot}0022656\theta$, do not deviate from the observed values more than ±0·003. The law does not hold good for substances whose molecules in the liquid and gaseous states have a different complexity.[10]

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CHAPTER V

COMBINATION BY VOLUME

§ 1. Gay Lussac's Law of Combining Volumes

Omnia mensura et numero et pondere disponsuisti—Thou hast ordered all things in measure, and number, and weight.—LIBER SAPIENTIAE.

NOT very long after John Dalton had directed the attention of chemists to the relations subsisting between the weights of bodies which combine in different proportions, J. L. Gay Lussac[1] established a similar correspondence between volumes of combining gases. A. von Humboldt, the naturalist and explorer, collected samples of air from different parts of the world, and with the aid of J. L. Gay Lussac, analysed the different samples with the idea of finding if the composition of air was variable or constant. J. L. Gay Lussac used Cavendish's process—explosion of a mixture of air and hydrogen gas. As a preliminary, A. von Humboldt and J. L. Gay Lussac investigated the proportion by volume in which hydrogen and oxygen combine, and found the ratio of hydrogen to oxygen, by volume, to be nearly as 2 : 1. If either hydrogen or oxygen was in excess of these proportions, the excess remained after the explosion, as a residual gas. A. von Humboldt and J. L. Gay Lussac (1805) found :

Vols. of oxygen.	Vols. of hydrogen.	Vols. of residue.
100	300	101·3 hydrogen
200	200	101·7 oxygen

After making corrections for impurities, etc., in the gases, J. L. Gay Lussac and A. von Humboldt stated that "100 volumes of oxygen required for complete saturation 199·89 volumes of hydrogen, for which 200 may be put without error." A. Scott (1893) found, as the result of twelve experiments on the volumetric composition of water, that oxygen and hydrogen combine very nearly in the ratio 1 : 2·00245 by volume.

Struck by the simplicity of the relation thus found, J. L. Gay Lussac (1808) followed up the subject by numerous experiments with different gases. As a result, in his *Mémoire sur la combinaison des substances gazeuses, les unes avec les autres* (1809), he concluded that "gases always combine in the simplest proportions by volume." For instance, one volume of hydrogen combines with one volume of chlorine forming two volumes of hydrogen chloride ; two volumes of hydrogen combine with one volume of oxygen forming two volumes of water vapour (which condenses to liquid water if the temperature be below 100°).

There are slight deviations with the gases which show deviations from the laws of Boyle and Charles, but the experimental results are such as to leave no doubt that J. L. Gay Lussac's generalization is valid, and accordingly, we define **Gay Lussac's law : when gases react together, they do so in volumes which bear a simple ratio to one another, and to the volume of the gaseous product of the action.** It is assumed, of course, that the initial and final products of the reaction are under the same conditions of temperature and pressure.

The remarkable way in which elements unite by weight was traced to a peculiarity in the constitution of matter ; so here, we are tempted to make a similar quest. It follows at once (1) if elements in a gaseous state unite in simple proportions by volume, and (2) if the elements also unite in simple proportions by atoms, then the number of atoms in equal volumes of the reacting gases must be simply related. With John Dalton, in his *A New System of Chemical Philosophy* (Manchester, 1808), let us make a guess. Assume that equal volumes of the different gases under the same physical conditions contain an equal number —say n—of atoms. Then, when two volumes of hydrogen react with one volume of oxygen to form two volumes of steam, we have $2n$ atoms of hydrogen reacting with n atoms of oxygen to form $2n$ " compound atoms " of steam. Hence, two atoms of hydrogen react with one atom of oxygen to form two " compound atoms " of steam. In that case, every atom of oxygen must be split into half to make two " compound atoms " of steam. This contradicts the fundamental postulate of the atomic theory expressed in John Dalton's aphorism : " Thou knowest no man can split an atom," meaning that atoms are assumed to be indivisible in chemical reactions.[2] Similar contradictions are encountered in nearly every case of combination between gases, hence J. Dalton regarded J. L. Gay Lussac's law as untenable : *Equal volumes of homogeneous gases, under like conditions of temperature and pressure, do not contain the same number of atoms.* There is such a marked uniformity in the deportment of elementary and compound gases with respect to variations of temperature and pressure, that it is not very probable any essential difference will be found in their constitution.

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§ 2. Amadeo Avogadro's Postulate

Advances in knowledge are not commonly made without the previous exercise of some boldness and licence in guessing.—W. WHEWELL.

J. J. Berzelius [1] thought it strange that J. L. Gay Lussac should have contented himself with having determined the combining ratios of gaseous substances, and should make no attempt to extend his discovery. Clearly with J. Dalton the faculty of speculation was predominant, and with J. L. Gay-Lussac experimentation. An epoch-making memoir entitled, *Essai d'une manière de déterminer les masses rélatives des molécules élémentaires des corps, et les proportions selon lesquelles elles entrent dans les combinaisons*, was published in 1811 by Amadeo Avogadro,[2] an Italian physicist. In his memoir A. Avogadro said—

> J'ai proposé une hypothèse pour expliquer le fait découvert par M. Gay Lussac, que les volumes des substances gazeuses qui se combinent entre elles, et des gaz composés qui en résultent, sont toujours dans les rapports très simples entre eux.

He pointed out that the difficulty with Dalton's hypothesis can be avoided if we distinguish clearly between elementary atoms and the small particles of a gas. Assume that the small particles of a gas are aggregates of a definite number of atoms ; then, using A. Avogadro's own words :

> Les molécules constituantes d'un gaz simple quelconque, c'est-à-dire celles qui s'y tiennent à une distance telle à ne pouvoir exercer leur action mutuelle, ne sont pas formées d'une seule molécule élémentaire mais résultent d'un certain nombre de ces molécules réunies en une seule par attraction.

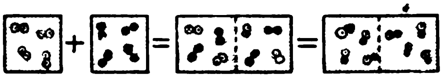
A. Avogadro called these aggregates molecules, in order to distinguish them from the ultimate atom. His actual term was *molécules constituantes* or *molécules intégrantes*—the former term was used for molecules of elements, the latter for molecules of compounds. The one term molecule (the diminutive form of the Latin word *moles*, a mass) is now applied to both Avogadro's *molécules constituantes* and *molécules intégrantes*. Each molecule of an elementary gas is supposed to contain the same number and kind of elementary atoms. What J. Dalton called atoms A. Avogadro called *molécules élémentaires*. The word "atom" does not occur in the latter's memoir. The modern meanings of the terms *atom* and *molecule* were clearly stated by A. M. Ampère[3] in 1832, and by A. Gaudin in the same year. Some years later these distinctions were emphasized by A. Laurent (1846) and employed in his posthumous book *Méthode de chimie* (Paris, 1854). A. M. Ampère used the term particle for an aggregate formed by the juxtaposition of molecules. He said:

> In the passage from liquid to the gaseous state, the molecules are separated from one another; and conversely, in passing from the gaseous to the liquid state, the molecules are drawn together. In the passage from the liquid to the solid state, I think that two or more molecules are drawn together. Mechanical forces alone can separate the particles; chemical forces are required to split the molecules.

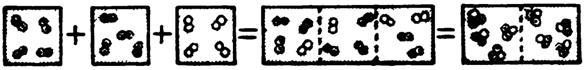
For the sake of simplicity, assume that each molecule of hydrogen gas is composed of two atoms of hydrogen, and make a similar assumption for oxygen gas; and assume with A. Avogadro that **equal volumes of all gases, at the same temperature and pressure contain the same number of molecules.** This postulate is now known as **Avogadro's hypothesis.** In A. Avogadro's own words:

> L'hypothèse qui se présente la première à égard et qui parait même la seule admissible, est de supposer que le nombre des molécules intégrantes dans la gaz quelconque est toujours le même à volume égal, ou est toujours proportionnel aux volumes. . . .

Suppose that two volumes of hydrogen contain $2n$ molecules of hydrogen, then one volume of oxygen will contain n molecules. These react to form $2n$ molecules of steam—each molecule of steam contains two atoms of hydrogen and one atom of oxygen. The idea can be more clearly illustrated by means of the subjoined diagrams. Each square represents one volume of a gas. Each volume contains n molecules. We do not know the numerical value of n, but, for the sake of simplicity, take $n=4$. It makes no difference to the final conclusion what numerical value we assign to n. Then we have:



Hence, although the atoms of oxygen cannot be split, yet a 2-atom molecule of oxygen can be subdivided so that one atom of oxygen enters the composition of each of two molecules of water. Again, with hydrogen and chlorine,



Diagrams similar in principle to these were used by M. A. Gaudin about 1832 in his *Recherches sur la structure intime des corps inorganiques définis.* It must not be supposed for one moment that what may be called Gaudin's diagrams are intended as pictures of the actual molecules. They are to be regarded as aids to the understanding of how Avogadro's hypothesis has led chemists to conclude that the molecules of gaseous elements are really compounded atoms, and how Avogadro's hypothesis reconciles the observed volume relations during the combination of gases with the atomic theory.

It has been assumed for the sake of simplicity, that the molecule of water contains three atoms, and that each molecule of hydrogen and oxygen contains two atoms. As a matter of fact, all we can infer from the observed facts is that the molecule of oxygen is split into halves, and, in the absence of evidence to the contrary, we assume for every substance the simplest molecular structure consistent with the observed facts.

A. Avogadro extended J. Dalton's atomic hypothesis and adapted it particularly to gases. We owe to the former the conception of two orders of minute particles : (1) the atom or unit of chemical exchange ; and (2) the **molecules are the smallest particles of an element or compound which exist free in a gas.** This definition of a molecule is usually extended into the less satisfactory definition : A molecule is the smallest particle of an element or compound which exists in a free state ; otherwise expressed, the molecules of an element or compound are particles so small that the specific properties of the substance depend upon the particles remaining intact. Hence, if molecules be subdivided the parts no longer have the specific properties of the original substance. If the molecules of steam, H_2O, be subdivided, two atoms of hydrogen and one atom of oxygen would be formed per molecule ; the atoms unite in pairs to form molecules.

Diatomic molecules for gaseous chlorine, hydrogen, and oxygen at ordinary temperatures furnish a satisfactory explanation of what we know to-day, but it is possible that at some future date, the evidence will compel us to consider these molecules to be tetra- or hexa-atomic. This will not materially affect the principle as indicated above. The molecule of mercury is supposed to be monatomic ; and the molecule of sulphur, hexatomic.

In 1814, A. M. Ampère advocated views similar to those of A. Avogadro, but he complicated the latter's simple hypothesis by an unsuccessful attempt to apply his conception of molecules to crystalline solids. Avogadro considered Ampère's extension unjustifiable. A. M. Ampère clearly emphasized the hypothetical nature of A. Avogadro's conception in a letter to M. le Comte Berthollet in 1814, when he said : If the consequences of the hypothesis be confirmed by further experiments, and the hypothesis be in agreement with known facts, *elle pourra acquérir un degré de probabilité qui approchera de ce qu'on nomme en physique la certitude.* Increasing knowledge has made A. Avogadro's hypothesis more and more probable ; it has been tested in hundreds of experiments, and never found wanting. The hypothesis has done such good service in giving a rational explanation of many different phenomena that it has been accepted as a fundamental truth. It gave chemists a clear definition of the atom, a method of determining the relative weights of the atoms, and of estimating the number of atoms in the molecule.

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§ 3. The Relative Weights of the Molecules

In order to bring into harmony all the branches of chemistry, we must have recourse to the complete application of the theory of Avogadro in order to compare the weights and the numbers of the molecules.—S. CANNIZZARO.

John Dalton in 1807 raised the query : " Are there the same number of particles of any elastic fluid in a given volume and under a given pressure ? " It is curious that in answering " No," J. Dalton[1] abandoned an hypothesis which afterwards proved to be one of the most fruitful suggestions in the development of chemistry, for, under the name of Avogadro's hypothesis, it has correlated what appeared antagonistic and contradictory, and has harmonized what seemed discordant and confused; it made Dalton's atomic hypothesis a clear, intelligible, and fertile theory. As C. A. Wurtz said in his *The Atomic Theory* (London, 1880), had it not been for this development, J. Dalton's hypothesis was in a fair way of being sentenced to sterility and oblivion. A fellow countryman of A. Avogadro, namely S. Cannizzaro, seems to have seen, more clearly than any other, the importance of A. Avogadro's hypothesis in putting J. Dalton's on a firm basis.

S. Cannizzaro's ideas were first published in a letter to S. de Luca embodying a *Sketch of a Course of Chemical Philosophy*,[2] given in the Royal University of Geneva in 1858. Before S. Cannizzaro published his paper, rank confusion prevailed in chemical literature. The terms atomic weight, molecular weight, and combining or equivalent weight were used and abused in every conceivable way. J. B. A. Dumas lost faith in the atomic theory and wrote in despair:

> Si j'en étais le maître j'effacerais le mot atome de la science, persuadé qu'il va plus loin que l'expérience : et jamais en chimie nous ne devons aller plus loin que l'expérience.

Avogadro's hypothesis was necessary for salvation; it lay dormant in chemical literature for nearly half a century; S. Cannizzaro brought the awakening, and showed chemists that the atom must be defined with reference to A. Avogadro's molecule. After reading S. Cannizzaro's pamphlet, Lothar Meyer (1860) thus describes his own conversion: "the scales fell from my eyes, my doubts disappeared, and a feeling of tranquil security took their place." A. Avogadro's hypothesis was thus made the basis of the current theory of chemistry.

By definition, the relative density of a gas is a number which represents how much heavier any volume of the gas is than an equal volume of the standard gas—generally hydrogen—measured at the same temperature and pressure—generally at 0° and 760 mm. pressure. Thus, the relative density of steam is 8·95. This means that any volume, say a litre of steam, is nearly nine times as heavy as the same volume of hydrogen.

Strictly speaking, the density of a gas is the weight of 1 c.c. of the gas at 0° and 760 mm. The density of a gas is usually expressed in terms of a litre of the gas because the number representing the weight of 1 c.c. would be inconveniently small. One litre of hydrogen at n.p.t. weighs very nearly 0·0896 grm. "So important is this standard weight-unit," said A. W. Hofmann in his *Introduction to Modern Chemistry* (London, 1865), "that a name is needed to denote it." He suggested *crith* (κρίθη, a barley corn, or small weight) to denote the weight of a litre of hydrogen at n.p.t. The weight of the same volume of oxygen would then be 16 criths, of nitrogen 14 criths, etc. The term has now dropped out of use, although for a time it served a useful purpose.

By Avogadro's hypothesis, equal volumes of gases, under like conditions of temperature and pressure, contain the same number of molecules, consequently, **the specific gravity or relative density of a gas is proportional to its molecular weight.** Let n represent the number of molecules in a volume v of each of two different gases, and if the molecules of each gas are all alike with the respective molecular masses M_1 and M_2, then the one gas will have a mass nM_1 and the other a mass nM_2. Let the densities of the respective gases be D_1 and D_2, then since density denotes the mass of unit volume, $D_1 : D_2 = nM_1/v : nM_2/v$; that is, $D_1 : D_2 = M_1 : M_2$ or

$$\frac{D_1}{D_2}=\frac{M_1}{M_2};\ \text{or}\ \frac{M_1}{D_1}=\frac{M_2}{D_2}\quad . \quad . \quad . \quad . \quad . \quad (1)$$

or the relative densities of any two gases are proportional to their respective molecular weights; and **the quotient of the molecular weight by the density is the same for all gases.** It is convenient to employ the term *molecular volume* for the quotient obtained by dividing the molecular weight M of a gas by its relative density

D; consequently, from the second of equation (1), **the molecular volumes of all gases are the same.**

If we accept this deduction, it enables us to determine the molecular weights of gases, once we have fixed an arbitrary standard for the density. Cannizzaro's unit, hydrogen=2, is frequently taken as the standard, or else hydrogen unity, that is, as S. Cannizzaro expressed it, "the quantity of hydrogen contained in a molecule of hydrogen chloride" is taken as unity. **The determination of the molecular weight of a gas is thus reduced to a laboratory measurement—the determination of the relative density of the gas.** Methods for measuring vapour densities are outlined later.

It has been shown within certain limitations, that the numerical values for the molecular weight and relative density of a gas referred to *the standard hydrogen*, 2, are the same. That is,

$$\text{Molecular weight} = \text{Relative density } (H_2=2) \quad . \quad . \quad . \quad (2)$$

For example, the observed density of steam is 18 ($H_2=2$), the molecular weight of steam is therefore 18 likewise. Again, if the relative density be referred to the standard *hydrogen unity, or oxygen* 16, the relative density is half the molecular weight; or the molecular weight is twice the density.

$$\text{Molecular weight} = 2 \times \text{Relative density } (H=1) \quad . \quad . \quad . \quad (3)$$

For instance, the density of steam is 9 ($H=1$), the molecular weight is therefore twice 9 or 18 as before. When the relative density is referred to oxygen 32, as is common in recent years, it is virtually assumed that there is an imaginary gas whose relative density is unity; and to avoid the hypothesis implied in the term molecular weight, the term **molar weight** is applied to the relative density of a gas referred to oxygen 32.

If the relative density be determined, as is frequently the case, with reference to *the standard air unity*, then, since the density of air with respect to hydrogen is 28·75 ($H_2=2$); or with reference to oxygen 28·98 ($O_2=32$), it follows that

$$\text{Molecular weight} = 28{\cdot}75 \times \text{Relative density (Air unity)} \quad . \quad . \quad (4)$$

For example, the relative density of cyanogen is 1·806 (air unity), the molecular weight is therefore $1{\cdot}806 \times 28{\cdot}75 = 51{\cdot}92$ ($H_2=2$). This is in agreement with the formula C_2N_2.

It is unfortunate that these different units are employed, even though all give the same final result. It shows the necessity for clearly understanding the particular meaning of terms employed before elaborating an argument. The method of determining the relative density of a gas by weighing a globe full of gas and then full of air, led to the use of air as a standard of reference. Thus, J. L. Gay Lussac (1815) found a 2½-litre globe weighed $w+2{\cdot}738$ grms. when filled with air, and $w+4{\cdot}946$ grms. when filled with cyanogen; consequently the relative density of cyanogen, air unity, is $4{\cdot}946/2{\cdot}738=1{\cdot}806$. The custom of referring all gas densities to air as a standard was gradually adopted. The system has been shown in recent years to be faulty when very accurate results are required because there are undoubtedly slight variations in the composition of air, and this causes the density of air—the standard of reference—to vary in a corresponding manner.

If the specific gravity of a gas is to be referred to water as *standard*, the relative density, air unity, is multiplied by the weight of one c.c. of air, *viz.* 0·001293; by 0·00008996 if hydrogen unity be the standard; and by 0·00004469 if oxygen be 32. Thus, the relative density of carbon dioxide is 1·57 (air unity); 22 (hydrogen unity); and 44 if oxygen 32 be the standard. Hence, also, the specific gravity with respect to water as standard is $1{\cdot}57 \times 0{\cdot}001293 = 0{\cdot}00203$.

It will be noted that if W denotes the weight of a litre of a gas of molecular weight M, and D denotes the relative density, air unity, $W=\frac{1}{2}M \times 0{\cdot}08996$; $D=M/28{\cdot}75$, and therefore $100(W-D)=M$, or *the molecular weight of a gas, is nearly* 100 *times the difference between the weight of a litre of the gas at n.p.t. and the relative density of the gas, air unity.*

Returning to S. Cannizzaro's important paper, S. Cannizzaro gave the following numbers, among others, for the densities of the different gases referred to hydrogen taken as 2, or to a semi-molecule of hydrogen taken as unity :

	Relative densities
Hydrogen	2·0
Oxygen	32·0
Chlorine	71·0
Nitrogen	28·0
Water vapour	18·0
Hydrogen chloride	36·5

If, therefore, the molecules of hydrogen, oxygen, nitrogen, and chlorine contain two atoms, the atomic weights of these gases will be half the respective molecular weights. Hence, making a selection from S. Cannizzaro's tables :

Table I.—S. Cannizzaro's Table of Atomic Weights.

Element.	Relative density of gas.	Atomic Weight, or Density ÷ 2.
Hydrogen	2	1·0
Oxygen	32	16·0
Chlorine	71	35·5
Nitrogen	28	14·0

In the case of compounds, if the molecule of hydrogen chloride contains an atom of chlorine and an atom of hydrogen, the molecular weight will be $35·5+1=36·5$; and the molecule of water vapour containing two atoms of hydrogen and one atom of oxygen—or, as A. Avogadro (1811) expresses it, *une demi-molécule d'oxygène avec une molécule ou, ce qui est la même chose, deux demi-molécules d'hydrogène*—will have a molecular weight of $16+2=18$. Hence, given the molecular weight of a compound gas, and the weights of the atoms of all but one of the elements, it is possible to compute the weight of the atom or atoms of that element in the molecule in question. The *modus operandi* will be discussed in two later sections.

A. Avogadro explicitly guarded against the assumption that the number of constituent atoms in the molecule of a gas must always be 2. There is really nothing in the facts to justify the assumption that the atoms themselves are simple particles. For all we know to the contrary, the atoms may be clusters of *n* particles. Indeed, we shall soon review some cogent evidence which has led many chemists to abandon Newton's solid impenetrable atoms, and to infer that **Dalton's atoms are not nature's irreducible minima.** Even if this inference be valid, each cluster of *n* particles which forms an atom has a definite weight—atomic weight—and enters into and is expelled from chemical combination as if it were a simple particle. If an atom be a cluster of particles, each cluster, so far as we can tell, has up to the present time behaved in chemical reactions as if it were an individual particle. The actual weight of a molecule is certainly not the molecular weight. When it is said that the molecular weight of hydrogen chloride is 36·5, this number simply means that we have conventionally agreed to fix the molecular weight of, say, oxygen as 32 units, and that the molecular weight of hydrogen chloride is to that of oxygen as 36·5 : 32. Consequently, like atomic weights, **molecular weights denote ratios, they are relative not absolute numbers.**

To deduce Avogadro's law from the relation between the relative densities and the molecular weights of the gases. Let M_1 and M_2 denote the weights of the molecules of two gases—A and B respectively ; further, let n_1 and n_2 respectively denote the number of molecules in unit volumes of the two gases. The weights of unit volumes (*i.e.* the densities) of the two gases will be M_1n_1 and M_2n_2. The observed fact is that the molecular weights (M_1 and M_2) of the gases are proportional to the densities (M_1n_1 and M_2n_2) of the gases ; or $M_1n_1 : M_2n_2=M_1 : M_2$, from which it follows that in unit volumes of the two gases $n_1 = n_2$. This is the symbolic way of stating Avogadro's rule. Hence, it has been claimed that Avogadro's postulate can be deduced from the relation between the molecular weights and the densities of two gases. It is easy to be misled by the apparent precision and rigorous accuracy conveyed to the mind by reasoning expressed in mathematical symbols, and to assume that the conclusions of such reasoning are certainties. Some affirm, on the strength of the simple demonstration just indicated, that "Avogadro's hypothesis is true." The reasoning is perfectly sound, but what about the premises, or statements upon which the reasoning is based? Avogadro's method for the determination of molecular weights tacitly assumes that the hypothesis is true. Hence, if the mathematical demonstration be employed to *prove* that Avogadro's hypothesis is true, the argument proceeds in a vicious circle. It is assumed in the premises what is "proved" in the demonstration. A conclusion proved by mathematics cannot be any more certain than the premises on which the reasoning is based.

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§ 4. The Formulæ of Compounds

Avogadro's hypothesis affords a bridge by which we can pass from large volumes of gases, which we can handle, to the minuter molecules, which individually are invisible and intangible.—W. A. Shenstone.

Since S. Cannizzaro's time, an enormous number of molecular weights have been determined by the vapour density method. If the molecule cannot be decomposed, it must be assumed that it is composed of one kind of matter only. If the substance is compound, it must be analysed so as to find the ratio, by weight, of its component elements referred to the oxygen standard (16). For instance, suppose that the analysis of a gaseous compound furnished: Nitrogen, 82·35 per cent.; hydrogen, 17·65 per cent. Using S. Cannizzaro's data, if hydrogen has an atomic weight of unity and nitrogen 14, the compound has the equivalent of $17{\cdot}65 \div 1$, or 17·65 hydrogen atoms for every $82{\cdot}35 \div 14$ nitrogen atoms; or 5·9 nitrogen for every 17·65 hydrogen atoms. By hypothesis we cannot have fractions of atoms. The nearest whole numbers are 3 hydrogen atoms for one nitrogen atom. Since the sum of the atoms in the compound must represent the molecular weight, it follows that the molecular weight must be $3n + 14n$, that is, the molecular weight is 17×1; 17×2; 17×3; . . . or $17n$. The formula is N_nH_{3n}. We can get no further until we know the molecular weight. If the vapour density of the compound (hydrogen $=2$) be 17, the molecular weight is 17. Hence, $17 = 17n$, or $n = 1$. The compound analysed can therefore be represented by the formula NH_3.

Examples.—(1) E. W. Morley (1895) found, in some careful experiments on the synthesis of water: Hydrogen used, 3·7198 grms.; oxygen used, 29·5335 grms.; water formed, 33·2530 grms. That is, one part by weight of hydrogen combines with 7·94 parts by weight of oxygen to produce 8·94 parts by weight of steam. A molecule of steam must contain n atoms of hydrogen, because parts of an atom do not take part in chemical changes. Hence, n parts by weight of hydrogen per $7{\cdot}94n$ parts by weight of oxygen give a molecule of steam of weight $8{\cdot}94n$. This all follows from the atomic theory. To apply Avogadro's hypothesis, with Cannizzaro's standard, the density of the steam must be determined. It lies between 16 and 20. It is difficult to determine the number exactly. If $n=1$, the density of the steam molecule will be near 8·94. This does not agree with the observed density 16 to 20. If $n=2$, the density of the steam will be 17·88; and if $n=3$, the density of steam will be 26·82. Hence, $n=2$. This means that each molecule of water vapour contains 2 atoms of hydrogen, atomic weight 1, and one atom of oxygen, atomic weight 15·88; or if we make our unit oxygen = 16, the atomic weight of hydrogen will be 1·008.

(2) Two different compounds have the same ultimate composition, namely: carbon 92·31 per cent., hydrogen 7·69 per cent., but the one has a relative density 26, and the other a relative density 78 (H = 2). What is the formula of each compound? There are 92·31 ÷ 12 = 7·7 carbon atoms per 7·7 ÷ 1 = 7·7 hydrogen atoms; but we cannot have fractions of atoms, hence dividing by 7·7 we get the ratio 1 : 1. That is, the formula of the compound is C_nH_n. The molecular weights of this series of compounds is $(12+1)n$ or $13n$. If $n = 2$, the molecular weight will be 26. Hence, one of the compounds is C_2H_2, and the other is C_6H_6.

In calculating formulæ for substances which cannot be vaporized, and one of the methods to be described later cannot be applied, it is usual to assume that the molecule has the simplest formula. In that case the formula is said to be *empirical*. Some prefer to use the term **formula weight** in place of molecular weight when the actual molecular weight has not been determined. The formula weight, like the molecular weight of a compound, is the sum of the atomic weights of the elements represented in the known or assumed formula of the compound.

EXAMPLES.—(1) 10 grams of pure tin when oxidized in air gave 12·7 grams of oxide. What is the formula of tin oxide? The atomic weight of tin is 119, and of oxygen 16. Hence, the ratio: Tin : oxygen = 10 ÷ 119 : 2·7 ÷ 16 = 0·084 : 0·17 = 1 : 2. The formula is therefore written SnO_2, although there is nothing to show why it is not Sn_2O_4; Sn_3O_6; . . . Sn_nO_{2n}.

(2) A sample of crystallized sodium carbonate furnished on analysis 37·2 per cent. of Na_2CO_3, and 62·8 per cent. of H_2O. What is the formula of the compound? The ratio $Na_2CO_3 : H_2O$ = 37·2 ÷ 106 : 62·8 ÷ 18 = 0·35 : 3·49 = 1 : 10. Hence, the formula is taken as $Na_2CO_3.10H_2O$, although there is nothing to show why it is not some multiple of this, say, $nNa_2CO_3.10nH_2O$.

(3) A. Jones (1892) analysed a sample of electric calamine, and found: Silica, SiO_2, 25·33; zinc oxide, ZnO, 67·15; and water, H_2O, 7·47 per cent. Show that this corresponds very nearly with the formula $Zn_2SiO_4.H_2O$.

(4) W. F. Hillebrand and W. H. Melville (1892) analysed some crystals obtained by the action of sulphuric acid on uranium oxide, and found: UO_2, 53·99; SO_3, 36·95; H_2O, 14·13 per cent. Show that the molecular ratio of these three constituents is 1 : 2 : 3·94, and that this corresponds with the formula $UO_2(SO_3)_2$, $4H_2O$ or $U(SO_4)_2.4H_2O$.

(5) G. Fernekes (1902) analysed a salt obtained by treating a solution of mercuric chloride with potassium ferrocyanide, and found: Potassium, 15·82 per cent.; mercury, 40·63; iron, 11·45; and cyanogen, C_2N_2, 31·78. Show that the simplest empirical formula for the compound is $K_2HgFe(CN)_6$.

§ 5. The Relative Weights of the Atoms

> Atoms are so inconceivably little that their aggregates are alone the ostensible subject of experiments.—S. BROWN.

It has already been stated that the conceptions molecular weight and atomic weight are quite independent of our theories about the nature of atoms and molecules; nor are the conceptions much affected by the actual weights of the atoms and molecules because the terms under consideration are definite expressions of Avogadro's hypothesis coupled with observed facts. It might therefore have been misleading to head this paragraph: *Weighing the Atoms*. There are reasons for supposing that the molecular weight of some compounds in the liquid or solid condition is a multiple of the molecular weight of the same substance in the gaseous condition. The molecule of steam approximately corresponds with the formula H_2O; but in liquid water there are reasons for supposing the molecule is either $(H_2O)_3$ or $(H_2O)_4$, that is, the formula for liquid water is not H_2O, for it contains molecules corresponding with H_4O_2, H_6O_3, or H_8O_4.

Refer back to the difficulty in fixing the atomic weight of carbon from the ratio of the weights of carbon and oxygen in the two oxides of carbon which we encountered in applying J. Dalton's atomic theory. Suppose that we do not know the atomic weight of carbon, but that we do know the composition of a number of volatile carbon compounds as well as their relative densities or molecular weights, Table II.

TABLE II.—MOLECULAR WEIGHTS OF SOME CARBON COMPOUNDS.

Volatile compound of carbon.	Composition by weight.	Molecular weight.	Amount of carbon per molecule.
Carbon monoxide	Carbon 12; oxygen 16	28	12
Carbon dioxide	Carbon 12; oxygen 32	44	12
Methane	Carbon 12; hydrogen 4	16	12
Ethylene	Carbon 24; hydrogen 4	28	12×2=24
Propylene	Carbon 36; hydrogen 6	42	12×3=36
Carbon disulphide	Carbon 12; sulphur 64	76	12

The smallest weight of carbon in a molecule of any of its known compounds is 12, and consequently this number is assumed to be the atomic weight of carbon. The atomic weights of a great number of the elements have been determined in a similar manner.

The determination of atomic weights.—According to J. Sebelin's *Beiträge zur Geschichte der Atomgewichte* (Braunschweig, 1884), when J. J. Berzelius was asked how he was able to get such excellent analyses, analyses which have been the admiration of generations of chemists, he answered:

> Try to find that method of analysis in which the accuracy of the result is least dependent upon the skill of the operating chemist; and when this method has been selected, consider what unavoidable conditions are present which are likely to affect the result with errors; and then ascertain whether the errors will increase or diminish the result. Then make another determination in which the opposite effects can alone be produced. If the two results are the same, the determination was correct.

The actual method used in finding the atomic weight of an element really requires:

(1) An exact analysis of a series of compounds containing the given element; and consequently the compounds investigated must be such as lend themselves to exact analysis, and which can be prepared in a highly purified condition.

(2) It is an advantage if the compound be volatile without decomposition, so that its vapour density can be determined. There are several other methods of computing the molecular and hence also the atomic weights of the different elements; and in several, the compound need not be volatile. Fortunately, atoms and molecules possess other qualities besides mass, which are dependent upon their atomic weights and which can be readily measured. Some of these will be described later.

(3) The smallest proportion of the element under investigation contained in all the compounds whose molecular weights are known is finally selected as the atomic weight of the given element.

J. A. Wanklyn (1894)[1] once claimed to have discovered a series of hydrocarbons, one member of which contained carbon 102 parts by weight, and hydrogen 17 parts, and had a vapour density of nearly 116 (hydrogen 2). Assuming the atomic weight of carbon is 12, and of hydrogen 1, these numbers give formula $C_{8\cdot5}H_{17}$. If this statement had been corroborated, and we were quite sure that Wanklyn's hydrocarbons were not mixtures, it would be necessary to make the atomic weight of carbon = 6, and write the formula of the compound in question $C_{17}H_{17}$, and this in spite of the fact that thousands of compounds of carbon are known, and all agree with the number 12 for the atomic weight of carbon. The formula of carbon monoxide—CO—would then be written C_2O, etc.—but J. A. Wanklyn's claim has never been established.

These remarks emphasize the importance of examining as large a number of volatile compounds as possible when fixing the atomic weight of an element. The importance of this principle was recognized as early as 1859, for F. A. Kekulé then wrote:

> It is of exceptional importance for chemists to determine the relative masses of particles which are not subdivided in chemical reactions. In order to determine the atomic or molecular weights of the elements and their compounds with some degree of probability, it is necessary to investigate a very great number of compounds and a very great number of chemical reactions.

If only a small number of compounds be examined, there is always a possibility, and perhaps a probability, that the actual minimum weight does not occur amongst the set of compounds taken. It follows, therefore, that the **atomic weight of an element is the least amount of that element—relative to the standard oxygen, 16—which is present in any molecule of all its known volatile compounds.** The value so obtained is the maximum possible value; the real value may afterwards prove to be a submultiple of this. The atomic weight must be equal to a whole multiple or submultiple of its combining weight. Owing to the fact that the molecular weights of so many volatile compounds of carbon are known, it is not very probable that the atomic weight of carbon is less than 12.

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§ 6. Methods for Measuring the Vapour Densities of Gases, and of Volatile Liquids and Solids

> The history of science shows that even during that phase of her progress in which she devotes herself to improving the accuracy of the numerical measurement of quantities with which she has long been familiar, she is preparing the materials for the subjugation of new regions, which would have remained unknown if she had been contented with the rough methods of her early pioneer.—J. C. MAXWELL.

When determinations of molecular weights are made to decide between quantities widely different, minor corrections, necessary for exact values, are not required. For instance, if chemical analysis showed that the molecular weight of a compound is some multiple of 20, then a molecular weight of 83, by vapour density methods, indicates that $4 \times 20 = 80$ is the molecular weight of the substance. With ordinary vapour density determinations, therefore, the weight of 22·4 litres of the gas or vapour at 0° and 760 mm. is to be computed from measurements with hydrogen $= 2$ or oxygen $= 32$ as standards of reference. No new principle is involved. If an intermediate value between two possible values for the molecular weight of a substance is consistently obtained, there is a disturbance—possibly association or dissociation—which must be investigated more closely.

These remarks do not apply when the molecular weights of gases are estimated from their densities in order to serve as a control for the atomic weights. The densities are then determined with as great an accuracy as possible. In the fourth century B.C., Aristotle made an unsuccessful attempt to determine the weight of air contained in a bladder; and, about 1632, G. Galilei established the fact that air has weight; R. Descartes (1638) said that G. Galilei's primitive method of weighing air *n'est pas mauvaise*. Robert Boyle, in his *Hydrostatics* (Oxford, 1666), gives the specific gravity of air 0·00125—with water unity as standard. The air of tartar, which consists of a mixture of carburetted hydrogen and carbonic acid gases, was weighed in a bladder by S. Hales,[1] and he compared the weight so obtained with that of the same bladder filled with air; F. Hauksbee determined the specific gravity of the mixture of carbon dioxide and nitrogen obtained by passing air over red-hot iron. The specific gravity of these mixed gases was so near that of air that the experimenters, by their methods, did not establish a difference. J. Mayow supposed but did not prove that the nitro-igneous constituent of air was heavier than the residual air from which it was separated. H. Cavendish, however, in his *Experiments on Factitious Airs*, in 1766, first established the difference in the specific gravities of air, carbon dioxide, and hydrogen, and this has been cited as the first conclusive proof of a plurality of elastic fluids. J. Priestley tried to weigh the different kinds of air in glass flasks by the displacement of water in a pneumatic trough, but the drops of water which adhered to the inside of the flask introduced too many errors. J. Priestley then used a bladder, and added that although the determination "cannot be done with precision in a bladder, as used by Mr. Cavendish, because the degree of distension cannot be measured with much accuracy, yet the circumstance is more than counterbalanced by being able to change the air, with compressing the bladder, without wetting it." J. Priestley found the bladder filled with—

	dwts.	grains.
Phlogisticated air weighed	7	15
Nitrous air	7	16
Common air	7	17
Dephlogisticated air	7	19

The early chemists apparently thought the determination of the density of a gas to be so simple an operation that details would be redundant; and they considered it was necessary merely to weigh a bladder or a flask first evacuated, and then filled with the required gas. Towards the end of 1779, F. Fontana [2] devised a much better method of measuring the specific gravities of different gases.

The stoppered globe *A*, Fig. 1, of known capacity is unscrewed from the gas stoppered receiver *B*, exhausted, weighed, and again screwed to the receiver; meanwhile, the receiver is filled over a mercury pneumatic trough with the gas under investigation. The stopcocks are opened, the cylinder *B* depressed in the mercury until the surface of the mercury is the same inside and outside the cylinder. The stopcocks are then closed, the difference of the two weighings is taken to represent the weight of the gas in the globe This result, divided by the capacity of the vessel expressed in cubic inches, gives the weight of a cubic inch of the gas in question.

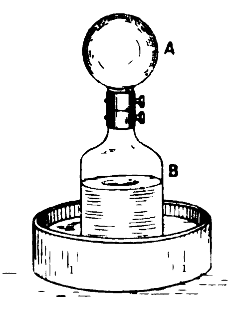

FIG. 1.—Fontana's Apparatus for Measuring the Density of Gases.

J. B. Biot and F. J. Arago (1806) determined the density of undried gases by means of a globe between 5 and 6 litres capacity. The results were corrected for the air displaced by the globe; the residual air in the evacuated flask; the cubical expansion of glass; and the hygroscopic moisture in the gas. The results were reduced to normal temperature and pressure, to sea-level, and to a latitude of 45°. For a long time J. B. Biot and F. J. Arago's measurements were considered to be a model for the work of others. J. J. Berzelius and P. L. Dulong (1820) and J. B. A. Dumas and J. B. J. D. Boussingault (1841) followed J. B. Biot and F. J. Arago's method, but they dried the gases.

A new era was inaugurated by H. V. Regnault in 1847. He introduced many vital improvements in J. B. Biot and F. J. Arago's procedure—chiefly in the use of a counterpoise balloon, and in the filling and exhausting of the globes while they were surrounded by a bath of melting ice. Modern work follows closely on the lines marked out by H. V. Regnault. Every known precaution which will conduce to the accuracy of the result is taken: (1) Attention is paid to the extreme purification of the gases to be measured; (2) the difference in the buoyancy in air of the weight and of the substance to be weighed is eliminated by reducing the weighings to the vacuum standard; (3) Lord Rayleigh's correction (1893) for the difference in the volume of the evacuated and filled balloon holding the gas is applied; (4) the expansion of the glass with variations of temperature is considered; (5) corrections are made for the deviations of the gas under investigation from Boyle's and Charles' laws; (7) an allowance is made for a slight condensation of gas on the inner walls of the measuring vessel; etc. In measuring the relative density of a substance which is gaseous at ordinary temperatures, three methods are available:

A. Weighing a known volume of the gas. The balloon method was worked out by H. V. Regnault (about 1847), and it has been much used in more recent work, where the general tendency has been to reduce the size of the balloons. H. V. Regnault worked with balloons about 10 litres capacity; E. W. Morley (1896)[3] with balloons 8–21 litres capacity; A. Leduc (1897), 2·3 litres; Lord Rayleigh (1888–95), 1·8 litres; P. A. Guye and C. Davilla (1905) used globes of capacity 0·38 to about 0·82 litre for nitric oxide; E. P. Perman and J. H. Davis (1906), 0·5 litre; and R. W. Gray (1905), 0·267 litre. The determinations made with small balloons are quite as concordant among themselves as those made with balloons of larger volume.

In this method the glass globe of volume v is counterpoised on the balance by a second tare balloon of approximately the same volume so as to eliminate corrections necessary for the buoyancy of the air. By repeated exhaustions and re-fillings, the balloon is filled with the gas under investigation. The temperature and pressure are respectively θ and p. Let w denote the difference between the weights of the full and empty balloon. The volume v_0 of the gas at 0° and 760 mm. pressure is first calculated in the ordinary manner:

$$v_0 = v\left(\frac{p}{760}\right)\left(\frac{273}{273+\theta}\right); \text{ or } v_0 = \frac{0\cdot3592vp}{273+\theta} \quad . \quad . \quad . \quad (1)$$

From Avogadro's hypothesis the molecular weight of a gas represents the weight of 22·3 litres of a gas if hydrogen $= 2$ be taken as the standard. Consequently, if w grams of a gas occupy v_1 c.c. at 0° and 760 mm. pressure, 22,300 c.c. will weigh $22{,}300w \div v_1$ grms., and this represents the molecular weight, or the uncorrected relative density of the gas, hydrogen $= 2$. For a high degree of accuracy, it is of course necessary to include correction terms as indicated above.

EXAMPLES.—(1) 585 c.c. of carbon dioxide measured at 18° and 756 mm. pressure weighed 1·076 gram. What is the molecular weight of the gas? 585 c.c. of gas become, at 0° and 760 mm., 546·1 c.c. Hence, the molecular weight is $22{,}300 \times 1\cdot076 \div 546\cdot1 = 43\cdot9$.

(2) H. V. Regnault (1845) filled a 10-litre globe with air at a pressure of 761·19 mm. at the temperature of melting ice. In addition to the tare balloon 1·487 grms. were required to balance the globe. The globe was then exhausted to a pressure 88·43 mm., and 14·141 grms. were now required to restore equilibrium. The globe was then filled with dry oxygen at 0° and 750·22 mm. pressure, 0·172 grm. was needed in addition to the tare to balance the globe. The globe was then exhausted to 4·59 mm. pressure and weighed, again 14·033 grms. were required. The globe lost 12·654 grms. of air at $761\cdot19 - 8\cdot43 = 752\cdot76$ mm. pressure and 0°. This corresponds with 12·776 grms. of air at 760 mm. Similarly with the oxygen: 14·1281 grms. at 760 mm. and 0°. The weights refer to equal volumes, and therefore the relative density of the oxygen (air unity) is $14\cdot1281 \div 12\cdot776 = 1\cdot10563$.

B. Measuring the volume of a known weight of the gas.—The volume occupied by a known weight of gas is measured in a suitable voluminometer, and the gas required to fill the balloon is weighed in another vessel either (*a*) by finding the loss of weight due to the escape of gas from the generating apparatus, or (*b*) by absorbing the gas in suitable apparatus. In the former case, given the temperature and pressure of the confined gas, the capacity of the balloon, and the loss of weight in the vessel from which the balloon was filled, the density follows directly. This method was used by E. W. Morley (1896) for hydrogen, and by A. Jaquerod and A. Pintza (1904) for sulphur dioxide. In a variation of this procedure, the measuring vessel is filled with the purified gas and its temperature maintained at 0°, while the pressure (approximately 760 mm.) is determined. The gas is then absorbed in a suitable apparatus previously evacuated and connected with the voluminometer by a tightly fitting joint. The weight of the absorbed gas completes the required data. This method was used by P. A. Guye and A. Pintza (1904–5) for nitrous oxide, carbon dioxide, and ammonia; by E. P. Perman and J. H. Davis (1906) for ammonia; and by R. W. Gray and E. P. Burt (1909) for hydrogen chloride.

C. Measuring the buoyancy of the gas in atmospheres at a known pressure.—A good analytical balance will indicate 0·0001 grm. when carrying a load of 100 grms.;

the balances used for assaying will indicate 0·00001 grm. with a load of 10 grms. The sensibility of instruments for detecting variations of mass has been so sharpened that the latest form of **micro-balance** will carry a maximum load of 5×10^{-3} grms., and is sensitive to $3\cdot3\times10^{-8}$ grm. The weighing of minute masses is called **micro-weighing**.[4] Probably the first micro-balance was made by E. Warburg and T. Ihmori in 1886. The beam of this balance was made of thin quartz rods to which were cemented razor knife-edges; the deflections of the beam were read from a mirror and scale without taring the weights. The sensitiveness of this balance was about the same as the assay balances. In 1906, W. Nernst and E. H. Riesenfeld devised a torsion micro-balance in which a quartz fibre was cemented to the prongs of a vertical brass fork; and a thin glass rod likewise fixed horizontally to the quartz fibre. One end of the rod is intended to serve as a pointer on a silvered scale, and the other carries a tiny pan. The load causes a slight torsion of the quartz fibre. The maximum load is 2 mgrm., and the lower limit of sensibility is 5×10^{-6} grms. In another type, the principle of Archimedes is applied, and a gas manometer takes the place of a set of weights. This apparatus was improved by B. D. Steele and K. Grant (1909), and W. Ramsay and R. W. Gray (1911), so that a weight 0·0000001 grm. can be accurately determined. In some of the improved forms a still greater sensibility has been attained. In this way, the density of less than 0·75 cubic millimetres of the emanation from radium has been determined, and the corresponding molecular weight computed from the result. This is a triumph of manipulative skill.

If air at the same temperature and pressure as the ambient atmosphere be confined in a quartz bulb, it will apparently weigh nothing, but if the outside air be reduced in density, the air inside the quartz bulb will appear to have a positive weight. Given the pressure of the ambient air, the weight of the confined air can be readily calculated as indicated in the subjoined example. The beam of the instrument is a framework of thin rods of silica arranged to swing on a central knife-edge resting on a central support. A scale-pan or bucket and a sealed air bulb of known volume are suspended from the framework by quartz threads, and counterpoised by a weight. All is enclosed in an air-tight metal case fitted with a mercury gauge. A mirror reflects a beam of light from the window to a scale a few feet away. The tube containing the gas under investigation is placed in the bucket, and the pressure noted at which the beam is in equilibrium. This is indicated by the spot of reflected light. The bulb containing the gas is broken, and all the glass splinters are placed in the bucket. The gas is removed by evacuating the metal case a few times. The pressure of the air again required to bring the spot of light to equilibrium is noted. Suppose, by way of example, that the pressure of the air required to bring a tube of xenon gas in the equilibrium position be 70 mm.; and similarly the empty tube, 52·9 mm. The difference, 17·11 mm., corresponds with a weight 608 millionths of a milligram. A correction is required for differences in the weight of the glass vessel at pressures of 70 mm. and 52·9 mm. It is 15 millionths mgrm. Again, the effect of the reduced pressure on the buoyancy of the glass bulb and the silver counterpoise is different. By substituting a counterpoise of silica the difference was found to be 91 millionths of a mgrm. Hence the weight of the gas in question is $608-91+15=532$ millionths of a milligram.

The micro-balance has been used by F. W. Aston (1914) to compare the densities of two gases. The gas to be investigated, density D, is admitted to the balance case, and the pressure p determined at which the balance beam is in a given position. The corresponding pressure p_1 for a gas of known density D_1, say, oxygen is then determined. The densities of the two gases D and D_1 are inversely proportional to the pressure p and p_1, or the density D of the required gas is p_1D_1/p.

The vapour density of solids and liquids which can be vaporized without decomposition can be obtained by the following methods:

A. Weighing a known volume of the vapour.—In **J. B. A. Dumas' process** (1826)[5] the substance is vaporized in a weighed glass bulb at atmospheric pressure. The bulb is then sealed up, and the weight of the vapour determined. The capacity of the bulb is then measured. From the resulting data, the vapour density of the gas follows directly.

EXAMPLE.—The following data were obtained by H. E. Roscoe (1878) for vanadium tetrachloride: Weight of globe filled with air (9°, 760 mm.), 24·4722 grams; weight of sealed globe (9°, 760 mm.), 25·0102 grams; temperature of bath when sealing the globe, 215°; barometer when sealing the globe, 762 mm.; and the weight of bulb full of water, 194 grams. The globe held less, 24·4722 = 169·5 grams of water at 9°. This represents very nearly 169·5 c.c. of water, or the capacity of the globe is 169·5 c.c. The apparent weight of the substance at 9° is 25·0102 − 24·4722 = 0·538 gram. The empty globe was buoyed up, during weighing, by its own bulk of air at 9° and 762 mm., and since 1 c.c. of air weighs 0·001293 grams, 169·5 c.c. of air at 9° and 762 mm. weigh at (0·001293 × 169·5 × 273 × 762) ÷ (760 × 282) = 0·213 gram. This added to 0·538 gram, gives 0·751 gram, the weight of the vapour in the globe at the time of sealing. The 0·751 gram of vapour occupied 169·5 c.c. at 215° and 762 mm. pressure, or 95·10 c.c. at 0° and 760 mm. pressure. Hence, 22,300 c.c. of vapour at normal temperature and pressure weigh 176·1 grams. This number also represents the molecular weight of vanadium chloride.

Vessels made of porcelain have enabled H. St. C. Deville and L. Troost (1858), H. E. Roscoe (1878), and others to determine vapour densities by this process at temperatures far exceeding those at which even hard glass softens. The objection to Dumas' process is the amount of material which has to be vaporized in order to drive out the air from the bulb. This waste is avoided in the two succeeding methods—Hofmann's and Meyer's processes. By using porcelain or platinum vessels, Dumas' process has been employed for bodies volatilizing at high temperatures.

B. Measuring the volume of a known weight of the vapour.—J. L. Gay Lussac (1811) showed that the vapour density of a substance can be determined by measuring the volume of a known weight of the vapour in such a way that the volatile substance is confined in a small vessel of known capacity by means of mercury or any other substance which boils at a high enough temperature—*e.g.* Wood's fusible alloy. When the vessel has been heated the bath is removed. After cooling, the volume of the vapour at the highest temperature of the bath can be calculated from the weight of, say, mercury remaining in the vessel. J. L. Gay Lussac's process was perhaps the oldest method used for measuring vapour densities. He placed a known weight of the substance under investigation in a graduated glass tube, about 40 cm. long, and filled with mercury. The tube dipped in mercury and was surrounded by a hot jacket so as to vaporize the substance. The temperature and volume of the confined vapour were measured. In **A. W. Hofmann's process** (1868) the measuring tube is over 760 mm. in length.

EXAMPLE.—The following data were obtained for carbon tetrachloride, CCl_4: Weight of liquid in bulb, 0·3380 grm.; the volume of vapour, 109·8 c.c.; the temperature of vapour, 99·5°; the barometer, 746·9 mm.; and the height of mercury in tube, 283·4 mm. The pressure of the vapour is the barometric height less the weight of the column of mercury in the Hofmann's tube, that is, 746·9 − 283·4 = 463·5 mm. Hence, 0·3380 gram of vapour at 99·5° and 463·5 mm. pressure occupy 109·8 c.c., and 49·09 c.c. at 0° and 760 mm. Hence, 22,300 c.c. of the vapour at normal temperature and pressure weigh 153·6 grams, and this number represents the molecular weight of carbon tetrachloride.

A. W. Hofmann's process is useful when only a small amount of the substance is available for a determination; and for a substance which decomposes when heated at a temperature in the vicinity of its boiling point at ordinary atmospheric pressures. In **V. and C. Meyer's process** (1877) [6] the apparatus is simplified by measuring the volume of air displaced by a given weight of the substance vaporized in a suitable vessel.

If the substance be vaporized too slowly, vapour will be carried forward with the expelled air, and be condensed, thus reducing the volume of air (or gas) measured in the gas burette. It is considered that the vaporization vessel should be at least 30° above the boiling point of the substance in order to secure rapid vaporization. If the gas be collected over water instead of over mercury and is filled with ordinary moist air instead of with dry air, *a correction for the pressure of aqueous vapour* may be applied. If air contains a per cent. of moisture; and f denotes the pressure of aqueous vapour at the room temperature; and p, the barometric pressure, the actual pressure of the confined gas is taken to be $p-(1-\frac{1}{100}a)f$. This refinement is usually ignored.

Example.—The vapour density of water was determined, and the following data were obtained. Xylene, boiling at about 138°, was used in the hot jacket *E*. It was found that the weight of the water in the stoppered tube was 0·0102 grm.; the temperature of the gas in the burette, 16·5°; the barometer, 703·8 mm.; and the volume of gas, 16·6 c.c. The 16·6 c.c. of vapour at 16·5° and 703·8 mm. becomes 14·496 c.c. at 0° and 760 mm. This is the volume of 0·0102 gram of vapour. Hence, 22,300 c.c. of the vapour will weigh 15·7 grams. This number represents the molecular weight of water vapour.

V. Meyer's apparatus has been modified in various directions without altering the fundamental principle. J. S. Lumsden (1903) proposed a modification in which the increase of pressure was measured while the volume of the apparatus was kept constant. Glass vessels are suited for this determination only at comparatively low temperatures; vessels made of hard porcelain have been used by J. Mensching and V. Meyer (1886) for temperatures up to about 1500°; platinum, platinum-iridium alloy, vitreous silica by J. Dewar and A. Scott (1879), L. F. Nilson and O. Pettersson (1886), and by J. Mensching and V. Meyer (1886); and vessels of iridium lined inside and outside with a magnesian cement, and heated in an electric furnace, enabled W. Nernst (1903) and H. von Wartenberg (1908) to measure vapour densities at temperatures as high as 1800° and even 2000°.

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§ 7. The Struggle of Avogadro's Hypothesis for Recognition

The first attempt at generalization seldom succeeds; speculation anticipates experience, for the results of observation accumulate but slowly.—J. J. Berzelius (1830).

A. Avogadro's hypothesis had a long struggle for recognition in spite of the fact that his memoir was followed three years later by A. M. Ampère's note addressed to M. le Comte Berthollet and entitled, *Sur la détermination des proportions dans lesquelles les corps se combinent, d'après le nombre et la disposition respective des molécules dont leurs particles intégrantes sont composées* (1814), advocating similar views. Half a century elapsed before the hypothesis was generally accepted. Among the many reasons for its failure was the fact that comparatively few substances which could be vaporized were then known, and hence the molecular weights of but few compounds had been determined with precision. At that time, an accurate knowledge of the weights of the elements was considered to be the most pressing subject of investigation. J. Dalton's atomic theory had just been born, and accurate data were also needed before that theory could be utilized. Referring to J. Dalton's theory J. J. Berzelius said :

> I recognized that if the newly arisen light was to be spread, it would be necessary to ascertain with the utmost accuracy the atomic weights of all elementary substances. . . . Without such work, no light would follow the dawn.

Something more than the mere accumulation of experimental data was necessary to find a method for determining the number of atoms in a molecule, in order that the atomic weight of the constituent elements could be obtained. Dalton pointed out that in fixing the atomic weight of oxygen with respect to hydrogen unity, he assumed that water is a binary compound of one atom of hydrogen and one of oxygen. If water be really a ternary compound containing two atoms of hydrogen and one of oxygen, it will be necessary to double the atomic weight of oxygen determined on the former assumption ; and if water contains two atoms of oxygen and one of hydrogen, the atomic weight of the oxygen would have to be halved. Similarly with other compounds. *The uncertainties in the application of J. Dalton's atomic theory are due to the arbitrary nature of the assumption of the number of atoms in a molecule.*[1]

W. H. Wollaston (1814).—In 1810, T. Thomson gave a list of the weights of various acids and bases which neutralized one another, and showed that these numbers were independent of the hypothesis of Dalton. W. H. Wollaston, in his paper *A synoptic scale of chemical equivalents* (1814), proposed to substitute the term *equivalent* in place of Dalton's *atom*. He claimed that his numbers were not warped by the uncertainties of the atomic theory, and that for practical purposes it is not necessary to know hypothetical atomic weights when equivalent weights are known. Wollaston thus proposed to do for the elements what J. B. Richter (1791–1802) had done for the acids and bases, and he accordingly used the term equivalent proposed by H. Cavendish in 1788. Starting with oxygen 10 as the unit of reference, he found the equivalent of hydrogen to be 1·3—meaning that 1·3 parts of hydrogen unite with 10 parts of oxygen to form water. In this sense, equivalent weights are identical with combining weights. Wollaston, however, got into difficulties in dealing with substances like carbon with two combining weights, for he was obliged to assume that in carbon dioxide two equivalents of oxygen were united with one of carbon so that equivalents and combining weights were no longer the same. Since 7·5 parts of carbon unite with 20 parts of oxygen by weight to form carbon dioxide, W. H. Wollaston said the formula of the compound is CO_2 ; and because 7·5 parts of carbon unite with 10 parts of oxygen by weight to form carbon monoxide the formula is CO. W. H. Wollaston might just as arbitrarily have said 3·75 of carbon unite with 10 parts by weight of oxygen to form carbon dioxide, and the formula is accordingly CO ; and in carbon monoxide 7·5 parts of carbon unite with 10 parts of oxygen by weight, and therefore the formula is C_2O. Hence, W. H. Wollaston's equivalents leave the difficulty with J. Dalton's atoms just as it was. Ignoring this uncertainty, the former computed the equivalents of 12 elements, and 45 compounds from various analyses. A. Ladenburg (1869) [2] is severe on W. H. Wollaston, for he says that Wollaston's views involved a retrograde step, for W. H. Wollaston believed that he was dealing with unambiguous conceptions free from all hypothesis ; and in introducing the term equivalent, he confused the conceptions of the equivalent and the atom, and rendered a vigorous struggle necessary before the two concepts could be clarified.

J. J. Berzelius (1810–26).—J. J. Berzelius seems to have regarded the investigation of the laws of combining proportions to be one of the most important objects of his life's work, and in a memorable work, *Essai sur la théorie des proportions chimiques et sur l'influence chimique de l'électricité*, published in Sweden in 1814, and at Paris in 1819, he developed his conceptions of the atomic theory, and collected together the results of his arduous work on the combining proportions of the elements which he had published between 1810 and 1812. In his *Lehrbuch der Chemie* (Dresden, 1825), J. J. Berzelius remarked that it did not matter much whether the particles which combine chemically be called atoms, molecules, chemical equivalents, or any other terms, but he preferred to use the term atom. In spite of Dalton's demonstration that Gay Lussac's law does not mean that equal volumes of elemental gases contain the same number of atoms, J. J. Berzelius used this erroneous *Volumtheorie* as a guide in determining the numerical values of the atomic weights of the elements which were gaseous at ordinary temperatures. He said, one volume of an elementary substance in the gaseous state corresponds with one atom, and he called the smallest particles *Volumatome*. This erroneous theory gave him satisfactory results in deducing the composition of water, and of the two carbon oxides; and consequently also of the atomic weights of oxygen, hydrogen, and carbon. J. J. Berzelius (1818) was not so fortunate with some of the metallic oxides, particularly the sesqui-oxides. It is illogical, said he, to express the composition of a series of oxides of an element A by the formulæ A_2O_2, A_2O_4, A_2O_6 . . ., and declared that in a series of compounds of the two elements one compound must always be represented as containing a single atom of one of the elements, and accordingly he wrote the formulæ AO, AO_2, AO_3 . . . If the simplest oxide were A_2O_2 Berzelius said that the atoms of the elements A would be divisible mechanically. J. Dalton saw the fallacy in this argument for fixing the number of atoms in a molecule of the solid oxides, but, led on by the erroneous argument, Berzelius (1818) wrote the formulæ for ferrous oxide FeO_2 instead of FeO ; and ferric oxide, FeO_3 instead of Fe_2O_3, and thus obtained numbers for the atomic weights of iron, chromium, etc., double the values of those now accepted. The chemical similarities of iron with chromium led him to symbolize chromic oxide CrO_3 by analogy with FeO_3 ; similarly he formulated the metal oxides ZnO_2, MnO_2 . . . by analogy with FeO_2. In 1826, however, he wrote—

> Assuming that chromic oxide contains three atoms of oxygen ; and that chromic anhydride contains six atoms, in forming neutral salts, chromic anhydride neutralizes an amount of base containing one-third as much oxygen as it itself contains. By analogy with sulphuric anhydride, and other anhydrides with three atoms of oxygen, it is most probable that chromic anhydride contains three atoms of oxygen to one of chromium, consequently chromic oxide will contain three atoms of oxygen to two of chromium, and the formulæ for chromic oxide will be Cr_2O_3, and for chromic anhydride, CrO_3. The isomorphic law will then make ferric oxide, Fe_2O_3, instead of FeO_3 ; and aluminium oxide, Al_2O_3, instead of AlO_3.

These considerations led J. J. Berzelius in 1826 to halve the atomic weights of the metals published in his 1818 Table of Atomic Weights. The following table represents atomic weights of a few elements selected from Berzelius' 1818 and 1828 Tables, and recalculated for the standard oxygen 16 instead of 100 used by Berzelius. The modern values also are given by way of comparison.

TABLE III.—BERZELIUS' ATOMIC WEIGHTS.

Elements	1818.	1828.	1919.
Carbon . . .	12·12	12·25	12·0
Oxygen . . .	16·0	16·0	16·0
Sulphur . . .	32·3	32·24	32·06
Mercury . . .	406	202·86	200·6
Iron . . .	109·1	54·36	55·84
Sodium . . .	93·5	46·62	23·00
Silver . . .	433·7	216·61	107·88

Berzelius never succeeded in deciding whether the binary compounds he analyzed contained two or more atoms per molecule. Without any rules to guide him, said J B. A. Dumas (1832), but guided mainly by analogies, he fixed by intuition the atomic weights of a number of elements which subsequent experience has only tended to confirm. When all is said, however, this method is unsatisfactory, because it is arbitrary, and liable to be capriciously modified by each worker. In addition to his volume law, Berzelius also used Dulong and Petit's rule of specific heats, and Mitscherlich's isomorphic law to assist him in fixing the atomic weights of the elements.

J. B. A. Dumas (1826–37).—In 1826, J. B. A. Dumas[3] published an important memoir *Sur quelques points de la théorie atomistique :*

> The object of these researches is to replace by definite conceptions, the arbitrary data on which nearly the whole of the atomic theory is based.

Dumas accepted the hypothesis of Avogadro as propounded by Ampère, namely, that equal volumes of gases contain an equal number of particles, and in the case of the simple gases, that these particles are subdivided during chemical reactions. J. B. A. Dumas thus recognized the importance of measuring the relative densities of gases and vapours, and he devised his well-known method for determining these constants. In 1832, he had determined the relative vapour densities of mercury, iodine, phosphorus, sulphur, arsenic, etc., and noted some irregularities with sulphur, mercury, phosphorus, and arsenic. He spoke of *un demi-atome* in the same way that Avogadro spoke of *une demi-molécule.* J. J. Berzelius appears to have been obsessed by his dualistic theory (*q.v.*), in which he assumed that the ultimate particles (molecules) of elementary substances cannot be split when they form a binary compound ; so that he wrote the formula of hydrogen chloride H_2Cl_2 ; or else he misunderstood J. B. A. Dumas, owing to the confusion of the words atom and molecule, and was led to say (1826) :[4] "It is usually supposed that an hypothesis ought to be abandoned as soon as it leads to an absurd conclusion ;" and if Avogadro's hypothesis involves the subdivision of an atom, it must be condemned.

In his *Leçons sur les philosophie chimique* (Paris, 1837), J. B. A. Dumas applied Avogadro's volume law—equal volumes, an equal number of atoms—to explain the formation of hydrogen chloride, HCl, and nitric oxide, NO, from the elementary gases, and he showed that the physical atoms must be split during the reaction. Hence, said J. B. A. Dumas, *la chimie coupait les atomes que la physique ne pouvait pas couper,* so that Avogadro's molecules are Dumas' physical atoms. Here again there was some confusion owing to the unfortunate use of the word atom in place of Avogadro's molecule. J. B. A. Dumas then went on to show that while Avogadro's volume law gives satisfactory values for the atomic weights of oxygen, nitrogen, chlorine, bromine, and iodine, difficulties are encountered with phosphorus, arsenic, mercury, and sulphur. For instance, ammonia is formed by the union of three volumes of hydrogen and one volume of nitrogen ; and phosphine, a similar gas, is presumably formed in a similar manner so that phosphine should be produced by replacing the nitrogen of ammonia by an equal volume of phosphorus gas. Consequently, it was argued that the density of phosphorus vapour ought to be 31·4 (hydrogen unity—in the original, oxygen 100 is the standard of reference) ; experiment gives a number twice as great ! A similar discrepancy was found with arsenic. This can only mean that equal volumes of the vapours of nitrogen, phosphorus, and arsenic do not contain the same number of atoms. Again, J. B. A. Dumas showed that about 200 parts of mercury unite with 16 parts of oxygen to form mercuric oxide, and therefore the atomic weight of mercury must be nearly 200 ; but judging from the density of mercury vapour, the atomic weight of this element is nearly 100. Consequently, *le chaleur diviserait les particles du corps plus que l'action chimique.* Equal volumes of gases sometimes contain an equal and sometimes an unequal number of atoms, and therefore the determination of the densities of vapours cannot be a trustworthy guide in evaluating the atomic weights of the elements. The facts seemed to be against Avogadro's hypothesis and J. B. A. Dumas accordingly gave it up in despair. He then tried an application of Dulong and Petit's rule, but here again he was disappointed with the exceptions; and finally, after trying Mitscherlich's isomorphic rule, he said, *tout considéré, la théorie atomique serait une science purement conjecturale, si elle ne s'appuyait pas sur l'isomorphisme.*

W. Prout (1833) and A. Gaudin (1835).—W. Prout, in his work *Chemistry . . . considered with reference to Natural Theology* (London, 122, 1833), adopted the hypothesis of Avogadro's, *viz.* " under the same pressure and temperature, all bodies in a perfectly gaseous state contain an equal number of self-repulsive molecules," to explain the volume relations of hydrogen, oxygen and water, and of hydrogen, chlorine, and hydrochloric acid. W. Prout's explanation is almost as clear as if it had been written to-day. From the observed results, said he,

> It follows irresistibly that every self-repulsive molecule of oxygen has been divided into two, and consequently must have originally consisted of at least two elementary molecules, somehow or other associated, so as to have formed one self-repulsive molecule.

M. A. Gaudin, in his papers *Recherches sur la structure intime des corps inorganiques*, published in 1833, had previously pointed out that J. B. A. Dumas' difficulty with mercury and phosphorus could be explained by assuming that the mercury molecule is monatomic, and that of phosphorus tetratomic; evidently J. J. Berzelius did not like this mode of evading the discrepancy observed by J. B. A. Dumas, and considered it to be *nur ein Spiel der Phantasie*, although M. A. Gaudin's suggestion is now generally accepted; so also is Gaudin's happy use of the terms mono-, di-, tri-, . . . atomic for indicating the number of atoms in a molecule.

Failures with Avogadro's hypothesis.—Towards the middle of the nineteenth century, as a result of these failures to apply Avogadro's hypothesis, the atom was abandoned by the majority of chemists as a discredited theory. In illustration, J. B. A. Dumas said in 1837: *Si j'en étais le maître, j'effacerais le mot atome de la science.* Wollaston's equivalents were used, notably by L. Gmelin in his popular *Handbuch der theoretischen Chemie* (Frankfurt-am-Main, 1817–9). In the early editions of this book Gmelin used the term *Mischungsgewichte*—mixing weights—and in a later edition (1843), the term *stoichiometric numbers* in place of equivalents. Gmelin said, if an atom is the smallest quantity of a body which enters into combination, the equivalents must represent atoms; the atomic notation of Dalton is based on hypothesis, equivalents are a reality. The inconsistencies involved in W. H. Wollaston's equivalents were thus ignored. The whole subject at this time (1840–50) was in a very confused state. In addition to the muddling of the terms atom, molecule, and equivalent, there were tables of atomic weights, equivalents, H. V. Regnault's *équivalents thermiques* (1849) based upon Dulong and Petit's rule; H. Rose's (1857) and J. C. G. de Marignac's *équivalents isomorphiques* (1855) based upon Mitscherlich's rule; and M. Faraday's *electrochemical equivalents* (1834).[5] Different chemists used different standards for their equivalent and atomic weights. The same chemical formula was used for different compounds, and different formulæ for the same compound—for instance, F. A. Kekulé in his *Lehrbuch der organischen Chemie* (Stuttgart, 1861) indicated nineteen different formulæ which had been proposed for acetic acid. Inorganic chemists thus failed to establish the conception of an atom, but fortunately organic chemists had begun to see more clearly.

C. F. Gerhardt and A. Laurent (1842–56).—In 1842, in a memoir entitled *Recherches sur la classification chimique des substances organiques*, C. F. Gerhardt was groping for a method of distinguishing between equivalent and atomic weights, and he put forward some important views respecting the equivalents of certain elements taking part in organic reactions. He showed that when an organic reaction gave rise to water, carbon dioxide, carbon monoxide, or ammonia, the smallest amounts produced are those represented by the formulæ H_4O_2, C_2O_4, C_2O_2, S_2O_4, NH_3

respectively, on the assumption that the equivalent or atomic weights are H=1, O=8, C=6, S=16, N=14. Hence, the quantities indicated by the formulæ must represent an equal number of equivalents. It seems strange, said he, that no reaction in organic chemistry can give rise to less than a single molecule of water, H_4O_2, or carbon dioxide, C_2O_4; and that these quantities of gases occupy equal volumes. Consequently, H_4O_2 and C_2O_4 represent either one or two equivalents; the former hypothesis fits the facts best, and therefore he argued that the equivalents of the elements O=8, C=6, and S=16 should be doubled so that the preceding formulæ can be written H_2O, CO_2, CO, SO_2, and NH_3 respectively. C. F. Gerhardt thus obtained numbers for the equivalents of the elements, hydrogen, oxygen, carbon, sulphur, and nitrogen in agreement with the atomic weights used by Berzelius in 1826.

C. F. Gerhardt also advocated the adoption of a common standard for comparing chemical formulæ with one another, and he recommended the use of what is known as the *two-volume standard*: those quantities by weight which occupy two volumes when in the gaseous state and when the volume of atomic hydrogen is taken as unity. Hence, Avogadro's hypothesis is sometimes called the *Avogadro-Gerhardt law*. In a later part of his paper, Gerhardt showed that his notions of atomic weights, the volume theory, and equivalents were not clear, because he stated that all these concepts coincide. A. Laurent (1846), however, obtained a clear grasp of the meanings to be attached to these terms, and he adopted Gerhardt's happy idea that chemical formulæ should represent comparable quantities; he also adopted the two-volume standard, but in doing so he was obliged to admit that there are some exceptions—*e.g.* the vapour of ammonium chloride, and sulphuric acid—which seemed to correspond with a four-volume standard. The names of Laurent and Gerhardt are usually linked together; it is, indeed, difficult to isolate the particular contributions made by each because they published a great deal jointly, and, being intimate friends, they probably discussed the whole subject together. A. Laurent's posthumous *Méthode de chimie* (Paris, 1854) and C. F. Gerhardt's *Traité de chimie organique* (Paris, 1856),[6] did much to clear the conceptions of equivalents, atoms, and molecules; and their definitions of these entities, and most of their formulæ for organic and inorganic compounds are virtually in use to-day. Laurent represented the union of hydrogen and chlorine by the equation (HH)+(ClCl) =(HCl)+(HCl); to-day we write, $H_2+Cl_2=2HCl$; similarly the synthesis of water was symbolized, (HH)+(HH)+(OO)=(HH)O+(HH)O; to-day we write, $2H_2+O_2=2H_2O$. A. Gaudin (1832) employed special diagrams to symbolize these reactions.

Several other systems of symbolizing chemical operations have been proposed. A. C. Brown (1867), for example, used Greek letters to represent different chemical actions, thus ϕ represented the replacement of hydrogen in a molecule by the radicle CH_3, and if a denotes a molecule of ammonia, NH_3, the symbol ϕa represented the substitution of one hydrogen atom in ammonia to form CH_3NH_2. In view of the great variety of chemical processes and compounds, such a system would be more cumbrous and throw greater strains on the memory than the present system. B. C. Brodie proposed a new notation in his *Calculus of Chemical Operations* (1867), which he regarded as "a rigid expression of fact," independent of the atomic hypothesis. B. C. Brodie's system, however, involved assumptions even more drastic than the atomic theory, and the notation was so confusing that it died as soon as it was born.

S. Cannizzaro (1857–8).—In 1857, S. Cannizzaro stated his belief:

> There are no exceptions to the universal law that equal volumes of gases contain equal numbers of molecules, and that the apparent exceptions will disappear when more searching experiments are made.

He showed that the apparent exceptions to C. F. Gerhardt's two-volume law, pointed out by A. Laurent, are not real, for the work of H. St. C. Deville (1857) has shown that ammonium chloride and sulphuric acid are decomposed by heat, and therefore the observed vapour densities are the densities of mixtures of the decomposition products and not of homogeneous compounds to which Avogadro's hypothesis alone refers. Similar conclusions were deduced independently and almost simultaneously by H. Kopp (1858)[7] and F. A. Kekulé (1858). Immediately afterwards, S. Cannizzaro published his celebrated *Sunto di un corso di filosofia chimica fatto nella Reale Universita di Genova* (1858), which placed Avogadro's hypothesis at the foundation of the system of chemistry which obtains to-day—witness, among other works, W. Nernst's popular *Theoretische Chemie vom Standpunkte der Avogadroschen Regel und der Thermodynamik* (Stuttgart, 1916). The atomic theory of the present-day chemistry is the work of many minds. In the words of G. Chrystal (1885):

> Few scientific ideas spring up suddenly without previous trace or history; a close examination always shows that the sprite was in the air before the Prospero came to catch him. . . . There are long periods in science in which great improvements were effected which cannot be traced to any individual, but seem to have been due merely to the working of the minds of scientific men generally upon the matter, one giving it this little turn, another that, in the main, always for the better.

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§ 8. Deviations from Avogadro's Law

> When a fact appears to be opposed to a whole train of deductions, it invariably proves to be capable of bearing some other interpretation.—SHERLOCK HOLMES.

It is sometimes said that a phenomenon "ought to take place," but it does not; the phenomenon is then said to be abnormal or anomalous. These terms are not very happily chosen, and they are sometimes used rather carelessly; they are not intended to imply that nature is erratic, arbitrary, and lawless. The words simply mean that in groping for the truth, an unexpected result has been obtained, which once stood, or now stands, challenging investigators to show how the unexpected should have been expected. In this sense it has been said that abnormal phenomena do not occur in nature. Some of the most treasured generalizations in science have been won by investigating the abnormal. This applies both in the laboratory and in the study.

Abnormal vapour densities.—According to Avogadro's hypothesis, if the relative density of hydrogen be taken as unity, the quotient $M/D=2$, where M denoted the molecular weight, and D the relative density of the gas. Some puzzling exceptions to this rule were encountered during the early application of the hypothesis, for several substances do not conform to the ratio when molecular weights deduced by the ordinary chemical methods are employed, and, in consequence, these substances were said to possess abnormal vapour densities. This led chemists to look upon Avogadro's rule with suspicion, and there were some controversies as to whether (i) substances with abnormal vapour densities really follow Avogadro's rule;

or whether (ii) substances with an abnormally low vapour density are dissociated into simpler molecules, and substances with an abnormally high vapour density are associated into more complex molecules. J. B. A. Dumas (1836)[1] thought that the abnormal vapour densities invalidated the hypothesis, while M. A. Gaudin (1833) considered that the alleged failure was due to a peculiarity in the molecules of the gas, which, when taken into account, left the hypothesis quite valid. Independent proofs of the validity of M. A. Gaudin's inference are discussed later on when the particular substances are treated. As soon as M. A. Gaudin's interpretation had been demonstrated experimentally, Avogadro's hypothesis won its way into the heart of chemical science.

There are two possible deviations with compounds; the ratio

$$\frac{\text{Molecular weight}}{\text{Density}} \text{ may be greater or less than 2}$$

when the density of hydrogen is taken unity. In the case of elementary gases, S. Cannizzaro (1858) showed that the atomic weight A is equal to half the vapour density of the gas, if hydrogen 2 be the unit, or to the vapour density itself, $A/D=1$, if hydrogen be unity. Here, again, there are two possible deviations:

$$\frac{\text{Atomic weight}}{\text{Density}} \text{ may be greater or less than unity}$$

when hydrogen unity is the standard of reference. The interpretation of the results in the two cases are similar.

The molecules of the substance are decomposed or dissociated; the molecules are actually less complex than corresponds with the simple chemical formulæ, and the ratio M/D is greater than 2, or the ratio A/D is greater than unity. For example, the vapour density of steam is 9 ($H=1$), the molecular weight 18, and the ratio $M/D=2$; at a very high temperature, there are reasons for supposing that the vapour density would be 6, and the ratio M/D would appear to be 3. This corresponds with the value of M/D on the assumption that the steam is dissociated into its elementary molecules: two volumes of hydrogen, and one volume of oxygen, so that the density of a mixture is involved and not that of a homogeneous substance as is required if Avogadro's rule is to be applied. The density of such a mixture will be $(2+16)\div3=6$; the assumed dissociation thus gives a number in agreement with observation. If the observed density were 8, this would represent a mixture with $33\frac{1}{3}$ per cent. of dissociated, and $66\frac{2}{3}$ per cent. of undissociated steam. The cases with phosphorus pentachloride, PCl_5; ammonium chloride, NH_4Cl; sulphuric acid, H_2SO_4; mercurous chloride, $HgCl$; nitrogen peroxide, N_2O_4; and hydrogen iodide, HI, are discussed later. With elementary gases, J. B. A. Dumas (1832) found that mercury vapour has a density of 100 corresponding with an atomic weight of 100, but the atomic weight deduced by chemical methods is 200, consequently $A/D=2$ instead of 1. It is therefore assumed that the molecule of mercury vapour is monatomic and $M/D=2$, while $A/D=1$. The cases with iodine, the metal vapours, etc., are discussed later.

The molecules of the substance are associated or condensed; the molecules are more complex than corresponds with the simple chemical formulæ; and the ratio M/D is less than 2, or the ratio A/D less than unity. The molecular weight of acetylene, C_2H_2, is 26, the vapour density is 13, and the ratio M/D is normal. Benzene has exactly the same chemical composition, and its vapour density is 39 (H unity); if the molecular weights of the two gases be the same, the ratio M/D for benzene would be 0·67, but if benzene be more complex than acetylene, say $(C_2H_2)_3$ or C_6H_6, the molecular weight of the complex molecule will be 78, and the ratio M/D becomes normal. Hence, for this and other reasons, benzene is regarded as if it were a product formed by the condensation of three molecules of acetylene. Phosphorus trioxide and pentoxide, and other examples, are discussed later. With elemental gases, J. B. A. Dumas (1832) found that the density of phosphorus vapour is 62·8, and the atomic weight deduced by chemical methods, by analogy with nitrogen, is 31·4, so that the ratio A/D is one-half. This is taken to mean that the molecular weight of phosphorus is not that equivalent to P_2, but is rather equivalent to P_4. Sulphur and arsenic are discussed later.

The effect of changes in the molecular weight of a gas on the laws of Boyle and Charles.—The gas equation,

$$\frac{pv}{T}=\frac{p_1v_1}{T_1}$$

must now be revised in order to allow for changes in the molecular weight of the gas when it changes from one state to another. Remembering that the density D of a gas is equal to the molecular weight M divided by the volume v, or $M=Dv$, the gas equation can be written,

$$\frac{p}{TD}=\frac{p_1}{T_1D_1}$$

provided $M=M_1$. Let M, D, and v respectively denote the molecular weight, density, and volume of the gas by one condition of temperature and pressure; and M_1, D_1, and v_1, the same constants for another condition of temperature and pressure, then, by substitution in a preceding equation, $pv/MT=p_1v_1/M_1T_1$. If the volume v_1 at some standard temperature T_1 and pressure p_1 be taken, the numbers p_1, v_1, and T_1 will always have one fixed value. Let R denote this constant value of p_1v_1/T_1. The gas equation then assumes one of the forms :

$$\frac{pv}{MT}=\frac{p_1v_1}{M_1T_1}\text{; or, }pv=\frac{M}{M_1}RT\text{; or, }pv=iRT$$

where i stands in place of the ratio of the molecular weights of the gas in the two conditions, M/M_1. If the molecules of the gas neither dissociate nor polymerize when the conditions change, $M=M_1$; or $pv=RT$ because $i=1$. Again, if the gas molecules polymerize or condense so that, say, two molecules combine together to form one molecule, there will be only half as many molecules in a given space as before : $M=\frac{1}{2}M_1$, and $pv=\frac{1}{2}RT$. If, however, the gas dissociates or decomposes so that each molecule of the gas forms two molecules of another gas or gases, then $M=2M_1$, and $pv=2RT$. Hence, **the ordinary gas equation, $pv=RT$, is a special case of the more general relation, $pv=iRT$, where the numerical value of i indicates whether or not the gas keeps the same molecular concentration during the change. If $i=1$, there is neither dissociation nor polymerization ; if i be less than unity, the gas polymerizes ; and if i be greater than unity, the gas dissociates when the conditions are changed.**

The effect of deviations from Avogadro's hypothesis on Gay Lussac's law of volumes.—The molecular volumes of many gases are not all the same, and they thus exhibit small deviations from the law $M/D=2$ (hydrogen unity). This is shown for a few gases at 0° and 760 mm. in the following table :

TABLE IV.—A COMPARISON OF THE MOLECULAR VOLUMES OF SOME GASES.

Gases.	Molecular weight M.	Observed density (O=16).	Molecular volumes M/D.
Oxygen, O_2	32	16	2·000
Nitrogen, N_2	28·02	14·00	2·001
Carbon monoxide, CO	28·00	14·01	2·000
Carbon dioxide, CO_2	44·00	22·15	1·988
Methane, CH_4	16·03	8·03	1·998
Ethane, C_2H_6	30·05	15·20	1·980
Ethylene, C_2H_4	28·03	14·28	1·966
Acetylene, C_2H_2	26·02	13·12	1·984

In calculations involving gaseous volumes, the errors due to the deviations of the molecular volumes from the theoretical may be greater than the experimental errors. Instead of writing the reaction, $2CO+O_2=2CO_2$, in the form, 2 Vols. CO+1 Vol. O_2=2 Vols. CO_2: it becomes necessary to write $2\times0{\cdot}994=1{\cdot}988$ volumes of carbon dioxide, and the equation becomes 2 Vols. CO+1 Vol. O_2=1·988 Vols. CO_2. Similarly, with equations involving other discrepant gases. If the partial pressure of the deviating gas be less about 25 per cent., the discrepancy may be disregarded since **the lower the partial pressure of the gas, the more nearly does it behave like an ideal gas.** Thus, the lower the pressure confining carbon dioxide, CO_2, at 20°, and of ethane, C_2H_6, at 0°, the more nearly do the molecular volumes approach the value 2 for ideal gases.

Pressure	100	300	500	600	700	760 mm.
Carbon dioxide	1·998	1·996	1·994	1·992	1·990	1·988
Ethane	1·998	1·992	1·988	1·984	1·982	1·980

Correction of the ratio M/D for gases which deviate from Boyle's law.—It follows from Avogadro's hypothesis: (i) The molecular volumes—*i.e.* the quotients of the molecular weights M by the respective densities D—of all gases are the same, so that $M_1:D_1=M_2:D_2$, and (ii) the molecular weights of all gases are proportional to their densities, so that $M_1:M_2=D_1:D_2$. These deductions can be true only for gases in which the pressure is not affected by intermolecular attractions as is the case with gases which follow the simple gas laws. Densities calculated for gases which do not conform with Boyle's law do not agree satisfactorily with observations unless the gases are attenuated or rarefied, thus showing that Avogadro's hypothesis is not strictly accurate with gases under normal pressure. Similarly, the experiments of H. V. Regnault [2] (1847) and others have shown that Boyle's and Charles' laws approach exactitude only when the pressures are very small. Gases approach the so-called ideal state when their pressures are reduced; and, at the limit, when the pressures are indefinitely small, Avogadro's hypothesis is strictly valid. Otherwise expressed, **the molecular volumes of all gases are exactly the same only when the gases are extremely rarefied**; and the limiting value of the ratio of the densities D_1 and D_2 of two gases will be equal to the ratio of their molecular weights M_1 and M_2 only when the pressures of the respective gases approach zero. The deviation of a gas from Boyle's relation $p_0v_0/pv=1$, or $1-p_0v_0/pv=0$, can be symbolized:

$$A=1-\frac{p_0v_0}{pv} \qquad (1)$$

where p_0 and v_0 respectively denote the atmospheric pressure and volume of the gas at 0°; and p and v the corresponding values at some small pressure. For the so-called permanent gases, Regnault's experiments show that the coefficient A is very nearly constant between one and six atmospheres pressure. Consider two gases under a very small pressure p; let each be subjected to atmospheric pressure p_0 when the volumes become respectively v_1 and v_2; then, $v_1=vp(1-A_1)/p_0$; and $v_2=vp(1-A_2)/p_0$; and by division,

$$\frac{v_1}{v_2}=\frac{1-A_1}{1-A_2} \qquad (2)$$

This means that the molecular volumes of the two gases under atmospheric pressures have the proportional values $1-A_1$ and $1-A_2$. Let D_1 and D_2 denote the respective densities of the gases under atmospheric pressures—temperature constant—then, the ratio of the molecular weights $M_1:M_2$ is equal to the ratio of the products of their molecular volumes by the corresponding densities; that is, to the ratio $D_1(1-A_1):D_2(1-A_2)$; or,

$$\frac{M_1}{M_2}=\frac{D_1(1-A_1)}{D_2(1-A_2)} \qquad (3)$$

If A for the two gases be zero the expression reduces to that required by Avogadro's rule. The densities employed in calculations with formula (3) are the weights in grams of a normal litre of the respective gases; the evaluation of the coefficients A is a problem for the physicists. A number of values have been determined, but the task is a difficult one, and is subject to some uncertainty since it involves an extrapolation of the pv and p-curve. The following values for A_0^1 between atmospheric and zero pressures are compiled from data by A. Leduc (1898), R. W. Gray and F. P. Burt (1909), and A. Jaquerod and O. Scheuer (1908)[3]:

TABLE V.—NUMERICAL VALUES OF THE COEFFICENT A.

Gas.	A_0^1	Gas.	A_0^1
Hydrogen	$-0·00056$.	Nitrous oxide . . .	$+0·00750$
Oxygen	$+0·00096$	Hydrogen chloride . .	$+0·00786$
Nitrogen	$+0·00044$	Sulphur dioxide . .	$+0·02314$
Carbon monoxide . .	$+0·00060$	Methane	$+0·00175$
Nitric oxide	$+0·00114$	Ethane	$+0·01194$
Carbon dioxide	$+0·00678$	Methyl chloride . .	$+0·02468$
Ammonia	$+0·01504$	Ether	$+0·02587$

If oxygen be the standard gas with $M_2=32$, $D_2=1·4290$, and $A_2=0·00096$, it follows that if the numerical values of the density D and the deviation a be known, the

$$\text{Molecular weight}=22·5739D(1-A)$$

The results computed by this method are in fair agreement with the values obtained by chemical processes. For example, with oxygen, 32, as standard

	Hydrogen.	Nitrogen.	Carbon monoxide.	Nitric oxide.	Methane.
M (Chemical) . .	2·015	28·019	28·009	30·006	16·039
M (Physical) . .	2·016	28·020	28·000	30·010	16·032

These results are in close agreement. This physical method thus rivals in accuracy the molecular weights of the permanent gases determined by chemical processes. There are not so many complications with physical methods as are involved in conducting a series of chemical operations with pure substances. This physical method is known as **D. Berthelot's limiting density method of determining molecular weights.**[4] The data required for the application of Berthelot's method are (i) the densities, and (ii) the compressibility of the gas under investigation; and also (iii) the compressibility of the standard gas.

With the more easily liquefiable gases, the coefficient A changes rapidly with changes of pressure, and consequently A cannot be assumed constant without sensible error. It is therefore necessary to use values for the coefficients A determined for the variations of pressure near to those under which the density has to be determined. The available data are not sufficiently exact to enable the method to be used for accurate molecular weights of such gases, the coefficients A are usually too high, and the molecular weights correspondingly low. For instance:

	Carbon dioxide.	Nitrous oxide.	Ethylene.	Ammonia.	Sulphur dioxide.
M (Chemical .	44·000	44·020	30·048	30·034	64·070
M (Physical) .	44·013	44·003	30·037	30·018	64·063

where the comparison is not so favourable.

According to D. Berthelot,[4] the molecular weight M of a normal liquid is related with its critical density D_c, critical pressure p_c, and critical temperature T_c by the formula

$$M=22·4\frac{D_c}{3·6}\cdot\frac{T_c}{273}\cdot\frac{1}{p_c}$$

where 3·6 represents the mean value of the actual to the theoretical density at the critical temperature for normal or non-associated liquids. E. Mathias has also shown that in accord with the law of rectilinear diameters, the critical density of a substance is related to the densities of the liquid D_l and of the saturated vapour D_v at a temperature T by the expression

$$D_c = \frac{D_l - D_v}{2\left(2 - \frac{T}{T_c}\right)}\text{; or, } D_c = \frac{D_l}{2\left(2 - \frac{T}{T_c}\right)}$$

when the temperature does not exceed the boiling point of the liquid under atmospheric pressure. Consequently, by substitution of the second of these equations in that of Berthelot,[5]

$$\text{Molecular weight} = 11{\cdot}4\,\frac{D_l T_c}{p_c\left(2 - \frac{T}{T_c}\right)}$$

The molecular weights of substances which are liquid at ordinary temperatures, calculated by this expression, are often a little too high. For example—

	Cy_2	SO_2	CCl_4	CS_2	NH_3	H_2O	$SnCl_4$
Calculated . .	50	65·1	152·3	73·4	19·2	25·1	252·4
Formula weight . .	52	64	153·8	76	17	18	260

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§ 9. Radicals or Radicles

For the chemist, each molecular compound is proximately made up of less compound atoms which are indivisible by forces which can divide their product, and these in turn can be separated by chemical agents into simple atoms.—S. Brown.

In 1815, J. L. Gay Lussac,[1] after studying the properties of hydrocyanic acid, reported cyanogen $(CN)_2$, to be "a remarkable example, and at present, a unique example, of a body which, although a compound, plays the part of a single body in its combinations with hydrogen and the metals." Indeed, if chemists did not know how to resolve cyanogen into its constituent elements, this compound would very probably be classed as an element, and further, it would probably be assigned a place in the halogen family of elements to be studied later. Since Gay Lussac's discovery a great number of similar groups of what might be called *pseudo-elements* have been found. For convenience, they are commonly called *radicals* or, following the custom of the London Chemical Society, *radicles*. There have been periodic discussions on the spelling of the term—radicle or radical. The latter is taken to be historically correct, and the former etymologically correct.[2] The word *radical* was previously employed by G. de Morveau (1787) and by A. L. Lavoisier[3] with a different meaning, for with A. L. Lavoisier a radicle could be a simple or compound body; he says, *le carbone est le radical de l'acide carbonique*, and added that vegetable acids contain *le radical oxalique, tartarique*, etc. The definition: **a radicle is a group of atoms which can enter into and be expelled from combination without itself undergoing decomposition,** is virtually that given by J. von Liebig in 1838. Each radicle acts as an unchanging constant in a series of compounds; and each can be replaced by an equivalent element or elements. In very few cases has it been possible to isolate the radicle, but the definition has nothing to say about the independent existence of radicles. " Radicles," said A. Kekulé (1858), " are not firmly closed atomic groups, but they are merely aggregates of atoms placed near together which do not separate in certain reactions, but fall apart in other reactions." For convenience, the term radicle is sometimes applied to an atom in a compound which can be replaced by another atom or radicle without a further change in the nature of the compound; in that case, the radicle is said to be a *simple radicle*, in contrast with *compound radicles*, which are groups of atoms.

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§ 10. The Atomic Weights of the Elements

> Every chemical element is regarded as having a distinct and definite nature of its own, which nature, moreover, determines all its activities.—B. P. BROWNE.
>
> The ratio between the atomic weights of oxygen and hydrogen is the base-line upon which our entire system of atomic weights depends. —F. W. CLARKE (1896).

What are the best representative values for the atomic weights of the elements? —The best available determinations of the value of the oxygen-hydrogen ratio give numbers ranging between 1·005 and 1·008 when the standard reference is oxygen 16. **All measurements made by man are affected by unavoidable errors of experiment; and measurements of the numerical value of all constants differ within certain limits amongst themselves.** It is convenient to select one representative value from the set of different observations ranging between the limits 1·005 and 1·008. The majority of chemists have agreed to let the *International Committee of Atomic Weights* decide what are the best representative values for the atomic weights of all the elements year by year. Hence, the generally accepted ratio for the atomic weights of hydrogen and oxygen is **1·008 : 16.** Every time new and more refined methods of measurement are employed, a change—generally insignificantly small—may be necessary. It must be recognized that the **true atomic weights** cannot be altered by the votes of the majority of the members of the International Committee of Atomic Weights.[1] There is an uncertain factor in the accepted values of the atomic weights, as there is in all our judgments. Aristotle was no doubt right, " Nothing can be positively known, and even this cannot be positively asserted." This doctrine, however, if rigorously applied, would paralyze all action. Accordingly, sound-minded people are accustomed to balance the evidence and then act. A careful consideration of all the available evidence considerably reduces the risk of error, and this method adopted by the Committee appears to be the most satisfactory solution of the problem.

The atomic weights of the elements are indicated in the following table. The numbers are those recommended by the International Committee on Atomic

Weights (1920). The atomic number, indicated in the same Table, will be discussed later.

TABLE VI.—INTERNATIONAL ATOMIC WEIGHTS (1921). O=16.

	Atomic number.	Symbol.	Atomic weight.
Aluminium	13	Al	27·1
Antimony	51	Sb	120·2
Argon	18	A	39·9
Arsenic	33	As	74·96
Barium	56	Ba	137·37
Beryllium (Glucinum)	4	Be	9·1
Bismuth	83	Bi	208·0
Boron	5	B	10·9
Bromine	35	Br	79·92
Cadmium	48	Cd	112·40
Cæsium	55	Cs	132·81
Calcium	20	Ca	40·07
Carbon	6	C	12·005
Cerium	58	Ce	140·25
Chlorine	17	Cl	35·46
Chromium	24	Cr	52·0
Cobalt	27	Co	58·97
Columbium (Niobium)	41	Cb	93·1
Copper	29	Cu	63·57
Dysprosium	66	Dy	162·5
Erbium	68	Er	167·7
Europium	63	Eu	152·0
Fluorine	9	F	19·0
Gadolinium	64	Gd	157·3
Gallium	31	Ga	70·1
Germanium	32	Ge	72·5
Glucinum (Beryllium)	4	Gl	9·1
Gold	79	Au	197·2
Helium	2	He	4·00
Holmium	67	Ho	163·5
Hydrogen	0·95	H	1·008
Indium	49	In	114·8
Iodine	53	I	126·92
Iridium	77	Ir	193·1
Iron	26	Fe	55·84
Krypton	36	Kr	82·92
Lanthanum	57	La	139·0
Lead	82	Pb	207·20
Lithium	3	Li	6·94
Lutecium	71	Lu	175·0
Magnesium	12	Mg	24·32
Manganese	25	Mn	54·93
Mercury	80	Hg	200·6
Molybdenum	42	Mo	96·0
Neodymium	60	Nd	144·3
Neon	10	Ne	20·2
Nickel	28	Ni	58·68
Niobium (Columbium)	41	Nb	93·1
Niton (radium emanation)	86	Nt	222·4
Nitrogen	7	N	14·08
Osmium	76	Os	190·9
Oxygen	8	O	16·00
Palladium	46	Pd	106·7
Phosphorus	15	P	31·04
Platinum	78	Pt	195·2
Potassium	19	K	39·10
Praseodymium	59	Pr	140·9
Radium	88	Ra	226·0
Rhodium	45	Rh	102·9
Rubidium	37	Rb	85·45
Ruthenium	44	Ru	101·7
Samarium	62	Sa	150·4
Scandium	21	Sc	44·1
Selenium	34	Se	79·2
Silicon	14	Si	28·3
Silver	47	Ag	107·88
Sodium	11	Na	23·00
Strontium	38	Sr	87·63
Sulphur	16	S	32·06
Tantalum	73	Ta	181·5
Tellurium	52	Te	127·5
Terbium	65	Tb	159·2
Thallium	81	Tl	204·0
Thorium	90	Th	232·15
Thulium	69	Tm	168·5
Tin	50	Sn	118·7
Titanium	22	Ti	48·1
Tungsten	74	W	184·0
Uranium	92	U	238·2
Vanadium	23	V	51·0
Xenon	54	Xe	130·2
Ytterbium (Neoytterbium)	70	Yb	173·5
Yttrium	39	Yt	89·33
Zinc	30	Zn	65·37
Zirconium	40	Zr	90·6

For ordinary calculations involving the use of atomic weights, most of these constants, excepting chlorine (35·5), copper (63·5), and zinc (65·5), are rounded off to the nearest whole numbers. The elements just named are then assigned the constants indicated in the brackets. The atomic weight table made by J. J. Berzelius in 1826 has excited admiration on account of its accuracy. With the standard O=16, most of J. J. Berzelius' numbers are remarkably close to those we are using to-day. For instance, with the common elements :

	O.	H.	N.	Cl.	S.	P.	Pb.	Cu.
Berzelius' atomic weights	16	1	14·15	35·47	32·2	31·4	207·4	63·4
To-day's numbers	16	1·008	14	35·46	32·07	31·0	207·1	63·5

This is a testimony to the accuracy of J. J. Berzelius' work and particularly so when the state of the knowledge of analytical chemistry in Berzelius' time is borne in mind.

Are atomic weights whole numbers ?—It must be added that although we are compelled to take the numbers as we find them, yet, the experimental errors involved in a complex operation are great, and these errors are sometimes so obscured by a cloud of auxiliary calculations that they are not always easy to detect. Consequently, G. D. Hinrichs (1893) suggests that **the true atomic weight of an element must be regarded as a limit to which the observed values approach as the disturbing factors are eliminated.**[2] It required a century of measurements on the density of atmospheric nitrogen before the presence of 1 per cent. of argon was detected therein. Accordingly, many chemists firmly believe that the rounded numbers are the best representative values of the atomic weights, and that the small deviations from the rounded numbers indicated in the International Table represent real, if unrecognized, errors of experiment; M. Rudolphi (1901) also attributed the deviations of the atomic weights from whole numbers to the presence of small quantities of unknown elements whose properties are closely allied to the elements with which they are mixed.

Why is oxygen 16 taken as the standard in preference to hydrogen unity ?—During the latter part of the nineteenth century, J. Dalton's (1803) standard hydrogen unity, was used for the atomic weights instead of oxygen 16. Hydrogen was selected as a standard for gas densities and atomic weights because it is the lightest element known. In determining atomic weights, it will be observed that one of them, say A, is arbitrarily fixed as a standard, and the atomic weights of the other elements are fixed through the relations $B=k_1A$; $C=k_2B$; $D=k_3C$; . . . where k_1, k_2, k_3, . . . k_n are numerical ratios. Here, obviously, the numerical ratios referred to the element A as standard are :

$$\frac{B}{A}=k_1\,;\ \frac{C}{A}=k_1k_2\,;\ \ldots\ \frac{N}{A}=k_1k_2\ \ldots\ k_n$$

Hence, since each observed ratio k embodies unknown errors, the errors will accumulate most on that particular ratio which is least directly connected with the standard of reference, A. Consequently, J. S. Stas (1860–65) pointed out, as J. J. Berzelius (1818) did before him, that the determination of the atomic weight of an element should be connected with the standard as directly as possible. Very few compounds of the metals with hydrogen are suitable for an atomic weight determination, while nearly all the elements form stable compounds with oxygen. Hence, if hydrogen be the standard, it is necessary to find the exact relation between the given element and oxygen, and then calculate what that relation would be on the assumption that the relation between hydrogen and oxygen is known. C. W. Blomstrand expressed similar ideas in his *Die Chemie der Jetztzeit* (Heidelberg, 1869) ; he said the atomic weights of practically all the elements are compared with hydrogen through the intervention of oxygen. Hydrogen compounds—hydrides—are comparatively rare ; oxygen compounds—oxides—are common. Hence, the weight ratio between oxygen and hydrogen must be known with great accuracy since a small error becomes cumulative and it becomes serious in elements with a large atomic weight—*e.g.* with uranium, the experimental error is multiplied about 15 times. Every improved determination of the relation between hydrogen and oxygen would then be followed by an alteration in the weight of every other element whose value, with respect to hydrogen as a standard, has been determined by the indirect process just indicated, for as J. J. Berzelius said in 1816, oxygen is a kind of nucleus about which chemistry has grown. The determination of the exact relation between hydrogen and oxygen appears to be more difficult than many other determinations, and hence, the majority of chemists think it better to refer the atomic weights of the elements to oxygen 16 as the standard instead of making the atomic weights depend on the more or less uncertain relation H : O. Hydrogen is a theoretical standard, oxygen is the real basis. The standard oxygen 16 is quite arbitrary. G. D. Hinrichs (1893) proposed carbon (diamond)=12 as the standard of reference. T. Thomson (1825) used oxygen 1; W. H. Wollaston (1814), oxygen 10; J. S. Stas (1860–65), oxygen 16; and J. J. Berzelius (1830) oxygen 100 as standard. The latter number makes the atomic weights of many elements inconveniently large, and if the atomic weight of oxygen be any whole number less than 16, fractional atomic weights will be required. The use of the oxygen O=16 unit involved the least change in the number in vogue when hydrogen unity was the standard.

This question of a standard is not of mere academic interest, because, in buying and selling ores on the percentage amount of contained metal, a difference in the atomic weight selected may involve appreciable differences in the estimated value of the ore. For instance, if oxygen be taken 16, the corresponding atomic weight of antimony is 119·9, and of uranium 239·61; if hydrogen be taken as unity, these values become respectively 118·9 and 237·65—differences of one and two units.[3]

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§ 11. The Relation between the Molecular Weights and the Volumes of Gases

The theory of molecules is an ideal conception placed by the mind like another Atlas underneath a measureless world of facts to give them intelligible cohesion and hold them up to view.—S. BROWN.

The molecular weight of any gas is numerically equal to the weight of any volume of the gas when the weight of an equal volume of hydrogen under the same physical conditions of temperature and pressure is 2. Two grams of hydrogen, taken as the standard, occupy **22·3** to **22·4** litres at normal temperature—0°—and normal pressure—760 mm. of mercury. Hence, it follows directly from Avogadro's hypothesis that **the molecular weight of any gas, expressed in grams, occupies approximately 22·3 litres at 0° and 760 mm. pressure.** Consequently, to find the molecular weight of a gaseous substance, weigh 22·3 litres of the gas at a convenient temperature and pressure; calculate the corresponding volume at 0° and 760 mm. pressure, and calculate by proportion the weight of 22·3 litres.

EXAMPLE.—A litre of gas at 20° and 730 mm. weighs 1·764 grams, what is the molecular weight of the gas? By the method of calculation indicated in the next chapter, one litre of a gas at 20° and 730 mm. pressure contracts to 894·5 c.c. at 760 mm. and 0°. Hence, if 894·5 c.c. weigh 1·764 grams, 22·3 litres will weigh 43·97 grams. Hence the molecular weight of the gas is nearly 44.

It must here be mentioned that the number 22·3 is not quite right for all gases. Many gaseous molecules have a slight attraction for one another, so that the molecules are slightly more closely packed than is represented by Avogadro's hypothesis. The greater the intermolecular attraction, the greater the weight of 22·3 litres, and consequently, the less the volume of a molecular weight of the gas expressed in grams. Thus, experiment shows:

Hydrogen.	Oxygen.	Nitrogen.	Chlorine.	Hydrogen chloride.	Carbon dioxide.	Steam (0°, 760 mm.).	Mercury.
22·40	22·39	22·45	22·01	22·22	22·26	22·39	22·55

The deviation from 22·3 can be neglected in ordinary chemical calculations.

The molecular weight of a compound not only tells us a weight, but it also tells us that if the molecular weight be expressed in grams, the substance when gaseous will occupy 22·3 litres at 0° and 760 mm. Further, **the molecular weight of a gas, expressed in kilograms, occupies, approximately, 22·3 cubic metres at 0° and 760 mm. pressure.** By mere chance, the number of avoirdupois ounces in a kilogram is 35·26, which is very nearly the same as the number of cubic feet in a cubic metre (35·31)—J. W. Richards.[1] The difference is only one-seventh of 1 per cent. Hence, the **molecular weight of any gas, expressed in avoirdupois ounces, occupies, approximately, 22·3 cubic feet at 0° and 760 mm. pressure.** These factors are useful in calculations involving cubic feet, cubic metres, and litres.

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§ 12. Chemical Equations and Chemical Arithmetic

> In his calculations, the chemist relies on the supposed numerical relations of the invisible, intangible, immeasurable particles he calls atoms. These relations have been determined by others in whom he has confidence, and the accuracy of these relations has to be accepted on faith.—H. C. BOLTON.

The molecular weight of an element or compound is the sum of the atomic weight of each of the atoms of the constituent elements.—Let a molecule be composed of n_1 atoms of one element, n_2 atoms of another, n_3 atoms of a third, and so on; further, let A_1, A_2, A_3, . . . , denote the atomic weights of the respective elements, then the molecular weight of the compound will be $n_1A_1+n_2A_2+n_3A_3+$ . . . For example, with the approximate atomic weights, the molecular weight of hydrogen, H_2, is 2; of water, H_2O, 18; of sulphuric acid, H_2SO_4, 98; and of ferrous ammonium sulphate, $FeSO_4.(NH_4)_2SO_4.6H_2O$, 392—since the summation furnishes $56+32+4\times16+2(14+4)+32+4\times16+6(2+16)=392$.

The process or art of calculating the numerical relations of the elements and their compounds is sometimes called **stoichiometry**—from the Greek στοιχεῖα, a fundamental constituent; μετρέω, I measure. The term appears to have been devised by J. B. Richter, in his book, *Anfangsgrunde der Stöchyometrie oder Messkunst chymischer Elementes* (Breslau, 1792–3), or, *The rudiments of stoichiometry or the numerical relations of the chemical elements*, for that branch of chemistry which deals with the numerical proportions in which substances combine. To-day the term is sometimes extended to comprise molecular and atomic weight determinations and also the general measurable properties of solids, liquids, and gases; solutions and mixtures; etc.—witness, S. Young, *Stoichiometry* (London, 1908).

When the initial and final products of a chemical reaction as well as the composition and proportions of the molecules concerned in the reaction are known, the facts can usually be symbolized or abbreviated into a kind of shorthand expression which takes the form of a chemical equation. There are some limitations which will be described later.

The equation indicates the nature of the different substances concerned in the reaction; as well as the proportions of the different substances which occur in the initial and final products of the reaction.—For instance, when mercury is heated in air and mercuric oxide, HgO, is formed, the reaction can be represented in symbols: $2Hg+O_2=2HgO$. We here ignore the nitrogen of the air because, so far as we can tell, it plays no direct part in the chemical reaction. Similarly, when mercuric oxide is heated to a high temperature, it decomposes, forming metallic mercury and oxygen. In symbols, $2HgO=2Hg+O_2$. The symbol = or → is used instead of the words "produces" or "forms," and the symbol + is used for "together with" on the right side of the = sign, and for "reacts with" on the left side. The latter equation reads: "Two molecules of mercuric oxide, on decomposition, produce a molecule of oxygen and two molecules of monatomic mercury." The number and kind of the atoms of the two sides of the equation must always be the same (persistence of weight).

The equation indicates the proportions by weight of the substances concerned in the reaction.—The atomic weight of mercury is 200, and the atomic weight of oxygen is 16, hence, the molecular weight of mercuric oxide is 216, and of oxygen 32. The latter equation can therefore be read: "432 grams (ozs. or tons) of mercuric oxide in decomposing form 32 grams (ozs. or tons) of oxygen gas and 400 grams (ozs. or tons) of metallic mercury." Hence, the chemical equation can be employed in all kinds of arithmetical problems dealing with weights of substances formed or produced.

Examples.—(1) How much mercuric oxide is required to furnish 20 grams of oxygen gas? Write down the proper equation; write 432 below the mercuric oxide, and 32 below the oxygen. We are not concerned with the mercury in this problem. Since we read from the equation: 32 grams of oxygen are furnished by 432 grams of mercuric oxide, one gram of oxygen will be furnished by $432 \div 32 = 13{\cdot}5$ grams of mercuric oxide; and 20 grams of oxygen will come from $20 \times 13{\cdot}5 = 270$ grams of mercuric oxide.

(2) Show that $2\frac{2}{9}$ grams of oxygen and $27\frac{7}{9}$ grams of mercury can be obtained theoretically from 30 grams of mercuric oxide. Obviously, 432 grams of mercuric oxide will give 32 grams of oxygen, therefore 30 grams of mercuric oxide will give $2\frac{2}{9}$ grams of oxygen.

The equation indicates the proportion by volume of the gases concerned in the reaction.—We have seen in the preceding section that if we express

Molecular weight in	Volume at 0° and 760 mm. per molecular weight.
Grams	**22·3 litres**
Kilograms	**22·3 cubic metres**
Ozs. (avoir.)	**22·3 cubic feet**

Consequently, the idea conveyed by the equation, $2HgO=O_2+2Hg$, can be expressed in these words: "432 grams (kilograms or ozs.) of mercuric oxide will furnish 32 grams (kilograms or ozs.) of oxygen, or 22·3 litres (cub. metres or cub. ft.) of oxygen gas at 0° and 760 mm. and 400 grams of mercury."

Examples.—(1) What volume of oxygen will be obtained by heating 30 grams of mercuric oxide? 432 grams of mercuric oxide will furnish $30 \times 22{\cdot}3 \div 432 = 1{\cdot}55$ litres of oxygen gas at 0° and 760 mm. pressure.

(2) How much mercuric oxide will be needed for 10 cub. ft. of oxygen gas at 0° and 760 mm. pressure? Here 22·3 cub. ft. of the gas come from 432 ozs. of mercuric oxide, hence, $432 \times 10 \div 22{\cdot}3 = 193$ ozs., or 12 lbs. 1 oz. of mercuric oxide are required.

It will be observed that in these examples it has been assumed that the reactions go to an end. This is an idealized imaginary condition which rarely obtains in practice where other factors—temperature, concentration, unequal mixing, etc.—introduce disturbances. In practice, there are nearly always some losses, and the actual yield is x per cent. of that theoretically possible on the assumption that the idealized equation is the limit or goal of perfection. In order to make sure that a reaction will proceed to an end, y per cent. excess of the initial products may be required. Each reaction, in this respect, has its own specific character. For example, the formation of nitric acid, HNO_3, by heating sulphuric acid, H_2SO_4, with sodium nitrate, $NaNO_3$, is represented by the equation: $2NaNO_3+H_2SO_4=2HNO_3+Na_2SO_4$, where 170 parts of sodium nitrate apparently require 98 parts of sulphuric acid to produce 126 parts of nitric acid. The manufacturer, however, has found by a process of trial and failure that under his conditions, an excess of about 80 more parts of sulphuric acid are needed to convert the 170 parts of sodium nitrate into nitric acid. The equation would then be more correctly written: $2NaNO_3+1·817H_2SO_4=2HNO_3+Na_2SO_4+0·817H_2SO_4$, where the excess $0·817H_2SO_4$ on both sides of the equation does not cancel out when the reaction is applied under industrial conditions. This, however, makes no difference to the general principles of chemical arithmetic here discussed. If the limitations of the stoichiometrical rules be not appreciated by the industrial chemist, his work will be considerably hampered. In general, the rigid application of fixed (scientific) principles, without a due appreciation of their limitations, is disastrous in the application of scientific methods in industrial work where success is estimated, not by the profoundness of a theory, but by the results achieved, or dividends secured.

§ 13. The Relation between Atomic and Combining Weights—Valency

Die Valenz nur ein Ausdruck des Gesetzes der multiplen Proportionen ist.—C. W. Blomstrand (1869).

Each atom carries into its combinations two things: first, its own proper energy; and second, the faculty of expending this energy in its own way, in attaching other atoms to itself, not indiscriminately, but definite atoms and in definite numbers.—C. A. Wurtz (1869).

Observation shows that the relative combining weights of oxygen and hydrogen are very nearly as O : H=8 : 1; and that the atomic weights of oxygen and hydrogen, deduced from the atomic theory and Avogadro's hypothesis, are very nearly as O : H=16 : 1. In fine, the atomic weight of oxygen is twice its combining weight. For carbon in carbon dioxide, the combining weight is 3, while the atomic weight of carbon is 12, that is, the atomic weight of carbon is four times the combining weight. In the case of hydrogen and chlorine, the atomic and combining weights are the same. In A. W. Hofmann's *Introduction to Modern Chemistry* (London, 1865), it is emphasized that the *atomic weight* of an element represents the minimum quantity of an element which can take part in forming a molecule of a compound; the equivalent, or combining weight of an element, represents the minimum quantity of an element which is required to fix one atom of hydrogen taken as a standard; and the *valency* or *valence* (*valens*, worth), or the atom-fixing power of an element, represents the number of times the combining or equivalent weight is contained in the atomic weight. In illustration,

	Hydrogen.	Chlorine.	Oxygen.	Nitrogen.	Carbon.
Atomic weight .	1	35·5	16	14	12
Combining weight .	1	35·5	8	4·67	3
Valency . . .	1	1	2	3	4

Consequently, as a first approximation,

$$\frac{\text{Atomic weight}}{\text{Combining weight}}=\text{Valency.}$$

Elements, however, may have more than one equivalent or combining weight, and since the atomic weight remains constant, an element may have more than one valency. Consequently, an atom not only has the power of fixing an atom of another element, but, under definite conditions, it has a definite number of such powers.

Although valency is primarily a number or a numerical ratio, the term is also used to express a general characteristic of the elements. **The valency of an element (or radicle) represents the general property of an atom (or radicle) to combine with a certain definite number of other atoms (or radicles).** In order to avoid confusing valency a number with valency a property, some restrict the use of the term so that *valency is reserved for the property, and valence for the number*; thus, mercury is an element with a valency of one or two, and in mercuric chloride, $HgCl_2$, mercury has a valence of 2, and in mercurous chloride, HgCl, a valence of one. This suggestion is good when there is any risk of confusion.

The meaning of valency can be represented another way. Numerous observations indicate that there is generally a limit to the number of atoms which can unite with a given atom, so that the atoms of an element appear to differ from one another with respect to the number of other atoms with which they habitually combine; valency may then be regarded as representing a *habit* of an element for combination; it has nothing to do with the force holding the atoms together. The valence of an element is obtained by finding—directly or indirectly—how many atoms of hydrogen can combine with or be replaced by an atom of the given element. The valence of hydrogen is always taken as unity. Hence the definition: **The valence of an element is a number which expresses how many atoms of hydrogen, or of other atoms equivalent to hydrogen, can unite with one atom of the element in question.** Strictly speaking, *valency is only applicable to those gases and liquids whose molecular weights have been determined;* and it is extended to solids by analogy with gases. We do not know the molecular weights of solids, and we therefore do not know if the valency concept can be extended to solids; it may possibly require modification.

Chemical affinity and valency are both peculiar but essentially different properties of the atom, and they must not be confounded. The terms, however, are sometimes used synonymously, since valency could not be manifested between two elements which have no affinity for one another. **Affinity refers to the act of chemical combination; valency governs the form of chemical combination.** The intensity of the chemical energy displayed by hydrogen, oxygen, nitrogen, and carbon, in the act of combining with chlorine, is very different—chlorine unites with hydrogen with great avidity; with carbon the action is so sluggish that it requires a powerful stimulant: while, the union of chlorine with oxygen and nitrogen is so difficult that it can only be effected indirectly, not directly. On the other hand, however vigorous the act of combination, the hydrogen atom is so constituted that it can unite with only one atom of chlorine, while carbon can unite with four, nitrogen with three, and oxygen with two. If the energy of the combination of chlorine with these four elements be represented by the amount of heat, evolved (+) or absorbed (—) during the combination, the chemical affinity is approximately:

	HCl.	OCl_2.	NCl_3.	CCl_4.
Chemical affinity .	+22·0	−8·9	−12·8	+5·2 units
Valency . .	1	2	2	4
	Stable.	Unstable.	Very unstable.	Stable.

A. S. Couper (1858), one of the pioneers in clarifying our ideas about valency, distinguished the two concepts by calling the former *affinity of kind*, and the latter *affinity of degree*. Affinity of kind, said he, is the specific affinities manifested by the elements the one for the other; affinity of degree is the grades or limits of combination which the elements display.

According to the law of multiple proportions, the states of saturation of the elements change *per saltum;* so also according to the doctrine of valency the affinities of the elements are exhausted by stages. The two conceptions are not identical. According to the latter, each element has a capacity for saturation which is definite for a given combination, but which varies from element to element. In 1858, S. Cannizzaro explained the difference by comparing the two series of chlorides: $HgCl$ and $HgCl_2$; $CuCl$ and $CuCl_2$; etc., and he added that the law of multiple proportions asserts that the quantities of an element contained in different molecules must be whole multiples of one and the same quantity; but this law cannot foresee that one atom of the element is equivalent in one case to one atom of hydrogen and in the second case to two atoms of hydrogen.

Nomenclature.—With hydrogen and chlorine, the atomic and combining weights are the same, and the valency is unity. These elements are accordingly said to be univalent, or monads; for similar reasons, oxygen is bivalent, or a dyad; nitrogen is tervalent, or a triad; carbon is quadrivalent, or a tetrad; and so on to octovalent elements or octads. The valency of an element is frequently represented by attaching the necessary numbers, in dashes or Roman numerals, to the top right-hand corner of the symbol for the element, as suggested by W. Odling in 1855. Thus, the symbols H^{I} and Cl^{I} respectively mean that hydrogen and chlorine are univalent; O^{II} means that oxygen is bivalent; N^{III} means that nitrogen is tervalent; and C^{IV} that carbon is quadrivalent. By collecting together a few compounds with their symbols the idea can be made clearer.

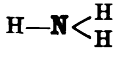
Univalent.	Bivalent.	Tervalent.	Quadrivalent.	Quinquevalent.	Sexivalent.
$H^{I}Cl^{I}$	$Ba^{II}O^{II}$	$H_3{}^{I}N^{III}$	$H_4{}^{I}C^{IV}$	$P^{V}F_5{}^{I}$	$S^{VI}F_6{}^{I}$
$Na^{I}Cl^{I}$	$Mo^{II}Cl_2{}^{I}$	$Fe^{III}Cl_3{}^{I}$	$C^{IV}Cl_4{}^{I}$	$W^{V}Br_5{}^{I}$	$U^{VI}F_6{}^{I}$
$K^{I}I^{I}$	$Zn^{II}Cl_2{}^{I}$	$Mo^{III}Cl_3{}^{I}$	$Mo^{IV}Cl_4{}^{I}$	$Mo^{V}Cl_5{}^{I}$	$Mo^{VI}F_6{}^{I}$

Some heptads and octads are known. Hence, the valency of all known atoms can be represented by an integer ranging from 0, 1, 2, . . . to 8. The elements generally combine in such a way that an equal number of valencies are opposed to one another.

No chemical compound is known to be formed by the union of the elements of the argon family, the so-called inert or noble gases. So far as our knowledge goes, these gases have therefore a **zero-valency**, and the elements appear to be **non-valent.** Any element existing free in a monatomic condition is non-valent in the sense that its atoms are not united with others by means of valency bonds; but the two cases differ in that the maximum valency of the latter is n units, while that of the inert gases is zero.

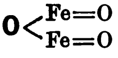
A few examples of radicles of different valency may be quoted: *Monad radicles*—OH, CN (generally written "Cy"), NO_3, NH_4 (sometimes written "Am"), COOH, etc. *Dyad radicles*—SO_4, SO_3, CO_3, SiO_3, etc. *Triad radicles*—PO_4, $FeCy_6$, etc. *Tetrad radicles*—$FeCy_6$, SiO_4, etc. There are some important hydrocarbon radicles—CH_3, called *methyl*; C_2H_5, *ethyl*; C_3H_7, *propyl;* C_4H_9, *butyl;* C_5H_{11}, *amyl;* etc. The members of the group of hydrocarbon radicles with the general formula C_nH_{2n+1}, are called the *alkyl radicles.* The members of the group, C_nH_{n-1} radicles—C_6H_5, *phenyl;* $C_6H_4.CH_2$, *benzyl,* etc.—are called the *aryl radicles.* There are also many other uni- and poly-valent hydrocarbon radicles.

Structural, graphic, or constitutional formulæ.—The valency of an element is sometimes represented by attaching the necessary number of hyphens to the symbol for the element. This enables the molecules of a substance to be represented by a kind of graphic formula. The symbol for hydrogen will have one hyphen; oxygen, two; nitrogen, three; carbon, four; etc.; a bivalent oxygen atom may be represented O^{II}, $-O-$, $O=$, $O<$, etc. The hyphens are usually attached so that the graphic formula occupies as little space as possible; they are drawn in the most convenient direction. The atoms of a molecule are then supposed to be joined together by their valencies; and this is represented diagrammatically by hyphens. The symbol for hydrogen chloride then becomes $H-Cl$; potassium iodide, $K-I$; water, $H-O-H$; mercuric oxide, $Hg=O$; a molecule of hydrogen, $H-H$; a molecule of oxygen, $O=O$; carbon dioxide, $O=C=O$; and



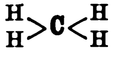
$$H-N{<}^{H}_{H}$$

Ammonia.



$$O{<}^{Fe=O}_{Fe=O}$$

Ferric oxide.



$$^{H}_{H}{>}C{<}^{H}_{H}$$

Methane.

Accordingly, the terms *bonds* or *links* are sometimes employed as well as *valencies.*

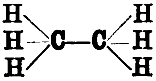
Graphic formulæ are also called structural or constitutional formulæ. *Structural formulæ primarily assume that the chemical properties of a substance are determined by the arrangement of the atoms in the molecules; and if the molecules of two compounds of the same chemical composition have their atoms differently arranged, the properties of the two compounds will be different.* Graphic formulæ are sometimes very convenient for representing the composition of compounds, but the student would err rather seriously if he supposed that the symbol given above for, say, methane represents the way the atoms are actually grouped in the molecule of methane. This would involve a leap far beyond our real knowledge, although the available evidence is in favour of the view that the atoms have a definite arrangement in the molecule, and, in some cases, the little knowledge we do possess can be better summarized by a graphic formula than in any other way. The graphic formula furnishes a clearer mental image of the curious way certain groups of atoms remain clustered together through a complex series of chemical changes than if the reaction were represented by ordinary symbols. The structural formula has a real and important signification ; it should symbolize the chemical character of the molecule. A graphic formula is thus a kind of dummy model illustrating the way a compound is formed, how it decomposes, and the relations between one compound and another. Indeed, chemists now investigate the position of a particular atom in a chain or ring of atoms, and find it to be at the side, in the middle, or in some other position relative to the remaining atoms. Without accepting C. F. Gerhardt's contention (1856) that *les formules chimiques ne sont pas destinées à représenter l'arrangement des atomes*,[1] it must not be believed for one moment that the model simulates reality since, for one thing, the formulæ are built on a plane two-dimensional surface, whereas the molecule probably extends into three dimensions ; again, graphic formulæ make the molecule appear as a fixed rigid structure, whereas there is some evidence indicating that the atoms within the molecule are in ceaseless rhythmic motion. The remarkable work which has been done by the aid of structural formulæ will always justify their use in the past and present, whatever future generations may think of them. The wonderful development of organic chemistry, said J. U. Nef (1904), is a consequence of the simple valency concept.

The doctrine of valency has furnished the chemist with a basis for calculation, and enabled him to deduce algebraically the existence of series of compounds previously unknown. It has been said that the theory of valency has enabled the chemist to predict reactions of unknown compounds with other known compounds, and enabled him to found a mechanics of the atoms which in another direction is as wonderful as the mechanics of the astronomer which has enabled him to fix the position and path of an invisible planet from its effect on the movements of one visible and known. Although the theoretical limitation seems valid in the majority of cases, yet there are several compounds whose existence appears contrary to the valency hypothesis—*e.g.* nitric oxide. However, where investigation is guided by a wrong theory, only those things which are sought are likely to be found, and the theoretical limitation may not have any real counterpart in nature. Hence, A. G. V. Harcourt [2] could say :

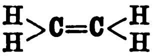
> A chemist who should depart from the general course, and set himself to prepare substances whose existence is not indicated by theory, would perhaps obtain results of more than usual interest.

Maximum and active valency.—Most elements have more than one valency. Stannous oxide has a composition corresponding with SnO ; and stannic oxide, with SnO_2. In the former case, the tin is said to be bivalent ; and in the latter, quadrivalent. There are thus two series of tin compounds—stannous and stannic. Similarly with copper, iron, etc. There are also two carbon oxides, carbon monoxide, CO, and carbon dioxide, CO_2. If carbon monoxide could be written $O{=}C{=}C{=}O$, and there is nothing in the analysis by weight which prevents this, all might be well ; but writing the formula in this manner would involve a contradiction of Avogadro's hypothesis, since the vapour density of carbon monoxide corresponds with the molecule CO, not C_2O_2. We cannot see the way clear to admit carbon monoxide as an exception to Avogadro's hypothesis, for that would introduce confusion into our system, and there would be no immediate prospect of restoring order. Some get over the difficulty by assuming that two of the free valencies in carbon monoxide mutually saturate one another, and write the graphic formula

$O{=}C\colon$; others assume that oxygen is quadrivalent, and write the graphic formula for carbon monoxide $C{\equiv}O$; and for carbon dioxide, $C{\lessdot}^{O}_{O}$, the two oxygen atoms are supposed to be doubly linked to one another and to the carbon atom. The question is therefore somewhat involved. The case of sulphur bivalent in hydrogen sulphide, $H{-}S{-}H$; quadrivalent in sulphur dioxide $O{=}S{=}O$; and sexivalent in sulphur trioxide $O_2{\equiv}S{=}O$, fits very well into this scheme. So do the series of compounds represented by ethane, C_2H_6 ; ethylene, C_2H_4 ; and acetylene. C_2H_2, which can be respectively represented by the graphic formulæ :



Ethane (with single bonds)



$$\begin{matrix}H\\H\end{matrix}{>}C{=}C{<}\begin{matrix}H\\H\end{matrix}$$

Ethylene (with double bonds)

$$H{-}C{\equiv}C{-}H$$

Acetylene (with triple bonds)

provided it be assumed that the respective carbon atoms are joined by single, double, and triple bonds. It may be added that the circumstantial evidence advanced by organic chemistry strongly favours this assumption.

Since chlorine or fluorine forms combinations with the metals far more generally than does hydrogen, it has been proposed to use chlorine or fluorine in place of hydrogen as the standard of valency. The hydrogen and fluorine valencies, however, are not always the same. For instance :

Hydrides . .	LiH	CaH_2	$(BH_3)_2$	CH_4	PH_3	SH_2	IH	—
Fluorides . .	LiF	CaF_2	BF_3	CF_4	PF_5	SF_6	IF	OsF_8

The maximum valency of the hydrides is thus attained with the tetrads ; but with fluorides, the maximum valency is reached with the octads. The preceding definition of valency is troublesome if applied to azomide, HN_3, although it works all right with ammonia, NH_3.

F. A. Kekulé (1866)[3] argued that valency is a fundamental property of the atom which is just as constant and invariable as the atomic weight ; the equivalent weight of an element may vary, the valency cannot. E. Frankland (1852) showed that the elements of the nitrogen family are sometimes ter- and sometimes quinquevalent. A controversy whether valency is fixed or variable was carried on about 1864 by F. A. Kekulé, C. A. Wurtz, A. Naquet, H. Kolbe, and A. W. Williamson. The controversy, after all, turned out to be nothing more than *ein Streit um ein Wort*. If valency means maximum saturation capacity, this property is unchangeable, but if valency means that this maximum power is always exerted, and that every atom exerts a constant invariable valency, the doctrine *est en désaccord flagrant avec les faits*. The discussion was then diverted to atomic and molecular compounds (*q.v.*). **Each element has a maximum valency towards certain other elements.** When an element appears to have a lower valency than its maximum valency, the compound is said to be an **unsaturated compound,** in contrast with a **saturated compound** in which the atoms are exercising their maximum valency. In many unsaturated compounds, the valencies appear to diminish in pairs. The pairs of *dormant* or *sleeping valencies*, *crypto-valencies* (κρυπτός, hidden), or *latent* or *passive valencies* are supposed to be self-saturated. Hence W. Odling (1855) proposed to call elements with an odd number of bonds *perissads* (περισσός, odd), and those with an even number of bonds *artiads* (ἄρτιος, even). It was also assumed that the sum of the valencies of the atoms forming a molecule is always an even number.

As a matter of fact, the hypothesis of the self-saturation of the bonds in pairs breaks down completely. The idea probably arose from the application of an inaccurate hypothesis—started in 1864 by E. Erlenmeyer[4]—which is stated in some of the older books on chemistry in words like these : " All chemical evidence shows that a body with unsatisfied bonds cannot exist by itself." All chemical evidence, as we shall see, shows nothing of the kind. Mercury and many other elements, when vaporized, give gases with one-atom molecules. The principle of self-saturation breaks down when applied to the nitrogen oxides, say nitric oxide, $N^{III}O^{II}$. The relative density (Avogadro's hypothesis) will not let us write N_2O_2, that is, $O{=}N{-}N{=}O$. We are therefore confronted with what appears to be an odd unsaturated valency in the molecule $-N{=}O$. Again, chlorine forms chlorine monoxide, Cl_2O, and chlorine peroxide, ClO_2; indium forms the three chlorides, InCl, $InCl_2$, $InCl_3$. The original form of the doctrine of valency is not tenable; elements cannot be classed as invariably uni-, bi-, ter-, quadri-, . . . valent, nor as artiads and perissads, since some elements can have any of these valencies according to circumstances. Chlorine, nitrogen, ruthenium, and manganese can be cited as examples; again, molybdenum forms a series of compounds with univalent chlorine or fluorine—$MoCl_2$, $MoCl_3$, $MoCl_4$, $MoCl_5$, and MoF_6; and vanadium forms VCl_2, VCl_3, VCl_4, and VCl_5. In view of facts like these, it is difficult to maintain the thesis that the apparent inconstancy of the valency of an element is due to the mutual saturation of pairs of valencies. Either a molecule can exist with free valencies, or Kekulé's maximum valency hypothesis breaks down when confronted with facts.

A great many ingenious hypotheses, more or less satisfactory, have been suggested to explain the difficulties. At present we are compelled to frankly admit with W. Lossen (1880) and A. Claus (1881) that **the active valency of an element is a variable habit of combination.** An explanation of the meaning of valency is thus left open. C. A. Wurtz (1864) distinguished between what he called *atomicité actuelle* and *atomicité virtuelle*, and in order to distinguish between the greatest valency an element is known to exhibit, and the valency which actually prevails in a particular compound, the terms **maximum or absolute valency** and **active or actual or free valency** may be respectively employed. So far as we can see, **the active valency of an element is dependent upon the properties of the atoms of the other elements with which it is combined as well as on the prevailing physical and chemical conditions to which the element is exposed.** Thus sulphur is bivalent towards hydrogen, but it can be sexivalent with fluorine; antimony, arsenic, and phosphorus are tervalent towards hydrogen, while phosphorus and antimony may be quinquevalent towards chlorine; arsenic is tervalent towards chlorine—and there is some doubt if the pentachloride, $AsCl_5$, has been made.

Werner's Nomenclature.—With a complex series of salts, instead of representing the number of times the acidic radicle is contained in the molecule—*e.g.* CuCl, copper monochloride; $CuCl_2$, copper dichloride; CuO, copper monoxide; $PtCl_4$, platinum tetrachloride, etc.—it is simpler, according to A. Werner.[5] to represent compounds with the same valency by names ending in the same suffix or letter. Thus, if M represents an atom of a basic element, and X an atom of acidic univalent element,

TABLE VII.—A. WERNER'S NOMENCLATURE OF SALTS.

Compound.	Valency.	Termination.	Examples.	
			Werner's name.	Old name.
MX	uni-	a	CuCl—cupr**a**chloride	copper monochloride
MX_2	bi-	o	$CuCl_2$—cupr**o**chloride	copper dichloride
MX_3	ter-	i	$MoCl_3$—molybden**i**chloride	molybdenum trichloride
MX_4	quadri-	e	$MoCl_4$—molybden**e**chloride	molybdenum tetrachloride
MX_5	quinque-	an	$MoCl_5$—molybd**an**chloride	molybdenum pentafluoride
MX_6	sexi-	on	MoF_6—molybd**on**fluoride	molybdenum hexafluoride
MX_7	septi-	in	Cl_2O_7—chlor**in**oxide	chlorine heptoxide
MX_8	octi-	en	OsO_4—osmium**en**oxide	osmium tetroxide

The suffixes have been chosen to make them differ as little as possible from those already in existence. The only serious objection appears to arise with salts like univalent and bivalent copper, mercury, etc., of the type $CuCl$, $CuCl_2$; and $HgCl$, $HgCl_2$, where cuprous becomes cupra-, and cupric, cupro-; and mercurous becomes mercura-, and mercuric, mercuro-.

The effect of external conditions on the valency of an element.—Active valency has been compared with friction in so far as it appears to be called into play by external causes which may vary from zero upwards, because the valency of an element is determined by the physical and chemical conditions under which the element is placed. For instance,

(1) *Temperature.*—The valency of an element generally diminishes with rise of temperature, *e.g.* sulphur trioxide, SO_3, when heated dissociates into sulphur dioxide, SO_2, and oxygen; and carbon dioxide, CO_2, into carbon monoxide, CO, and oxygen. Copper oxide, CuO, at 1110° becomes cuprous oxide, Cu_2O; and lead dioxide, PbO_2, at 615° yields lead monoxide, PbO.

(2) *Pressure.*—The valency of an element is often diminished with a decrease of pressure. Pressure usually facilitates chemical action. By heating bismuth with water at 280° under a pressure of 10,000 atm. the monoxide, BiO, is formed, but at higher temperatures and less pressure the sesquioxide, Bi_2O_3, is produced; similarly antimony is said to form the monoxide, SbO, and aluminium the monoxide, AlO, under conditions where the sesquioxides would normally be produced. Carbon monoxide, CO, under a pressure of 600 atm. at 320° is partially converted into the dioxide, CO_2, and free carbon.

(3) *Light or radiant energy.*—Numerous physical and chemical changes are induced by exposure to light, and the reactions may be accompanied by changes in the valency of some of the elements concerned. Thus, by exposure to light ferric oxalate, $Fe_2{}^{III}(C_2O_4)_3{}^{II}$, is reduced to ferrous oxalate, $Fe^{II}C_2O_4$—in symbols: $Fe_2(C_2O_4)_3=2FeC_2O_4+2CO_2$; and an aqueous solution of mercuric chloride, $HgCl_2$, is reduced to mercurous chloride, $HgCl$, under similar conditions: $4HgCl_2+2H_2O=4HCl+O_2+4HgCl$. Similar remarks, *mutatis mutandis,* apply to the effect of other forms of radiant energy.

(4) *Chemical reagents.*—Changes in the valency of an element are usually induced by oxidizing or reducing agents. Thus, ferrous chloride, $FeCl_2$, is oxidized to ferric chloride, $FeCl_3$, by the action of hypochlorous acid, $HClO$; the reaction is symbolized: $2Fe^{II}Cl_2+HCl+HClO=2Fe^{III}Cl_3+H_2O$; and ferric chloride is reduced to ferrous chloride by the action of sulphur dioxide, $2Fe^{III}Cl_3+SO_2+H_2O=2Fe^{II}Cl_2+2HCl+SO_3$. At the same time, it will be noticed, the sulphur dioxide, $O=S=O$, is oxidized to sulphur trioxide, $O=S\ll\begin{smallmatrix}O\\O\end{smallmatrix}$, where quadrivalent sulphur probably becomes sexivalent. Hence, **oxidation usually involves an increase in the valency of an element, and reduction a decrease.**

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§ 14. The Polarity of Valency

> The doctrine that the chemical forces by which the elements of bodies are held together or separated, are identical with the polar forces of electricity is now entirely established in the minds of the most profound and philosophical chemists of our time.—W. WHEWELL.

An agent exhibits polarity when it is characterized not only by a numerical value, but also by a sign indicating the direction in which it will act. For example, during the electrolysis of binary compounds some elements always accumulate at one particular electrode; the hydrogen, for instance, goes to the cathode, never to the anode; and conversely, the oxygen goes to the anode, not to the cathode. It is therefore assumed that hydrogen carries a positive electrical charge, oxygen a negative charge; otherwise expressed, oxygen has a negative polarity, hydrogen a positive polarity.

In 1881, in a paper *On the modern development of Faraday's conception of electricity*, H. von Helmholtz deduced from Faraday's work that during electrolysis the same quantity of either positive or negative electricity (96,540 coulombs) always accompanies each univalent atom, or each valency of a multivalent element, so that the same quantity of electricity passing through an electrolyte always sets free or transfers the same number of units of affinity (or valency) at each electrode. Otherwise expressed, an n-valent atom or radicle carries n unit charges of electricity. Electricity thus behaves as if it were divisible into definite elementary portions—positive or negative—which behave as if there were atoms of electricity. Following G. J. Stoney's proposal (1881), these unit or atomic changes of electricity are called *electrons*.[1] It may therefore be said that valency is a polar phenomenon, each valency being associated with a positive or negative electron. The valency of a univalent hydrogen atom carrying a positive charge can therefore be called a **positive valency,** and each valency of a bivalent oxygen atom carrying two negative charges a **negative valency.** Each positive valency can be represented by a + or · sign attached to the symbol of the element, say H^+ or $H^{\cdot}$; and, in a similar manner, each negative valency represented by a — or ′ sign, say O^{--} or O''. These symbols properly interpreted represent observed facts.

Again, during the electrolysis of certain compounds, some elements—arsenic, antimony, boron, bromine, carbon, iodine, nitrogen, phosphorus, selenium, silicon, sulphur, tellurium, etc.—act sometimes like hydrogen and sometimes like oxygen in that with some compounds a given element may accumulate at the positive pole and with other compounds at the negative pole. Otherwise expressed, the atoms of these elements sometimes carry positive and sometimes negative charges, so that in some compounds the atoms of these elements have positive valencies, and at other times negative valencies. R. Abegg (1904) called these elements with a dual nature *amphoteric elements* (ἀμφί, both). Hence, a description of the valency of an element in a particular compound should indicate whether the active valency is positive or negative. In further illustration, the sulphur in hydrogen sulphide, H_2S, has two negative valencies; and in sulphur trioxide, SO_3, the same element has six positive valencies, so that a change from sulphur with -2 valencies to sulphur with $+6$ valencies involves a change of eight units of electricity—the algebraic difference 8, not the numerical difference 4 units. Similarly, in methane, CH_4, the carbon atom has four negative valencies; in carbon tetrafluoride, CF_4, the carbon atom has four positive valencies; so that the passage from the former to the latter again involves a change of eight valency units. To avoid confusion with valency as a number, the term **polar number** has been employed to represent the algebraic number of negative charges which are lost, or positive charges gained by an atom of an element in the formation of a given compound. The valency and polar number of nitrogen in ammonia are 3 and -3 respectively; the valency of nitrogen in ammonium chloride is 5 and the polar number -3 (*i.e.* $-4+1$), as illustrated in the diagram, Fig. 4. In nitrous acid, HO.N : O, with oxygen negative, the polar number is $+3$, and the valency 3; whereas in $H-N\equiv O_2$, the polar number is still $+3$, but the valency is 5. In potassium permanganate, $KO.MnO_3$, the polar number of manganese is +7, and the valency 7.[2]

D. I. Mendeléeff (1871) assumed that the highest oxide (omitting the peroxide) gives the maximum valency of an element, and R. Abegg (1904) adopted practically the same suggestion for finding the maximum positive valency of an element; J. N. Friend (1908) suggested that the fluoride be employed for the same purpose. The hydrides usually give the numerical values of the negative valency of the non-metals. J. N. Friend (1908) has compiled the following Table VIII showing the positive and negative values of some amphoteric elements with respect to their hydrides and fluorides:

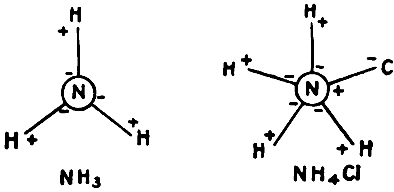

FIG. 2.—Polar Numbers of Nitrogen (−3).

TABLE VIII.—HYDRIDES AND FLUORIDES OF SOME AMPHOTERIC ELEMENTS.

Element.	Negative valency.		Positive valency.		Total valency.
	Hydride.	Active valency.	Fluoride.	Active valency.	
Antimony	SbH_3	3	SbF_5	5	8
Arsenic	AsH_3	3	AsF_5	5	8
Boron	BH_3	3	BF_3	3	6
Bromine	BrH	1	BrF_3	3	4
Carbon	CH_4	4	CF_4	4	8
Iodine	IH	1	IF_5	5	6
Nitrogen	NH_3	3	NOF	3	6
Phosphorus	PH_3	3	PF_5	5	8
Selenium	SeH_2	2	SeF_6	6	8
Silicon	SiH_4	4	SiF_4	4	8
Sulphur	SH_2	2	SF_6	6	8
Tellurium	TeH_2	2	TeF_6	6	8

It is interesting to note that the majority of the known amphoteric elements give 8 as the sum of the positive and negative valencies. R. Abegg (1904), indeed, assumed that all elements are amphoteric and possess 8 positive and negative valencies, but the observed facts with hydrogen, the alkali metals, and the inert gases do not favour this generalization. The positive valencies of the alkali metals appear to be so strong that they show little or no sign of their supposed negative valencies; and the negative valencies of fluorine are so strong that they show little or no sign of positive valencies. R. Abegg and G. Bodländer (1899) developed the hypothesis that elements have a different valency according as they are united with electropositive or electronegative elements; and that each element possesses the two kinds of valency—positive and negative. The usually accepted valencies of the non-metals are negative, and of the metals, positive; R. Abegg and G. Bodländer called these the **normal valencies** of the elements; and the secondary valencies of opposite polarity, active only under special conditions, were called **contra-valencies.** The normal valencies are supposed to be the stronger. The sum of the normal and contra-valencies, as indicated, is assumed to be 8, ranging over the different families of elements:

	Metals.			Non-metals.			
	Na	Mg	Al	Si	P	S	Cl
Normal valencies	+1	+2	+3	+4	−3	−2	−1
Contravalencies	−7	−6	−5	−4	+5	+6	+7
Polar number	−6	−4	−2	0	+2	+4	+6

Thus chlorine is univalent, polar number −1 in hydrogen chloride, HCl, where it is coupled with electropositive hydrogen; but it has its maximum heptavalency, polar number +7, when it is united with electronegative oxygen in chlorine heptoxide, Cl_2O_7. In particular cases, neither all the normal nor all the contra-valencies may be active. The contra-valencies in a particular family of elements increase in activity as the atomic weights of the elements increase; thus, in the halogen family, fluorine (atomic weight 19) does not form a compound with oxygen, while iodine (atomic weight 127) gives a stable oxide. All the normal valencies of an element are supposed to be equivalent, but if one be saturated, the remainder are weakened. Consequently, the active valency of an element depends upon the electrochemical character of the associated atoms—arsenic pentafluoride, AsF_5, for instance, is fairly stable (O. Ruff and H. Graf, 1906), while arsenic pentachloride, $AsCl_5$, is so very unstable that it is doubtful if it really has been prepared (C. Baskerville and H. H. Bennett, 1902). The formation of the so-called molecular compounds by the union of two or more molecules is attributed to the presence of *unsaturated*, *contra*, *or secondary valencies* in at least one of the constituent atoms.

There are some modifications of this theory of valency. Most are agreed about this interpretation of positive and negative valencies; and the formation of double and associated compounds is supposed to be due to the exercise of residual, contra or secondary valencies. L. Spiegel (1902) assumed that elements possess secondary valencies which can be called forth only in pairs of equal and opposite sign, so that when not externally saturated they neutralize one another and impart no electro-chemical characters to the element. Spiegel called these extra-valencies, *neutral affinities*. S. Arrhenius (1904) made a similar assumption and called them *electrical double valencies*, and J. N. Friend (1908) used a similar hypothesis and called the sleeping valencies, *residual or latent valencies*. I. Langmuir (1916) assumed that the aggregation of molecules into liquid and solid masses is due to the exercise of the secondary valencies, and thus the *cohesion* of solids and liquids is due to the exercise of an attraction similar in kind to chemical affinity. The electron hypothesis will be described later.

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§ 15. The Association of Atoms in Three Dimensions

The arrangement of the atoms of a molecule in one plane is equally convenient in diagrams, and improbable as a natural fact.—A. G. Vernon Harcourt (1875).

When our views are sufficiently extended as to enable us to reason with precision concerning the proportions of elemental atoms, we shall find the arithmetical relation will not be sufficient to explain their mutual action and we shall be obliged to acquire a geometrical conception of their relative arrangement in all three dimensions of solid extension. . . . When the number of particles (combined with one particle) exists in the proportion of 4 : 1, stable equilibrium may take place if the four particles are situated at the angles of the four equilateral triangles composing a regular tetrahedron. . . . It is perhaps too much to hope that the geometrical arrangement of primary particles will ever be perfectly known.—W. H. Wollaston (1808).

In order to explain why the atoms of diatomic molecules travel about in pairs, it seems to be necessary to assume that the atoms exert an attraction on one another, and that the position of the atoms in space must be conditioned by the attractive forces. As Isaac Newton said in his *Opticks* (London, 1704):

> How the particles which touch only in a few points can stick together and that so firmly as they do, without the assistance of something which causes them to be attracted or pressed towards one another, is very difficult to conceive.

When two univalent atoms unite with one bivalent atom, it is natural to imagine two points of contact, and two directions in which the bivalent atom exerts its power of combination. This conception of direction appears to be almost necessary in the case of carbon with its four valencies, and organic chemists have founded upon this what is known as **stereochemistry** (στερεός, solid), or *chemistry in three dimensions*, or *chemistry in space*, on lines dimly foreshadowed by W. H. Wollaston in 1808, and A. M. Ampère in 1814. Since then, many chemists have thrown out hints of a tridimensional arrangement of the atoms in a molecule—L. Pasteur (1861), F. A. Kekulé (1861), A. M. Butleroff (1863), E. Paternó (1869), A. Gaudin (1873), etc. Thus, in his celebrated lecture, *Recherches sur la dissymétrie moléculaire des produits organiques* (Paris, 1861), L. Pasteur asked: Are the atoms of *d*-tartaric acid grouped on the spiral of a helix winding to the right, or placed at the summits of an irregular tetrahedron, or disposed according to some other asymmetric grouping? and replied: We cannot answer these questions. It was not until the appearance of J. H. van't Hoff's paper, *On a system of atomic formulæ in three dimensions*, in Holland, September, 1874; [1] and J. A. le Bel's *Sur la relations qui existent entre les formules atomiques*, in France, November, 1874, that this idea was systematically developed as a working hypothesis in organic chemistry. After demonstrating the probability of the hypothesis that the carbon atom exerts its valencies in definite directions in tridimensional space, it appeared highly probable that other elements would be found to exhibit the same phenomenon, and thus arose a stereochemistry of nitrogen, sulphur, silicon, selenium, tin, etc. The relative directions of the four valencies of the carbon atom have been studied, and the attempt has been made to find the effect of the displacement of these directions upon the properties of the resulting compounds. It appears to be necessary to assume that the carbon atom is a material body with a certain shape and size, because K. Auwers (1890) has shown that in the case of two carbon atoms united by a double-bond, the linking forces probably act in such a way as to make an angle with each other and not a straight line joining the two points, because the existence of such forces acting from mere point-centres is highly improbable. Without making any suggestion as to the actual form of the tetrahedral arrangement of the valencies of the carbon atom—whether the attractive forces are concentrated at the apices (J. Wislicenus, 1888), or at the centres of the faces (A. Wunderlich, 1886)—organic chemists, following Wollaston's suggestion, find it convenient to represent graphically the four valencies of the carbon as acting in the direction of the line joining the centre with the apices of a regular tetrahedron. According to this hypothesis, the constitution of methane, CH_4, will be that represented in the diagram, Fig. 5, where the circles represent the relative positions of the hydrogen atoms with respect to the central carbon atom; similarly, for ethane, C_2H_6, with a pair of single-linked carbon atoms, Fig. 5, acetylene, C_2H_2, with a pair of triple-linked carbon atoms, Fig. 5; and benzene, C_6H_6, with a chain of six carbon atoms alternately single- and double-linked so as to form a closed chain or ring.

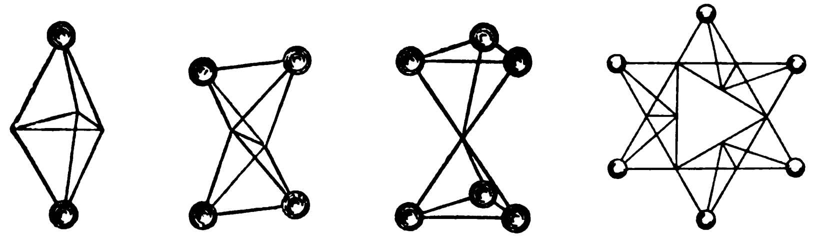
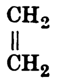


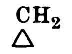
FIG. 3.—Diagrammatic representation of the Tetrahedron Theory of Quadrivalent Carbon with Single-, Double-, and Triple-linked Carbon Atoms.

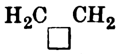
In the case of double- or triple-linked carbon atoms, are the lines assumed to be normally directed from the centre of the tetrahedron, bent with or without straining, or do the forces act rigidly in one fixed direction so that their components alone act in a direction parallel with the line joining the centres of the two tetrahedra? If it be assumed, with A. Naumann (1890), that the two valencies joining a pair of double-linked carbon atoms in, say, ethylene, C_2H_4, are directed from the centre of a tetrahedron towards the apices, and if each of these forces be resolved in two directions according to the parallelogram of forces, the sum of the components of each of these forces acting in the direction of the line joining the centres of the two tetrahedra, is effective in holding the two carbon atoms together. If the force with two single-linked carbon atoms be taken as unity, the force holding a pair of double-linked atoms will be $0{\cdot}577 \times 2$, and between a pair of triple-linked carbon atoms, $0{\cdot}33 \times 3$. This is not in agreement with J. Thomsen's thermal data.

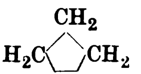
A. von Baeyer, in a paper *Ueber Polyacetyleneverbindungen* (1885), showed that if the four valencies of carbon are directed from a centre towards the four corners of a regular tetrahedron, the lines must make an angle of 109° 28′ with one another; and he made the assumption that if the direction of the attraction be diverted, there will be a corresponding strain; the greater the divergence, the greater the strain; and the greater the strain, the less the stability of the resulting molecule. The negative heat of formation of acetylene with its two carbon atoms connected by a triple bond, and the great instability of the acetylene compounds, show that the three linking bonds of the two acetylene carbons may be under some such strain; otherwise it might be anticipated that a pair of triple-linked atoms would be more stable than a pair of double-linked atoms, and the latter in turn more stable than a pair of single-linked carbon atoms. J. Thomsen's study of the heats of formation of the hydrocarbons (1882) shows that the breaking up of a double-bond requires 15·46 Cals. less thermal energy than a pair of single-bonds, and the breaking of a triple-bond requires 43·92 Cals. less thermal energy than is needed for three single-bonds.

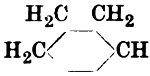
Consequently, **A. von Baeyer's strain theory** of valency—*Spannungstheorie*—assumes that the four valencies of the carbon atom normally act in the direction of the lines joining the centre with the apices of a regular tetrahedron making angles 109° 28′ with one another; and if these directions be bent or diverted, the lines are strained as if they were elastic wires, so that the greater the divergence the greater the strain, and the less the stability of the molecule. It follows that if the carbon atoms all lie in one plane, the angles of divergence with ethylene and with tri-, tetra-, penta-, and hexamethylene, C_nH_{2n}, will be


(C_2H_4), 54° 44′
Ethylene


(C_3H_6) 24° 44′
Trimethylene


(C_4H_8), 9° 44′
Tetramethylene


(C_5H_{10}), 0° 44′,
Pentamethylene


(C_6H_{12}), —5° 16′
Hexamethylene

and generally, for a ring compound of this type containing n carbon atoms in the ring, the angle of divergence will be 54° 44′ less $(n-2)\ 90° \div n$. H. Sachse introduced further developments.

This hypothesis explains how the members of the closed ring series increase in stability up to a maximum with pentamethylene, which should be more stable than all the other members of the series, for the higher members decrease in stability with increasing complexity; the theory also explains how organic compounds with open chains have a greater tendency to form closed rings with five and six members than closed rings of greater or less complexity. F. Stohmann and C. Kleber's measurements (1892) of the energy required to break such rings and add two hydrogen atoms are in approximate agreement with this deduction; so also is I. Traube's work (1899) on atomic volumes. There are, however, several series of compounds whose behaviour does not fit in quite so well with the hypothesis. For instance, it will be obvious that the strain theory itself cannot be a sufficient explanation of ring formation because it does not take the influence of chemical affinity into account —*e.g.* the influence of side-chains in facilitating the closing of the ring. H. N. Stokes (1900) applied a similar hypothesis to the phosphimic acids in which the phosphorus atoms form closed rings and the results were in general agreement with the hypothesis.

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§ 16. The Evolution of the Valency Concept

> The doctrine of valency is no mere speculation or hypothesis evolved by the brilliant fancy or imagination of one man; it is the logical outcome of knowledge acquired step by step. The conception has been one of slow growth, for it gradually incorporated itself into science as the necessity arose for devising a suitable explanation for accumulated observations.—E. P. Venable (1899).

While the mists which enveloped the concepts, molecule, atom, and equivalent, were being dispelled by illuminating rays of A. Avogadro's hypothesis, many theories to explain chemical composition were struggling for existence. In the resulting controversies—chiefly among J. J. Berzelius, J. B. A. Dumas, J. von Liebig, A. Laurent, and C. F. Gerhardt—the facts were interpreted by different hypotheses; and, as A. Ladenburg (1886) has shown, this was far more favourable for progress than if a single theoretical opinion had come too prominently in front. The differences of opinion quickened interest and experiment, and gave chemistry a very intimate knowledge of many classes of compounds, because the advocate of each hypothesis tried to support his own views by evidence which could be obtained only by a close study of the chemical characteristics of the compounds in dispute. It is difficult for chemists to appreciate the labour involved in clarifying the concepts which now appear so simple. As one writer has said:

> In the glamour of recent discoveries and the attractiveness of what is new and startling, the pioneer spade work of a bygone age is forgotten or undervalued, and A. Carrel adds: Almost every step in scientific progress which appears to be due to the efforts of one individual is, in reality, the result indirectly of the unknown scientific work of many others.

The radicle or radical theories.—In his *Traité élémentaire de chimie* (Paris, 1793), A. L. Lavoisier supposed that chemical compounds were formed by the union of two bodies, and stated his belief that the composition of organic bodies depended upon the existence of complexes or radicles in union with oxygen. Adopting a suggestion of Guyton de Morveau (1787), Lavoisier called that portion of a compound which is combined with oxygen, *la base* or *le radicle*. In developing his celebrated dualistic polar hypothesis, J. J. Berzelius (1817) extended Lavoisier's idea. The dominant feature of Berzelius' hypothesis is that chemical compounds can all be resolved with two distinct parts electrically different. When J. B. A. Dumas and P. F. G. Boullay (1828)[1] announced their belief that ether, $(C_2H_5)_2O$, consisted of two parts—water, H_2O, and a basic radicle, C_2H_4, which was called at the suggestion of J. J. Berzelius *ætherine*—the radicle etherine was thought to be always present in what are now called *ethyl compounds*. For instance, alcohol, C_2H_6O, would have been regarded as a binary compound, $C_2H_4.H_2O$; and ether, $C_4H_{10}O$, as $2C_2H_4.H_2O$. J. J. Berzelius at first opposed this hypothesis, but he afterwards incorporated the idea in his dualism. J. B. A. Dumas and P. F. G. Boullay's **etherine hypothesis** was not generally accepted because it did not adapt itself to the many new organic compounds soon afterwards discovered. The interesting feature about this hypothesis is that it represents *an attempt to find a similarity in the structure of a series of chemical compounds which possess like fundamental properties by showing that they are all derived from one common primitive stock or type.*

In 1815, in his memoir *Recherches sur l'acide prussique*, J. L. Gay Lussac[2] announced the discovery of the radicle cyanogen, C_2N_2 (κύανος, blue; γεννάω, I produce); and he showed that the group CN, or Cy, persists as a radicle through a whole series of chemical compounds.

Cy.H	Cy.Cl	Cy.Br	Cy.NH_2	$CH_3CO.Cy$
Cyanogen hydride.	Cyanogen chloride.	Cyanogen bromide.	Cyanamide.	Acetylcyanide.

Again, in 1832, J. von Liebig and F. Wöhler described a series of compounds of the radicle benzoyl, C_6H_5CO, of benzoic acid, in a memoir entitled *Untersuchungen über das Radikal der Benzoësäure.* The benzoyl radicle persists in many chemical compounds—among others

$C_6H_5CO.H$	$C_6H_5CO.OH$	$C_6H_5CO.Cl$	$C_6H_5CO.NH_2$	$C_6H_5CO.OC_2H_5$
Benzoyl hydride.	Benzoic acid.	Benzoyl chloride.	Benzamide.	Ethyl benzoate

The recognition of these two radicles—cyanogen and benzoyl—led to the development of what is now called the **older radicle theory.** On this hypothesis complex groups or radicles were supposed to exist unalterable in organic compounds, and to play the same rôle as elements do in inorganic compounds. According to J. von Liebig (1837),

> Cyanogen is a radicle (1) because it is a non-varying constituent in a series of compounds; (2) because in these latter it can be replaced by other simple substances; and (3) because in its compounds with a simple substance, the latter can be turned out and replaced by equivalents of other simple substances.

Hence, while this hypothesis was in favour, organic chemistry was regarded by J. B. A. Dumas and J. von Liebig (1837) as the *Chemistry of Compound Radicles.* The purpose of organic chemistry was supposed to involve the investigation and isolation of radicles as the more intimate components of organic compounds. Cyanogen and benzoyl, said A. Ladenburg (1869), were the pillars of the radicle theory, and this hypothesis received further support from the work described in R. Bunsen's brilliant memoirs, *Untersuchungen über die Kakodylreihe* (1839–43), in which it was shown that the so-called *Cadet's fuming liquid*—obtained by A. A. F. Cadet in 1760 by distilling potassium acetate with arsenious oxide—contained the oxide of a radicle, with the empirical formula, $As(CH_3)_2$, and which he called *kakodyl* or *cacodyl* (κάκωδης, ill-smelling). R. Bunsen succeeded in isolating the radicle itself, and also in preparing various salts—the chloride, bromide, fluoride, sulphide, etc. Modifications of the theory of radicles were discussed by J. J. Berzelius (1833) and J. von Liebig (1834–38), and the principle of radicles was generally accepted although it was not so much emphasized during the reign of the so-called type theories.

The type theories.—In 1834, J. B. A. Dumas[3] found that the hydrogen of many organic compounds could be replaced or substituted by chlorine in such a way that for every volume of chlorine introduced into a compound, an equal volume of hydrogen was lost; and, shortly afterwards, J. B. Dumas found that when oxygen displaces hydrogen, half a volume of oxygen takes the place of one volume of hydrogen. Otherwise expressed, while equal volumes of hydrogen and chlorine are equivalent, these elements possess only one-half the substituting value of the same volume of oxygen. A further study of substitution or metalepsis (μετάληψις, exchange), led J. B. A. Dumas, in his memoir, *Sur le constitution de quelques corps organiques et sur la théorie des substitutions* (1839), to the so-called **substitution theory.** J. B. A. Dumas discovered two important facts in his investigation of the action of chlorine on some organic compounds: (1) When a compound containing hydrogen is exposed to the dehydrogenating action of chlorine, bromine, or iodine, for each atom of hydrogen that it loses, it takes up an equivalent volume of chlorine, bromine, etc. (2) If a compound contains water, it loses the hydrogen without an equivalent substitution or replacement. The main *assumption* of the substitution theory hangs on the doctrine that the structure and character of organic compounds are not materially altered by the substitution of chlorine in place of hydrogen.

A. Laurent in a paper *Théorie des combinaisons organiques* (1836), and later, in his posthumous work, *Méthode de chimie* (Paris, 1854), tried to reconcile the radicle theory with these new facts discovered by J. B. A. Dumas. When the substitution occurs equivalent by equivalent, the residual body exhibits certain analogies with the original substance, for the substitution occurs without disturbing the structural type—chlorine, for instance, may occupy the place left vacant by hydrogen. A. Laurent argued that all organic compounds have definite forms or nuclei—*radicaux*—and consist either of *primary nuclei—radicaux fundamentaux*—or of *secondary or derived nuclei—radicaux derivés*—in which the hydrogen atoms have been replaced by others, or in which additional atoms have been taken up. This hypothesis was called the **nucleus theory**; it included the idea of substitution, and was based on the radicle theory; but it controverted the doctrine that radicles were unchangeable, for the atoms of a radicle can be replaced by others; it gave the first hint of what is now known as "chemistry in space." The nucleus theory was specially favoured by L. Gmelin in his celebrated *Handbuch der Chemie* (Heidelberg, 1843 *et seq.*), but it was not taken up by chemists generally.

In 1839, J. B. A. Dumas prepared trichloroacetic acid, $CCl_3.COOH$, in which three of the hydrogen atoms of acetic acid, $CH_3.COOH$, are replaced by chlorine, and the resulting compound retains the chief characteristics of the parent acid. This led him, in his *Mémoire sur la loi des substitutions et la théorie des types* (1840), to extend Laurent's nucleus theory to what is now known as the **older theory of types,** in which organic substances are supposed to be formed of particles which may be replaced or displaced, so to speak, without destroying the original substance. Compounds which have similar properties and a similar structure were classed as belonging to one *chemical type*—*e.g.* acetic acid and the chloroacetic acids. The relations between the members of a series of compounds belonging to one chemical type thus recall those assumed by A. Laurent to subsist between the original and the derived nuclei. J. B. A. Dumas also found it necessary to employ what he called the *mechanical type* to classify compounds which are related in structure but which manifest different chemical characteristics. Dumas rightly classed acetic acid and alcohol under the same mechanical type, which included a number of compounds which had little or no chemical relations with one another, though they may be regarded as belonging to one natural family because they may be derived by substitution one from the other—*e.g.* methane, CH_4; formic acid, $H.CO.OH$; carbon tetrachloride, $CCl_3.Cl$. J. B. A. Dumas' mechanical type resembled what H. V. Regnault (1838) had previously called the *molecular type*. If a substance changes without losing its mechanical type, it follows the law of substitution, but if it passes into another mechanical type, the law of substitution is not maintained during the reaction. By this statement, J. B. A. Dumas admits that his original idea of substitution is not always applicable, for an equivalent of hydrogen is not always evolved when another is introduced into the compound; and a compound is not regarded as consisting of two parts. but is supposed to be a uniform whole with its component parts related in an analogous fashion to the worlds of a planetary system in which the atoms are held together by affinity instead of by gravitation. Just as the stability of a planetary system depends not on the intrinsic nature of the planetary units, but rather on their relative position with respect to one another and to the sun, so J. B. A. Dumas supposed that the chemical properties of a compound are primarily dependent on the arrangement and number of the constituent atoms, and in a less degree on their chemical nature. Dumas thus regarded the planetary molecule as the *type* of a series of compounds with a similar structure; and therefore, he opposed a *unitary theory of chemical composition* in place of J. J. Berzelius' dualism. Between 1838 and 1844, J. J. Berzelius vigorously fought a losing fight in his *Jahresberichten* against these encroachments on his dualistic views. C. F. Gerhardt having suggested that in compounds of an organic base with an inorganic acid, the organic portion of the compound, termed the copula, was supposed to unite by *accouplement* (copulation) with the inorganic acid. J. J. Berzelius tried to explain the substitution products obtained by J. B. A. Dumas by arbitrarily assuming that they were formed by the copulation or pairing of imaginary copulæ; he explained the formation of trichloroacetic acid, for example, by assuming it to be formed by the union of carbon chloride, C_2Cl_6, with oxalic acid, $H_2C_2O_4$; and he assigned different rational formulæ to trichloroacetic acid and its parent—acetic acid. Berzelius' explanation broke down completely when L. H. F. Meslen (1842) showed that chloroacetic acid could be reconverted to the original acid by reduction with potassium amalgam. J. J. Berzelius obstinately opposed the theory of types with his last breath, but he fought practically alone. His one-time supporter, J. von Liebig, gave up the dualistic hypothesis when it failed to explain the newer facts.

In 1839, C. F. Gerhardt, in his memoir *Sur la constitution des sels organiques à acides complexes et leur rapports avec les sels ammoniacaux*, rejected the radicle theory and stated his belief that a compound must be regarded as a complex of atoms bound each to all, and all to each; but he could not help admitting that certain groups of atoms do recur in chemical compounds. Accordingly, C. F. Gerhardt attempted to reconcile his hypothesis with observation, by what he called his **théorie des résidus**—*theory of residues*—in which a group of atoms previously called a *compound radical* was termed *le reste*—a residue; unlike radicles, C. F. Gerhardt's residues were not supposed to be present as such in a compound, for, said C. F. Gerhardt, *je prends l'expression de radical dans le sens de rapport, et non dans celui de corps isolable ou isolé.* C. F. Gerhardt's molecule was *une système unitaire*—a simple edifice and not a double building; all assumptions of a binary structure were excluded. He argued that the constitution of a compound can be deduced only from its modes of formation and decomposition, and that according to the theory of radicles several rational formulæ and several radicles could be imagined in the case of one substance formed in different ways—*e.g.* barium sulphate formed by the reactions symbolized: (i) $BaO+SO_3$; (ii) BaO_2+SO_2; and (iii) $BaS+2O_2$. Consequently, a *chemical type is nothing more than a general system of reactions.* Acetic acid, water, and alcohol were classed in the same way because they undergo analogous reactions—say, when they are deoxidized to form aldehyde, hydrogen, and ethyl hydride, C_2H_5H, respectively. Gerhardt further supposed that when two substances react with one another, an element in the one combines with an element in the other to form one stable compound, and the residues also unite to form what he called *corps copulés* and later *corps conjugés*, meaning *copulated or conjugated compounds.* Thus, the copula benzene, C_6H_6, unites with nitric acid, HNO_3, to form water, H_2O, and the copulated compound nitrobenzene, $C_6H_5.NO_2$. In modernized symbols:

$$\left.\begin{matrix}\mathrm{NO_2}\\ \dot{\mathrm{O}}\mathrm{H}\end{matrix}\right\} + \left.\begin{matrix}\mathrm{C_6H_5}\\ \dot{\mathrm{H}}\end{matrix}\right\} = \left.\begin{matrix}\mathrm{H}\\ \dot{\mathrm{O}}\mathrm{H}\end{matrix}\right\} + \left.\begin{matrix}\mathrm{C_6H_5}\\ \dot{\mathrm{N}}\mathrm{O_2}\end{matrix}\right\}$$

Consequently, in a reaction between two substances, each molecule is split into two parts, and the resulting residues unite in such a manner that a *double exchange* takes place, and Gerhardt said: *J'appelle radicaux ou résidus les éléments de tout* *corps qui peuvent être ainsi transportés dans un autre corps par l'effet d'une double décomposition, ou qui y ont été introduits par une semblable réaction.* It is not very obvious why C. F. Gerhardt emphasized the distinction between his own type formulæ and those of J. B. A. Dumas. The former clearly supposes substitution to be effected by replacing an element in a compound by an equivalent of another element, or by the residues (radicles) of the reacting substances, and this is but a restatement of the views of J. B. A. Dumas and A. Laurent. C. F. Gerhardt's conception of radicles, said C. Schorlemmer (1879), soon supplanted the older views, and its introduction into the theory of types led to the fusion of both theories.

The discovery of the organic ammonias by C. A. Wurtz (1849) and A. W. von Hofmann (1850)[4] revealed the close relationship between the organic ammonia bases and ammonia itself, and the hypothesis that the former were derivatives of ammonia, NH_3, produced by the substitution of hydrocarbon radicles in place of hydrogen atoms:

$$NH_3 \qquad (C_2H_5)NH_2 \qquad (C_2H_5)_2NH \qquad (C_2H_5)_3N$$

furnished the only satisfactory explanation of the constitution of these compounds. In this way, said C. A. Wurtz, the ammonia type was founded. Similarly, A. W. Williamson's *Theory of Ætherification* (1850), dealing with the substitution of hydrocarbon radicles in place of the hydrogen atoms of water, established the water type. A. W. Williamson demonstrated the close relationship between

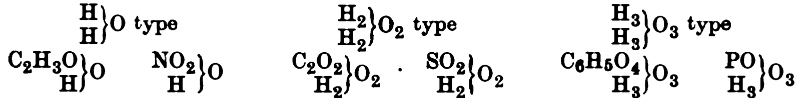
$$\underset{\text{Water.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} \qquad \underset{\text{Alcohol.}}{\left.\begin{matrix}C_2H_5\\H\end{matrix}\right\}O} \qquad \underset{\text{Ether.}}{\left.\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\right\}O}$$

In harmony with a prior suggestion made by A. Laurent in 1846, A. W. Williamson wrote: "I believe that throughout inorganic chemistry and for the best known organic compounds, one single type will be sufficient—it is that of water represented as containing two atoms of hydrogen to one of oxygen." Numerous nitrogen compounds were then referred to C. A. Wurtz and A. W. von Hofmann's ammonia type, and many oxygen compounds were likewise referred to A. W. Williamson's water type as *termes de comparaison*. C. F. Gerhardt in his *Traité de chimie organique* (Paris, 1853–6) added hydrogen and hydrogen chloride to the ammonia and water types, and he attempted to classify all organic compounds by reference to the four types: hydrogen, H_2; hydrogen chloride, HCl; water, H_2O; and ammonia, NH_3. In 1857, F. A. Kekulé, in an important memoir *Ueber die sogenannten gepaarten Verbindungen und die Theorie der mehratomigen Radicle*, proposed to add methane, CH_4, to the list of primitive or **simple types**, and to remove hydrogen chloride from the list because it is merely a special case of the hydrogen type. Thus arose the **newer theory of types** which now assumed the forms

$$\underset{\text{Hydrogen type.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}} \qquad \underset{\text{Water type.}}{\left.\begin{matrix}H\\H\end{matrix}\right\}O} \qquad \underset{\text{Ammonia type.}}{\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N} \qquad \underset{\text{Methane type.}}{\left.\begin{matrix}H\\H\\H\\H\end{matrix}\right\}C}$$

A. Laurent had suggested in 1846 that alcohol and ether as well as inorganic acids and oxides could be regarded as derivatives of water. In 1848–9, T. S. Hunt published several papers in which he showed that the composition of many oxygenated compounds might be derived from water as a type, and he also referred the formulæ of hydrocarbons to hydrogen as a type; but T. S. Hunt's work had little or no influence on the development of the theory of types since it was unknown to those who were working in Europe on this subject.

A. W. Williamson introduced the idea of **condensed types** in 1850; dibasic acids like sulphuric acids and oxalic were regarded as derived from two molecules of water, and the acid radicle was supposed to replace one atom of hydrogen in each of the two molecules of water. W. Odling, in his paper *On the Constitution of Acids* *and Salts* (1855), developed the idea still further, and formulæ like these were obtained:



$$\left.\begin{matrix}H\\H\end{matrix}\right\}O\ \text{type} \qquad \left.\begin{matrix}H_2\\H_2\end{matrix}\right\}O_2\ \text{type} \qquad \left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3\ \text{type}$$

$$\left.\begin{matrix}C_2H_3O\\H\end{matrix}\right\}O \quad \left.\begin{matrix}NO_2\\H\end{matrix}\right\}O \quad \left.\begin{matrix}C_2O_2\\H_2\end{matrix}\right\}O_2 \ \cdot\ \left.\begin{matrix}SO_2\\H_2\end{matrix}\right\}O_2 \quad \left.\begin{matrix}C_6H_5O_4\\H_3\end{matrix}\right\}O_3 \quad \left.\begin{matrix}PO\\H_3\end{matrix}\right\}O_3$$

Acetic acid. Nitric acid. Oxalic acid. Sulphuric acid. Citric acid. Phosphoric acid.

F. A. Kekulé (1857) also extended the type theory to include **mixed types** supposed to be formed by the union of two simple or condensed types. For example, chlorosulphuric acid, $(HO)ClSO_2$, can be referred to a mixed hydrogen and water type; and carbamic acid, $H_2N.COOH$, was referred to the mixed ammonia and water types:

$$\begin{matrix}\left.\begin{matrix}H\\H\end{matrix}\right\}\\\left.\begin{matrix}H\\H\end{matrix}\right\}O\end{matrix} \qquad \begin{matrix}\left.\begin{matrix}Cl\\SO_2\end{matrix}\right\}\\\left.\begin{matrix}SO_2\\H\end{matrix}\right\}O\end{matrix} \qquad \begin{matrix}\left.\begin{matrix}H_2\\H\end{matrix}\right\}N\\\left.\begin{matrix}H\\H\end{matrix}\right\}O\end{matrix} \qquad \begin{matrix}\left.\begin{matrix}H_2\\CO\end{matrix}\right\}N\\\left.\begin{matrix}CO\\H\end{matrix}\right\}O\end{matrix}$$

Mixed type. Chlorosulphuric acid. Mixed type. Carbamic acid.

The need for the introduction of condensed and mixed types showed the insufficiency of the type theory, for as the number and complexity of organic compounds increase, an indefinite number of types may be required. C. F. Gerhardt's type theory is now considered but an interesting phase in the evolution of systematic chemistry. The attempts to refer a large number of compounds to a limited number of types, and the consequent need for viewing individual compounds from many different *points de vue*, enabled chemists to see many analogies and contrasts previously hidden, and to realize dimly the remarkable relations the atoms of a compound bear each to each. It soon became evident that the theory of types represented an artificial arbitrary system of classification; even C. F. Gerhardt (1856) admitted *mes radicaux et mes types ne sont que des symboles, destinés à concréter en quelque sorte certains rapports de composition et de transformation*, and H. W. Kolbe (1843 *et seq.*) seemed to get at the root of the matter when asked: "Why are we to suppose that nature has restricted herself to forming all bodies on the models of these four types? Why on these models rather than on others? The four types are nothing but a vain artifice." He answered that "the grouping of organic compounds into types verges on empty formalism, and is merely playing with formulæ." He sought to replace the purely formal types by others which he considered to be related naturally with their derivatives. In a paper *Ueber die chemische Konstitution und Natur der organischen Radikale* (1851), H. W. Kolbe built up a **newer radicle theory** in which he eliminated those tenets which were not in harmony with fact; he showed, as J. J. Berzelius supposed, that in organic compounds there are definite radicles which behave like the elements in inorganic compounds. The discovery of the organometallic compounds—typified by zinc ethyl, $Zn(C_2H_5)_2$—by E. Frankland (1849), seems to exclude every doubt of the actual existence of compound radicles; and H. W. Kolbe (1850) electrolyzed aqueous solutions of the salts of the fatty acids, and believed that he separated the constituent hydrocarbon radicles—as a matter of fact, he obtained products of the union of two radicles. Thus, with potassium acetate, $CH_3.CO.OK$, he obtained gaseous carbon dioxide and ethane, $(CH_3)_2$ or C_2H_6; the potassium, simultaneously obtained, undergoes a secondary reaction with the solvent: The primary reaction in modern symbols is represented:

$$\begin{matrix}CH_3\cdot CO.O\,K\\CH_3\cdot CO.O\,K\end{matrix} \rightarrow \begin{matrix}CO_2\\CO_2\end{matrix} + \begin{matrix}CH_3\\\dot{C}H_3\end{matrix} + 2K$$

In conjunction with E. Frankland, H. W. Kolbe published a paper entitled *Ueber den naturlichen Zusammenhang der organischen mit den anorganischen Verbindungen, die wissenschaftliche Grundlage zu einer naturgemassen Klassifikation der organischen chemischen Körper* (1859), in which it was shown by numerous examples that organic compounds can be regarded as derivatives of inorganic compounds, and result from the latter—in some cases directly—by wonderfully simple substitution processes. Consequently, organic acids can be regarded as substitution derivatives of carbonic acid, and consequently, H. Kolbe argued that carbonic acid is a natural standard of reference for organic bodies because they are formed from this gas in the vegetable kingdom. He said: The carbonic acid type must therefore exist in the very nature of things, and it seems logical to refer all organic compounds to this type, since they are all in fact derived from it.

For example—translating Kolbe's symbols into modern practice, and starting from carbonic acid, $(HO)_2CO$—when a hydroxyl group, HO, is replaced by a hydrogen, H, atom, formic acid, H.CO.OH, is formed; replacing OH by CH_3 furnishes acetic acid, $CH_3.CO.OH$; replacing two OH-groups by two H-atoms yields formaldehyde, H CO.H. If an OH-group be replaced by an H-atom, and an O-atom by two H-atoms, methyl alcohol, $CH_3.OH$, results; and if an OH-group is replaced by CH_3, and an O-atom by two H-atoms, ethyl alcohol, $CH_3.CH_2.OH$, is formed.

H. Kolbe is here perhaps a little inconsistent, for C. A. Wurtz, in his *Histoire des doctrines chimiques depuis Lavoisier jusqu'à nos jours* (Paris, 1869), has pointed out that water and ammonia are agents as indispensable as carbonic acid in the processes of vegetable life. Kolbe's objections to C. F. Gerhardt's or F. A. Kekulé's types also apply to his own carbonic acid type.

The doctrine of valency.—In conformity with the general views of chemists early in the nineteenth century, J. L. Gay Lussac,[5] in his *Recherches sur l'acide prussique* (1815), regarded salts as products of the union of an equivalent of an acid with an equivalent of the base, but T. Graham's important *Researches on the Arseniates, Phosphates, and Modifications of Phosphoric Acid*, published in 1833, showed that phosphorus pentoxide can unite with one, two, and three equivalents of water to form definite acids which can respectively unite with but one, two, and three equivalents of the base to form definite salts with characteristic properties. Five years later, J. von Liebig, in his memoir *Ueber die Constitution der organischen Säuren* (1838), found other acids to behave in a similar manner, and he employed the terms *mono-, di-, tri-, and poly-basic acids* to indicate the saturation capacity of the acids for the bases. The idea of basicity was further extended to organic radicles; and, in 1834, J. B. A. Dumas showed that an atom of hydrogen could be replaced by an atom of chlorine, but only by the equivalent of half an atom of oxygen, so that these quantities of chlorine and oxygen are equivalent to an atom of hydrogen.

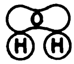
In his memorable paper *On a New Series of Organic Compounds containing Metals*, published in 1852, E. Frankland applied the idea of equivalency or saturation capacity to the elements. He showed that the power of the metals to combine with oxygen is reduced when the metal is copulated with compound radicles in such a way that, say, stannic ethyl oxide, $(C_2H_5)_2SnO$, is to be regarded as stannic oxide, SnO_2, in which one oxygen atom is replaced by two ethyl radicles; and stannic ethide, $Sn(C_2H_5)_4$, as stannic oxide with the two oxygen atoms replaced by four ethyl radicles. E. Frankland then remarked:

> When the formulæ of inorganic chemical compounds are considered, even a superficial observer is impressed with the general symmetry of their construction. The compounds of nitrogen, phosphorus, antimony, and arsenic especially exhibit *the tendency of these elements to form compounds containing three or five atoms of other elements*; and it is in these proportions that their affinities are best satisfied. . . . Without offering any hypothesis regarding the cause of this symmetrical grouping of atoms, it is sufficiently evident, from the examples just given, that such a tendency or law prevails, and that, **no matter what the character of the uniting atoms may be, the combining power of the attracting element is always satisfied by the same number of these atoms.**

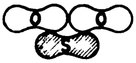
Thus Frankland led chemists to see that within certain limits the atoms of the elements possess definite saturation capacities; and he proved that copulation is a consequence of the saturation capacity of the elements. In 1877, Frankland added that the hypothesis just outlined "constitutes the basis of what has since been called the *doctrine of atomicity* or the equivalence of the elements." The far-reaching importance of the above quotation from Frankland was not realized until some years afterwards. A vague inkling of the operation of some such law among organic compounds was probably at the back of the minds of the founders of the different theories of types, for in representing chemical transformations as the result of substitutions of atoms or groups of atoms, the equivalency of the substituents must have been tacitly assumed; but they were prevented from realizing the importance of the principle by laying too much stress on the *position* rather than on the *nature* of the atoms concerned.

F. A. Kekulé seems to have considered himself to have been the originator of the doctrine of the valency, or, as he termed it, the *atomicity* of the elements. As a matter of fact, in 1854, two years after the publication of E. Frankland's paper, F. A. Kekulé did obtain a clearer vision of the doctrine, and, in 1857, he explained the existence of primitive types—simple and mixed—by means of the valency of the constituent elements. Soon afterwards, A. S. Couper, independently of F. A. Kekulé, published a paper, *Sur une nouvelle théorie chimique* (1858), in which he deduced constitutional formulæ for many compounds from the valency of the elements, or rather, what he called *affinity of degree* of the elements as contrasted with the ordinary manifestations of chemical affinity, or, as he called it, *elective affinity*. A. S. Couper, for the first time, also represented the composition of compounds by joining the symbols of the elements or compound radicles by means of hyphens or linking bonds. In his *Lehrbuch der organischen Chemie, oder der Kohlenstoff-Verbindungen* (Stuttgart, 1859), F. A. Kekulé symbolized the valency of an atom in graphic formulæ by means of a diagram whose size represented the valency as illustrated in the following examples:

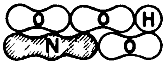
Hydrogen chloride, HCl



Water, H_2O.



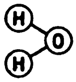
Sulphur dioxide SO_2.



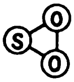
Nitric acid, HNO_3.

There was no intention, of course, to convey any idea of the relative dimensions of the atoms. In 1865, A. C. Brown suggested a system in which the symbol of the element was surrounded by a circle, with a number of radiating lines corresponding with the valency of the element. For instance,

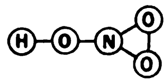
Hydrogen chloride, HCl.



Water, H_2O.



Sulphur dioxide, SO_2.



Nitric acid, HNO_3.

The grouping was not meant to indicate the physical but rather the chemical position of the atoms. E. Frankland adopted practically the same system in 1866, except that he omitted the circles round the symbols of the elements, and this method of pictorially representing the linking of the atoms of a molecule in definite order is virtually that employed by A. S. Couper, and it has persisted up to the present day. A. M. Butleroff (1861) followed up A. S. Couper's idea, and defined *the structure of a chemical compound* to be the mode in which the atoms are mutually linked together in the molecule. This does not afford any information of the position of the individual atoms in space. The chemical characteristics of a compound, said Butleroff, depend first upon the nature and relative quantity of its elementary constituents, and then on its chemical structure.

F. A. Kekulé (1857) classified the elements according to the replacing values of their atoms. Hydrogen, chlorine, potassium, etc., were called monobasic or monatomic elements; oxygen and sulphur were dibasic or diatomic; nitrogen, phosphorus, and arsenic were tribasic or triatomic; and carbon was classed as a tetrabasic or tetratomic element. There is an incongruity in the use of the terms *mono-*, *di-*, . . . *atomic*, since similar terms are employed to represent the number of atoms in a molecule; and the confusion in the use of the terms *mono-*, *bi-*, . . . *basic atoms* with J. von Liebig's polybasic acids, led E. Erlenmeyer (1860) to propose the terms *ein-*, *zwei-*, *drei-*, *and vier-werthig* which have come into use in Germany; the equivalent *uni-*, *bi-*, *ter-*, and *quadri-valent*, used by L. Meyer, or *mono-*, *di-*, *tri-*, *and tetra-valent*, with W. Odling's alternative terms (1864): *monad, dyad, triad, and tetrad* are now in use. J. Wislicenus used the terms *monaffin, diaffin, triaffin, and tetraffin*. In 1855, W. Odling placed dashes beside the symbol of the atom or radicle to express what he called the replaceable, or representative, or substitution value of the atoms, and he recognized, as E. Frankland did in 1852, that an atom can have more than one replaceable value. Various terms were used in place of valency during the clarification of the concept—e.g. *saturation capacity, combining capacity, atom-fixing power, affinity units, affinity of degree, basicity, and atomicity.* The two latter terms are objectionable. A. W. Hofmann (1865) considered that *atomicity* is a barbarous term; and is best reserved to express the number of atoms in a molecule of an element; the term *basicity* is also best retained to express the number of stages in which the replaceable hydrogen of an acid can be substituted by a metal. A. W. Hofmann did much to spread a knowledge of the doctrine of valency. He employed the term *quantivalence* "to designate the particular atom-compensating power inherent in each of the elements," and added "this power must by no means be confounded with the specific intensity of the respective activities of the atoms." H. Wichelhaus[6] shortened A. W. Hofmann's quantivalence to *valency* (or *valence*) in 1868; and H. Wichelhaus' term is now in general use.

The doctrine of valency introduced by E. Frankland and amplified by F. A. Kekulé soon stilled the controversies which had been waged between the advocates of the radicle and type theories. The nature of the problem was changed. Chemical formulæ were no longer employed to represent types of double decomposition, but rather to show the relations which subsisted between the constituent atoms of a molecule. The doctrine of valency enabled chemists to see, as in a glass darkly, the intimate structure of the molecules by establishing the way in which the atoms are bound together. Consequently, neither the type nor the radicle theory could claim a victory, for the theory of composition based upon valency absorbed and assimilated them both; it showed that chemists had really admitted a water type because there is a bivalent element oxygen; an ammonia type because there is a tervalent element nitrogen; and a methane type because there is a quadrivalent element carbon. As F. A. Kekulé's mixed metaphor expressed it: "Both sides had been striving towards the same goal by different paths; each side thereupon profited by the experience of the other, and with united forces sailed onward on the reunited stream."

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§ 17. Attempts to explain Valency

The general test of truth is evidence.—J. M. C. DUHAMEL.

The composition of all chemical compounds, says H. von Euler (1903), can be regarded as a function of a valency force—*Valenzkraft*—which is probably of an electric nature, and dependent on the temperature, pressure, and the nature of the solvent. Numerous attempts have been made to invent some peculiarities in the structure of the atoms which will explain that strange power manifesting itself as valency. Even Lucretius attributed the differences in the behaviour of his atoms to differences in their shape, size, and mode of motion. The subject has rather lent itself to hypotheses established by the absence of a knowledge of contradictory facts. A brief *résumé* of the more striking forms of these hypotheses may act as a danger beacon.

I. Differences in the valency of different elements have been explained by supposing that *an atom of an n-valent element is compounded of n units, each of which is capable of attracting one other unit.* A constant quantity of one element, said E. Erlenmeyer (1862),[1] never binds itself to more or to less than a constant quantity of another element—this he called *the law of constant affinivalencies.* W. Odling (1855) called these attracting units *sub-atoms;* G. Ensrud (1907), *Kernen* or *nuclei;* L. Knorr (1894), *Valenzkörper* or *valency bodies;* E. Erlenmeyer (1867), *affinivalencies;* A. W. von Hofmann (1865), *minimum atom-binding quantities* of an element; and J. Wislicenus (1888), *primitive atoms*, which are located in certain parts of the atom and from which they exert their influence. W. Lossen, in an important paper *Ueber die Vertheilung der Atome in der Molekul* (1880), pointed out that this hypothesis cannot be sound, for if a constant mass of, say, carbon binds itself to a constant mass of oxygen in the molecule of carbon dioxide, CO_2, the same mass of carbon is bound to half the same constant mass of oxygen in carbon monoxide, CO. Hence, the assumed constant mass must be variable. G. Ensrud (1907) supposed an atom to be compounded of an enveloping shell of a substance of small density with a nucleus of great density and eccentric shape. The envelopes of different atoms repel one another, the nuclei attract one another in the direction along which valency acts. An atom of an *n*-valent element has *n* nuclei. This hypothesis recalls J. F. Redtenbacher's *Das Dynamidensystem* (Mannheim, 1857). Some of these hypotheses appear to have arisen by confusing the fractional parts of an atom with fractional parts of its weight, and assuming that the former are equal to the latter. There is nothing to show that if the atom were divided up into a number of attracting portions, each would be the same fractional part of the weight of the atom. The modern electron hypothesis of valency is one form of this hypothesis—*vide* Vol. III.

II. Other hypotheses assume that *valency is an attracting force localized at certain parts of the atom.* The atoms are supposed to be joined together at these attracting points; in other words, some parts of the atom are less active than others. This hypothesis has taken various forms. E. Erlenmeyer (1867) and A. Michaelis (1872) suggested that the attractive forces are not exerted uniformly in all directions as is the case with gravitation, but are specially strong in certain definite directions so that a straight line joining two atoms directly bound together expresses the direction of the mutually exerted force. A. Michaelis supposed an n-valent atom to have n such directions, and, if it is bound by $n-x$ bonds, to have these mutual actions exerted in $n-x$ such directions. A. C. Brown (1861–79) assumed that each atom possesses two kinds of attractive forces—positive and negative—and the point towards which these forces act was called a *pole* or active point. He made no assumption as to the nature of the attractive or repellent forces. An n-valent element has n such positive and negative poles. When two atoms unite, the positive pole of the one attracts the negative pole of the other, and *vice versâ*. When a bivalent atom combines with two univalent atoms, the forces emanating from the bivalent atoms will be divided between its two poles in some proportion depending on the forces of the two univalent atoms. In order to support the assumption that valency is due to centres of attraction localized on the atom, subsidiary hypotheses have to be invented. For instance, it has been assumed (i) that the atoms are bound to one another through the attraction of electric or magnetic charges localized on the atoms; and also (ii) that the intensity of the attractive force is modified by the shape of the atom.

(i) *Electric charges localized on the atom.*—The idea that the reacting units are polarized, and carry definite electric charges, each charge representing one valency, naturally grew from Davy's and Berzelius' electrochemical hypothesis, and Faraday's work. There are many modified forms of the hypothesis. For example, V. Meyer and E. Riecke (1888) assumed that the carbon atom is surrounded by an æthereal envelope which, in the case of isolated atoms, has a spherical shape like that supposed to be possessed by the atoms themselves. The atom in the core carries the specific affinities; the æthereal envelope is the seat of the valencies. Each valency is determined by the presence of two opposite electrical poles—called double or *di-poles*—situated at the ends of a straight line which is small in comparison with the diameter of the æthereal shell. The four valencies of carbon are represented by four such di-poles each of which is able to move freely within the æthereal shell, and to turn freely about its middle point. The carbon atom attaches other atoms to its surface by the attractions of the di-poles. The modern form of the electric charge hypothesis will be discussed later.

(ii) *The shape of the atom.*—J. H. van't Hoff, in his *Ansichten über die organische Chemie* (Braunschweig, 1881), showed that the attractive forces emanating from an atom will be uniform in all directions if the atom is spherical, but if the shape be not spherical the intensity of the force, at short distances, will be more concentrated in certain spots than in others. Thus, if the atom were shaped like a regular tetrahedron, it would behave as if it were quadrivalent, for the centres of the four bounding faces would represent maximal attractions. Given the number of maximal points on the atom, it would be possible to deduce the valency, and conversely. There will be as many maximal points as the figure has sides. If the faces are unequally distant from the centre, the maximal points may not all have the same value, so that, when the nature of the united atoms also determines the attracting power, the number of effective valencies of the attracting atom will be affected, and a change of valency will be observed on comparing combinations of an element with other different elements. J. Wislicenus (1888) has expressed a similar idea; he said:

> It is not impossible that the carbon atom more or less resembles—perhaps very closely—the form of a regular tetrahedron; and further, that the causes of those attractions which are exhibited by the so-called units of affinity or bonds are concentrated at the apices of this tetrahedral structure, so that where there is least matter there is most force. These attractions are possibly analogous to the electrical state of a metal tetrahedron charged with electricity.

If the atoms be also in rapid vibratory motion, only the parts where the greatest attractions are exerted can retain their contacts, and therefore valency will be reduced by a rise of temperature, for a rise of temperature probably augments the vibratory motions of the atoms.

III. Another set of hypotheses has assumed that *valency is due to the need for harmonizing the motions of the combining atoms so as to form complexes whose parts move in stable equilibrium.* One form of this hypothesis is indicated later on. According to L. Meyer (1884), the atoms in a molecule are not in a state of rest, but they move rotationally about a centre of equilibrium; the orbits of similar atoms in the molecules of the same substance are the same so that equivalent atoms have the same paths, but the orbits of different atoms are greater, the greater the valency of the atom. E. Molinari (1893) suggested a modification of this hypothesis in a paper entitled *Motochemistry* (*móto*, motion). The valency of an atom in a molecule is determined by the nature or energy of its oscillatory motion; and he claims that the constitution of compounds is dependent upon the intramolecular movements rather than on the relative positions of the atoms in space. F. A. Kekulé (1872) considered that valency is determined by the relative number of impacts which an atom receives from other atoms in unit time; each of the univalent atoms in a diatomic molecule impinges once, while the bivalent atoms impinge twice in unit time. It is not very clear how this explains valency, and in 1878, F. A. Kekulé said that " the nature of the motion of atoms, unknown at present, may be imagined as an oscillatory one in such a way that the number of oscillations executed in unit time exactly represents the valency of the atoms." F. M. Flavitzky (1896), following N. N. Beketoff (1880),[2] supposed that the atoms move in curves which lie in planes parallel to one another; the atoms of different elements move in planes which are inclined at definite angles to one another; the motion of the atoms of one element can be completely counteracted by the motions of the atoms of another element only when the two planes of motion are parallel; otherwise, according to the size of the angle between the planes of motion, an atom of one element may require two, three, or more atoms of another element to balance it; and only those components come into action which are parallel to the plane of motion of another atom. Accordingly, F. M. Flavitzky refers the valency of an element to the difference in the angles between the planes of the orbits of the different rotating atoms. J. H. van't Hoff, in his *Die Lagerung der Atome im Raume* (Braunschweig, 1894), argued against the hypothesis which ascribed isomeric phenomena to the varied motions of the atoms because temperature presumably favours atomic motions, and yet the phenomena become less and less complex as the temperature rises, and constantly more complex as the temperature falls.

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§ 18. Atomic, Molecular, and Specific Volumes

> Modern developments in crystallography indicate with ever increasing distinctness that the chemical atom even when its individuality is shrouded by combination with other different atoms, exhibits characteristics which are essentially its own, and which are discernible in the compounds into which it enters.—W. J. POPE and W. BARLOW (1907).

So far as the balance can indicate, the weight, and by inference the mass, of an atom remains uniformly constant during all chemical changes; but the evidence is less clear with respect to the volume or space occupied by the atoms of an element when it enters into chemical combination. A. le Royer and J. B. A. Dumas [1] opened up the subject in 1821 with an attempt to determine the equivalent volumes of the elements by dividing their atomic weights by their respective specific gravities; the quotients were called *atomic volumes*.

The atomic volume of an element is obtained by dividing the atomic weight by its specific gravity; similarly the molecular volume represents the molecular weight divided by the specific gravity. Consequently, the atomic volume represents the space occupied by the aggregates of atoms, including the interstitial spaces, whose weights are proportional to the atomic weight; otherwise expressed, the volume occupied by a quantity of the element proportional to the atomic weight. The term *equivalent volume* was used before the concept of the atom had been clarified by Avogadro's hypothesis. At the suggestion of J. J. Berzelius, H. Schröder employed the term *molecular volume* in place of equivalent volume; and H. Kopp's term *specific volume* had the same connotation. It has been urged that the term specific volume is objectionable because the specific gravity of a body is the weight of unit volume, and the term specific volume by analogy suggests the volume of unit weight. The terms atomic volume and molecular volume here employed are defined by the ratio

$$\frac{\text{Atomic weight}}{\text{Specific gravity}}=\text{Atomic volume}\,;\quad \frac{\text{Molecular weight}}{\text{Specific gravity}}=\text{Molecular volume.}$$

Consequently, if the atomic or molecular weight be expressed in grams, the atomic or molecular volume respectively denotes the number of cubic centimetres occupied by a gram-atom or gram-molecule.

It follows from Avogadro's hypothesis that all gases have the same molecular volume. If the centres of gravity of the molecules of liquids were situated at the same average distance apart—as they probably are with gases—a given volume of different liquid would contain the same number of molecules; and the molecular weights of different liquids would be proportional to the specific gravities—as is also probably the case with gases. Similar remarks apply to solids. With liquids and solids, however, the molecules must be located at different distances apart because the molecular weights of different liquids and solids are not proportional to their specific gravities. The molecular volumes of liquids and solids do not exhibit the same uniformity as those of gases. This might have been predicted from the fact that while the coefficients of thermal expansion and the compressibilities of the different gases are approximately the same, each solid and each liquid has its own characteristic constant.

The molecular volume of gases can be compared at an arbitrarily defined standard temperature and pressure; but since liquids are obviously not in the same molecular condition, they are therefore not under comparable conditions at any one arbitrarily defined temperature. Consequently, H. Schröder[2] suggested that liquids would be more nearly in the same comparable state at the temperatures at which their vapour pressures are the same—*e.g.* at their boiling points under a standard pressure. In the case of solids, the effect of temperature is not so marked as with liquids, and in the first approximation, the specific gravity is taken at a convenient atmosphere temperature—say 0°, 4°, 15°, etc. A. Horstmann, W. Lossen, and A. Bartoli contend that (i) while the so-called atomic volume refers not only to the space filled by the atom, but also to the space in which the atom oscillates, it is not likely, *a priori*, that the molecules will be in the same state at 1°, the boiling point of butane, as they are at 317°, the boiling point of octadecane; (ii) relations similar to those established at the boiling temperature are likewise manifest at, say, the arbitrary temperature 0°; and (iii) the boiling point cannot be a strictly comparable state because it is affected by pressure to a different extent in the case of different liquids. G. Tschermak, F. Krafft, and G. le Bas take the melting point as a comparable state. In a valid corresponding state, the pressure, temperature, and volume should be expressed in terms of their critical values, and T. E. Thorpe has emphasized the fact that C. M. Guldberg has shown that the ratio of the critical temperature T_c to the absolute boiling point T_b approximates to a constant. Consequently, the boiling temperatures are approximately equal fractions of the critical temperatures. Consequently, properties like the molecular volume which change but slowly with temperature, are comparable at the ordinary boiling points. The results by the different methods do not show any very decisive evidence in favour of any one method, since relations which are revealed by the one may be obscured by the other. I. Traube emphasized the disturbing effects of molecular association and claimed that this can be eliminated by determining the molecular volume in dilute solution. The idea was applied many years previously by L. Playfair and J. P. Joule, who argued that "solution in water is the obvious means of destroying the cohesion of a body without at the same time altering its chemical properties."

From their observations on atomic volumes A. le Royer and J. B. A. Dumas tried to show that the atomic volumes are multiples of one and the same number and thus form an arithmetical series, but more extended investigations proved this tentative hypothesis was not in accordance with fact. At this period, the chemical combination of gases in volumetric proportions was attracting much attention, and attempts were made to show that solids likewise unite in definite volumetric proportions. For example, W. Herapath [3] tried to prove that the atomic volume of oxygen in a metal oxide bears a simple numerical relation to that of the metal with which it is combined. The same problem was attacked by C. J. B. Karsten (1832) and by P. F. G. Boullay (1840). Here again, more accurate observations falsified the hypothesis. F. Ammermüller (1840) concluded from his observations that the molecular volumes of compounds containing the same elements in different proportions are either the same, or else stand to one another in rational proportions. J. F. Persoz (1839) showed that equivalent amounts of many compounds of analogous composition have the same molecular volume, and he tried unsuccessfully to establish A. le Royer and J. B. A. Dumas' arithmetical rule.

H. Kopp's first publication, *Ueber die Vorausbestimmung des specifischen Gewichts einiger Klassen chemischer Verbindungen*, appeared in 1839 and his last publication on the subject was made in 1889. The earlier papers are mainly occupied in collecting material and in finding the best conditions for comparing the data. In 1844 H. Kopp tentatively concluded:

> (1) Equal differences in composition correspond with equal differences in specific volume. (2) Equivalent amounts of oxygen and hydrogen in liquid compounds occupy nearly the same volume. (3) The specific volume of a compound is equal to the sum of the specific volumes of its components. The same element almost invariably preserves the same specific volume. Isomeric compounds have the same specific volumes which stand to one another in the same relation as the molecular weights of the compounds. Variations in the chemical constitution of isomeric compounds are without effect on their specific volume. (4) Comparisons of specific volumes of liquids are only valid at temperatures at which the vapour pressures of the liquids are equal.

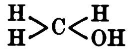
H. Kopp considered that these conclusions did not rest on a very firm experimental basis, and he therefore made accurate determinations of the physical constants required for testing them rigorously. The results of this work enabled him to take a general survey of the subject in his memoir, *Beiträge zur Stöchiometrie* *der physikalischen Eigenschaften chemischer Verbindungen*, 1855. His main conclusions were :

> (1) The selection of the temperature of equal vapour pressure as a basis of comparison seems to be warranted by the fact that regularities are thereby made evident which otherwise are not apparent. (2) Differences of specific volume are proportional to differences in chemical composition. (3) Isomeric liquids of the same chemical type have equal specific volumes. (4) The substitution of hydrogen for an equivalent amount of oxygen only slightly affects the specific volume. (5) One atom of carbon can replace two atoms of hydrogen without altering the specific volume.

The molecular volumes of the members of a homologous series of liquids which differ in composition by CH_2 increase nearly 22 units for each increment of CH_2. Thus, the molecular volume of formic acid, H.COOH, is 41·3 ; of acetic acid, CH_3.COOH, 63·6 ; and of propionic acid, C_2H_5.COOH, 85·6. Hence, the molecular volume of the group CH_2 is 22. Further, the replacement of one atom of carbon by 2 atoms of hydrogen in a compound usually makes no marked change in the molecular volume, and hence it is inferred that the atomic volume of carbon is nearly equal to the molecular volume of H_2. Since the molecular volume of CH_2 is 22, it follows that *the atomic volume of carbon is* 11. The difference, $22-11=11$, thus represents the molecular volume of H_2, and *the atomic volume of hydrogen is* 5·5. Again, the molecular volume of water is 18·8 ; deduct 11, the value of H_2, and *the atomic volume of oxygen* 7·8 remains. The molecular volumes of a large number of compounds can be calculated from the data so obtained, and compared with those obtained by actual experiment. The results for many carbon compounds are quite satisfactory. Thus, with alcohol, C_2H_5OH, the molecular volume will be $(2\times11)+(6\times5·5)+7·8=62·8$. The observed value is 62·2. Hence, if a compound contains n_1 atoms of atomic volume A_1 ; n_2 atoms of atomic volume A_2 ; . . . , the

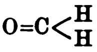
$$\text{Molecular volume, } v=n_1A_1+n_2A_2+\ \ldots$$

H. Kopp here over-emphasized the additive character of this property, but he did point out that the specific volume of a liquid is determined not only by its composition but also by its constitution, for he found that the relative position of the oxygen atom in a molecule affected the specific volume. The atomic volumes of the oxygen atoms in carbonylic and hydroxylic oxygen are respectively 12·2 and 7·8. The idea will be clear by comparing methyl alcohol, CH_3OH, with formaldehyde, H.COH, and with formic acid, H.COOH—



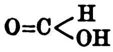
$$\begin{matrix}H\\H\end{matrix}\!>C<\!\begin{matrix}H\\OH\end{matrix}$$

Methyl alcohol
(Hydroxylic oxygen).



$$O=C<\!\begin{matrix}H\\H\end{matrix}$$

Formaldehyde
(Carbonylic oxygen).



$$O=C<\!\begin{matrix}H\\OH\end{matrix}$$

Formic acid
(Hydroxylic and carbonylic oxygen).

By applying similar methods to those described above, it is found that the atomic volume of carbonylic oxygen is 12·2. The molecular volume of methyl alcohol is accordingly $4\times5·5+11+7·8=40·8$; of formaldehyde, $2\times5·5+11+12·2=34·2$; and of formic acid, $12·2+7·8+2\times5·5+11=42·0$. Consequently, it is inferred that **one and the same atom may have different atomic volumes according to the conditions under which it is placed.** In further illustration, sexivalent sulphur has an atomic volume 12·0 ; quadrivalent sulphur, 22·6 ; and bivalent sulphur, 28·3. Nitrogen in ammonia and related compounds has an atomic volume 23 ; in cyanogen compounds, 28 ; and in nitroxyl compounds, 33. Hence, *the molecular volume can sometimes be used* (1) *for estimating the molecular weight of a liquid from its specific gravity and composition ; and* (2) *it may reveal peculiarities in the constitution of the molecule.* For instance, it may be used to show whether carbonylic or hydroxylic oxygen is present.

EXAMPLES.—(1) The observed molecular volume of acetic acid, $C_2H_4O_2$, is 63·7. The only molecular volume compatible with this is 64, deduced on the assumption that the compound contains one hydroxylic oxygen atom (7·8), and one carbonylic oxygen (12·2).

The formula for acetic acid is therefore written $CH_3-CO-OH$. (2) The density of phosgene, $COCl_2$, at its boiling point, is 1·415. What is the atomic volume of chlorine, on the assumption that the atomic volume of oxygen is 12·2; and of carbon 11·0 ? Ansr. $99/1{\cdot}415=12{\cdot}2+11{\cdot}0+2x$; x, the required atomic volume, is therefore 23·4.

A large number of solid and liquid compounds—over a thousand—have been examined. The pioneer work was done by H. Kopp and extended by many other workers.[4] With solids the data which have been accumulated are even more difficult to deal with, since the disturbing factors seem to be even more perplexing than is the case with liquids. Although many additive regularities have been detected ranging over a limited number of compounds, yet, almost every investigation has emphasized the constitutive nature of this property, and narrowed the range of the simple additive rule. Even the increment CH_2 in a homologous series, when determined at the boiling points, is not additive, for its effect becomes greater as the series is ascended, but, as A. Horstmann showed, the effect is not so marked when the comparison is made at equal temperatures, or, as F. Krafft has shown, at the melting points. H. Kopp thought that isomerides of similar structure had the same molecular volume, but P. Dobriner and R. Gartenmeister have shown that the effect is related with the boiling points, for the lower boiling isomer has the larger molecular volume; J. C. Brown, A. Zander, T. E. Thorpe, and W. Städel showed that isomers with an *iso*-structure also have the larger molecular volume. F. Neubeck showed that the molecular volume of the benzene derivatives is modified according as the groups occupy the ortho-, para-, or meta-position. P. Walden and T. Liebisch found that the racemic isomer of stereo-isomerides has the smaller molecular volume, and I. Traube that the trans-isomer has the greater molecular volume. H. L. Buff also showed that the atomic volume of an element varies according to its degree of saturation, and that an unsaturated carbon atom has a larger atomic volume than a saturated one. Hence, argued H. L. Buff, the atomic volume of an element decreases as saturation proceeds. This was confirmed by R. Schiff and W. Lossen, who found that on passing from a saturated carbon atom to one with the double ethylene linkage, the molecular volume decreases about 8·5 units, and on passing from the double ethylene to the triple acetylene linkage, the molecular volume decreases about 6·5 units. In a homologous series of ethylene linkages, the effect produced by each is rather less than the preceding one. A. Horstmann found that "unsaturated compounds with closed chain formulæ have considerably smaller molecular volumes than those with open chain formulæ and multiple linkages of the atoms." R. Willstätter showed that the contraction in the molecular volume which accompanies the conversion of a normal chain hydrocarbon to the ring or cycloid structure is larger than is caused in passing from a saturated to an unsaturated compound. Consequently, **molecular volumes are dependent upon differences in the structure of the compound as well as on the nature of the atoms in the molecule.**

The difference between the molecular volumes of the MO oxides and the atomic volume of M gives fairly constant values for the atomic volume of oxygen, but in other cases very different values are obtained. Thus, the oxygen in cupric oxide has an atomic volume 5·1, and in cuprous oxide 10·5. B. Brauner and J. I. Watts have investigated the atomic volumes of the oxides, and found the results are in accord with the periodic law, and conclude:

(1) In strong bases the oxygen has a negative value. (2) In the oxides of heavy metals and metalloids the volume of the oxygen is positive. (3) The earth metals unite with oxygen without any appreciable change of volume, and thus form a connecting link between acids and bases. (4) The higher the specific volume of the element in the oxide, the less positive or more negative is the specific volume of the oxygen. (5) The more negative the value of the oxygen, the greater is the affinity of the metal for the oxygen.

L. Playfair and J. P. Joule[5] noted that the molecular volumes of certain highly hydrated salts—*e.g.* sodium decaquocarbonate, and the alkali dodecaquophosphates and dodecaquoarsenates—are exactly equal to that of the water, considered as ice, which they respectively contain, so that the molecules of the salt proper seem to exist in the interstitial spaces of the water since they exert no apparent influence on the bulk. The relation does not hold with salts less highly hydrated—*e.g.* borax, sodium pyrophosphate, and aluminium sulphate—where the molecular volume is the joint effect of the water considered as ice, and of the salt. R. Schiff also showed that the members of certain classes of hydrated salts have practically the same molecular volume—*e.g.* the alums have a molecular volume of about 277; the double sulphates of the type $M_2'M''(SO_4)_2.6H_2O$ have a common molecular volume of about 207; and the vitriols of the type $M''SO_4.7H_2O$, isomorphous or not, have the same molecular volume 146. T. E. Thorpe and J. I. Watts have further shown that the volumes occupied by the several molecules of water in polyhydrates vary with the degree of hydration, for the molecular volumes of hydrated salts are not usually equal to the sum of the molecular volumes of the anhydrous salt and of the water (18·8). With the magnesium sulphates, for example,

$MgSO_4$ plus . . .	0	1	2	5	6	7 H_2O
Molecular volume .	45·3	55·6	67·0	112·4	130·8	146·4

The first molecule of water, the constitutional water or the water of halhydration of T. Graham, here occupies a less volume than the remaining molecules. The second molecule of water raised the molecular volume 11·4; the next three molecules of water raise the molecular volume an average of 11·8; the sixth molecule raises the constant 18·4, and the seventh, 15·6. T. E. Thorpe and J. I. Watts obtained analogous results with the series of sulphates $MSO_4.nH_2O$, when n varied from 0 to 6. This is in harmony with H. Kopp's general conclusion that the water molecules of a hydrated salt contribute in different degrees to the total molecular volume, for in salts containing a small number of water molecules (1 to 3), he found the average molecular volume of the water is 12·4; in others containing a larger proportion (2 to 7), the average molecular volume is 13·4; and in a third class, with the largest proportion of water molecules (3 to 10), the average molecular volume is 15·3. F. W. Clarke compared similarly the molecular volumes of a series of chlorides $MCl_2.nH_2O$, when n varied from 2 to 6; and for a series of hydrated oxides—$B_2O_3.3H_2O$; $I_2O_5.H_2O$; $K_2O.H_2O$; $CuO.H_2O$; $SrO.H_2O$; $BaO.H_2O$; $Al_2O_3.3H_2O$; $Mn_2O_3.H_2O$; $Fe_2O_3.H_2O$. In the former, the molecular volume of the water varied from 12·5 to 15·0, and in the latter from 7·4 to 19·4. F. W. Clarke's results emphasize the difference between water of crystallization and water of constitution in that the chemical differences implied by these expressions are connected with the relative magnitudes of the spaces occupied by chemically comparable quantities of the hydrated salts. The contraction which occurs in the dilution of sulphuric acid with water is indicated in Fig. 27, Cap. X.

The atomic volume of an element obtained by dividing atomic weight by its specific gravity is not the same as the atomic volume deduced by H. Kopp from the molecular volumes when the element is in combination. The two values are not usually the same. For instance,

	H.	C.	Cl.	Br.	I.	O.
H. Kopp, atomic volume .	3·5	11	22·8	27·8	37·5	7·8–12·2
Calculated from element .	11	3·4	22·2	25·1	25·6	14·3

In 1831, T. Thomson compiled a table of atomic volumes of the metals, and noted a correspondence in the atomic volume of the elements most nearly related with one another. When the atomic volumes are plotted against the atomic weights, L. Meyer[6] showed in 1869 that a periodic curve is obtained like Fig. 4 in Cap. VI, where (1) the waves increase in amplitude as the atomic weights increase; (2) the elements of similar chemical properties occupy corresponding positions on the waves; (3) the more volatile and easily fusible elements occur on the crests or rising portions of the curve, and the elements which fuse with difficulty are in the troughs or on the descending portions of the curve. The curve was found by W. Borchers to be more regular and the relations between the elements clearer if the equivalent volume—atomic weight÷maximum valency—be employed in place of the atomic volumes.

The molecular volume of an element varies with the conditions under which the molecules are placed. The atom is presumably always in oscillatory periodic motion, and this motion gives rise to volume; consequently, the molecular volume is a relative measure of the space inhabited by the molecule; it represents the smallest space which the molecule requires for itself under the existing conditions. Similar remarks apply to the atomic volume so that **each atom can be regarded as a material nucleus surrounded by an envelope, shell, or space—called the sphere of action or sphere of influence into which no other atom or molecule can penetrate.** The sphere of influence is thus regarded as the effective boundary surface of an atom. This is what is sometimes called the *vibratory or oscillatory volume of an atom*, that is, the space within which the material nucleus performs its oscillations. Such a space would have the quasi-rigidity characteristic of a material nucleus rapidly revolving about a mean position. There is, however, no need to make any assumptions as to the nature of the internal character of the atomic nucleus with its encircling shell; it is not even necessary to assume that the complex is spherical. Under ordinary circumstances the complex can be regarded as the atom itself, since the so-called sphere of influence is the actual boundary by which we know and measure the behaviour of the atom. This is the concept of the atomic volume as pictured by D. I. Mendeléeff (1889), O. E. Meyer (1899), T. W. Richards (1901), etc.

In J. D. van der Waals' equation $(p+av^{-2})(v-b)=RT$, the term b represents the volume occupied by the substance, *i.e.* the molecular volume at absolute zero, since at this temperature v becomes equal to b and represents the volume occupied by the substance of the atoms—the atom nucleus as it may be called—but it is said to be four times the actual volume of the molecule. It is not practicable to compare the values of b for different substances because of the lack of data; but from the theory of corresponding states, it may be shown that the critical volume v_c is three times the value of b, or $v_c=3b$; and the so-called critical coefficient, T_c/p_c, or, the ratio of the critical temperature and critical pressure, is related to b by the expression $T_c/p_c=8b/R$, where R is the gas constant $pv/273$.

F. Exner[7] showed that, according to R. Clausius and O. F. Mossotti, $(\mu^2-1)/(\mu^2+2)$ is equal to the ratio of the volume actually occupied by matter to the apparent volume of the substance, when μ represents the refractive index for waves of infinite wave length, and it is found that μ^2 is equal to the dielectric constant. Consequently, as P. A. Guye has shown, the product of $(\mu^2-1)/(\mu^2+2)$ with the molecular volume will be a measure of the space filled by matter in a gram-molecule of a substance. Consequently, the magnitude b of J. D. van der Waals' equation, the critical volume, and the critical coefficient may be represented as functions of the molecular refraction. I. Traube has shown that b is between 3·5 and 4 times as large as the molecular refraction, MR, and P. A. Guye found the relation $MR=18T_c/p_c$. From I. Traube's result, it follows that atomic refraction can be employed as a measure of the material nucleus of an atom composed of a material nucleus and an encircling shell or sphere of influence. The sphere of influence represents a kind of shell about the atom nucleus, and it is presumably that portion of the atom which is permeable to light, and constitutes a dielectric medium which enables electromagnetic radiations to be transmitted through a body at a speed which is characteristic of the particular substance.

T. W. Richards[8] has shown that while it is assumed that the molecules of a gas are particles moving independently at some distance apart, it is doubtful if there are such interstitial spaces in liquids and solids. The impermeability of glass to oxygen, nitrogen, and water for long periods does not lend support to the view that there are empty spaces between the molecules; and he limits the permeability which has been observed in rigid compact solids, to such substances as can enter into the chemical structure of the solids themselves. It is therefore inferred that in solids and liquids the atoms formed of material nuclei with enveloping shell are in close contact with one another at the boundary of their envelopes. Such atoms are considered to be compressible and elastic; they can contract and expand, or vibrate among themselves even when their surfaces are closely packed together; and they are quite capable of sustaining and transmitting the vibratory motions called heat. E. Grüneisen's observations show that the compressibility of a number of metals—copper, silver, aluminium, iron, and platinum—loses only 7 per cent. in cooling from the ordinary temperature down to that of liquid air, and by extrapolation very little more diminution will occur in passing down to the temperature of absolute zero, so that it is probable that metals are as compressible at absolute zero as they are at ordinary temperatures. The value of b in J. D. van der Waals' equation is fairly constant over a wide range of pressure, but it suddenly begins to diminish when very high pressures have been attained. Again, for carbon dioxide, the value of b increases as the temperature rises, thus, if $a=0{\cdot}00874$, and $v=$unity at 0° and 760 mm., then $b=51$ c.c. per gram-molecule at 0°, and 64 c.c. at 100°. For hydrogen likewise, b is 13·8 c.c. at 0° and 15·1 c.c. at 100°. On the other hand, H. K. Onnes has shown that the apparent volume b of helium atoms is smaller at high than at low temperatures; at 0°, b is 12 c.c., and at 100°, 10·4 c.c. per 4 grms. of helium. This is not what would be anticipated, and T. W. Richards makes the tentative suggestion that "the greater velocity of the colliding atoms at the higher temperature has a greater compressing effect so that at high temperatures the atoms seem to occupy less space than at lower temperatures."

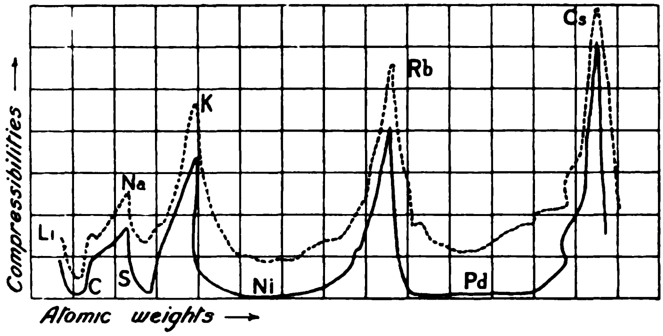


FIG. 4.—Compressibility and Atomic Volume Curves of the Elements.

T. W. Richards has shown that the compressibilities of the elements—*i.e.* the relative contractions in volume per megabar (0·987 atm.) per sq. cm.—are closely related to their atomic volumes, for the structure of the two curves is very similar as indicated in Fig. 4, where the atomic volume curve is dotted, and the compressibility curve is continuous. **The greater the densities of the elements the less their compressibility.** The elements with the larger atomic volumes are the more compressible and the more easily melted and volatilized. Consequently, the compressibilities of different substances are not only dependent on the magnitude of the applied pressure, but also on the internal pressure produced by the mutual cohesive attraction between the particles. In gases, the cohesive pressure is small, and accordingly the compressibility is large; in solids and liquids the cohesive pressure is large, and the compressibility is small. T. W. Richards' theory of compressible atoms thus reveals the existence of internal cohesive and affinity pressures holding the atoms and molecules together.

Cohesive pressure exerted by the cohesive forces which bind the molecules together.—Cohesion manifests itself in various ways; the most obvious is the mechanical resistance which a body offers to the separation of one part of a substance from another, and it appears more or less modified in such properties as ductility, malleability, tenacity, hardness, surface tension, volatility, etc. The density of a given substance is a manifestation of an internal pressure—the greater the density, the greater the internal pressure. When a rise of temperature produces a marked effect on the volume, it may be assumed that the internal pressure is less than when a rise of temperature produces only a slight effect on the volume. Substances in which the particles are held together by a high cohesive attraction are usually difficult to volatilize ; they have a small atomic volume ; a relatively large density ; a high surface tension ; high latent heat of evaporation ; and are least compressible. Conversely, if the atomic volume be relatively large owing to a small cohesive attraction, these substances will be most volatile and have the greatest compressibility. In illustration, T. W. Richards found that the three isomeric xylenes agree well with these deductions :

	o-Xylene.	*m*-Xylene.	*p*-Xylene.
Density (20°)	0·8811	0·8658	0·8611
Boiling point	144·0°	139·0°	136·2°
Compressibility (20°) . .	60×10^{-6}	$63{\cdot}5\times10^{-6}$	$66{\cdot}2\times10^{-6}$
Surface tension (20°) . .	3·09	2·96	2·92 mgrm. per mm.

T. W. Richards also compared some properties of two isomeric butyric esters, and found in each case :

	Specific gravity.	Compressibility.	Decrease in compressibility per 222 atm.	Coefficient of expansion.	Boiling point.	Surface tension.	Heat of vaporization.
Ethyl butyrate	0·8785	$76{\cdot}9\times10^{-6}$	$13{\cdot}6\times10^{-6}$	0·001247	120·8°	24·58	34·7
Ethyl isobutyrate	0·8710	$90{\cdot}8\times10^{-6}$	$15{\cdot}0\times10^{-6}$	0·001294	109·8°	23·30	33·9

The denser substance has the less compressibility, the less decrease in compressibility with an increase of pressure, the less coefficient of thermal expansion, the higher boiling point, the greater surface tension, and the greater heat of vaporization. All this is in accord with the assumption that a great cohesion produces an internal pressure which is effective in reducing the molecular volume. Hence it follows that not only is the atomic volume dependent upon the nature and location of the different atoms in the molecule, but also on the cohesive attraction of one molecule for another.

If the atomic volume be related with the cohesive pressure, and if the valency of an element in a compound be related with the atomic volume, it might be anticipated that the cohesion will be a function of the valencies of the combined elements. W. Sutherland found that the valencies of the elements in simple substances like sodium chloride influenced the cohesion, but he was unable to establish a relationship for more complex bodies. A. P. Mathews found empirically that the cohesion factor a of J. D. van der Waals' equation is related with Σv, the number of valencies, and the molecular weight M by the expression $a=0{\cdot}3125\times10^{-5}M\Sigma v$; and from the known relations of a to the critical constants T_c, v_c, and p_c, it follows that $Mp_c^{\frac{1}{2}}\Sigma v=0{\cdot}0043T_c^{3}$; and also that $M\Sigma v=4{\cdot}3\times10^{-5}(v_cT_c)^{\frac{3}{2}}$. A. P. Mathews uses these expressions for computing the valencies of chlorine, oxygen, sulphur, nitrogen, phosphorus, and the elements of the argon family.

Affinity pressure, produced by the chemical affinity or mutual attraction of adjacent atoms.—The atomic volume of an element depends on the nature of the associated atoms. In the middle of the eighteenth century, R. Kirwan sought to measure the force of the attraction between the atoms in a chemical compound from the diminution in volume which attended the union of two substances ; while H. Davy and others have alluded to the increase in density of the product of the union of two substances with a powerful affinity for one another. Thus, W. Müller-Erzbach (1881) said that in similarly constituted solids, those are the most stable which are formed with the greatest contraction—*e.g.* when lead replaces silver ; potassium, sodium ; or, when chlorine replaces bromine or iodine, contraction occurs, and the products of the replacement are the more stable. According to F. Ephraim and P. Wagner, the molecular volume of a stable compound is smaller than the sum of the volumes of its decomposition products, as shown by the schönites studied by A. E. H. Tutton. The double alkali magnesium sulphates have smaller molecular volumes than the copper or manganese salts, although the atomic volume of the metal is greater with the first than with the other two. The stability of the salts is more strictly parallel to their molecular volumes than to the atomic volumes of the free metals. The percentage contraction on the atomic volume rather than the actual contraction suffered by any particular atom is thus the important criterion of the stability of a compound.

D. I. Mendeléeff has shown that the greater the affinity of the elements for one another, the less the atomic volume of the resulting compound. Thus the contraction which occurs during the formation of potassium or sodium oxide is greater than in the formation of stannic oxide. As V. Braun expressed it, the specific gravity of solid chemical compounds is high in proportion to the intensity of the affinity which unites their components, and G. S. Johnson inferred that the affinity of iodine in potassium tri-iodide is small because combination occurs without contraction. W. Müller-Erzbach and I. Traube have emphasized the same idea. Other things being equal, **elements with the greatest densities have the least chemical affinity and suffer least change in their atomic volumes when they enter into combination**—these elements will be found distributed about the troughs of the curve, Fig. 4. Conversely, **elements with the smallest densities are usually most energetic chemically and suffer the greatest contraction in their atomic volumes when they form chemical compounds**—these elements will be found distributed about the peaks or crests of the curve, Fig. 4.

The fact that the less the density, or the greater the compressibility of an element, the greater its contraction on combination, is best illustrated by comparing the contractions occurring during the formation of similar compounds of the elements having widely different compressibilities but similar affinities. Strontium and lead are not very different in cohesive pressure as shown by the closeness of their boiling points. When a gram-atom of strontium unites with a gram-molecule of chlorine, there is a contraction of 32·6 c.c., and lead gives under similar conditions a contraction of 20·1 c.c. If affinity causes contraction this is just what would be anticipated because the affinity of strontium for chlorine is greater than that of lead; this is confirmed by the respective heats of formation 772 and 346 kilojoules per gram-molecule. The compressibilities of the elements of the alkali metals and the contractions which occur, in c.c. per gram-molecule, when the corresponding chloride is formed, are as follows:

TABLE IX.

Element.	Compressibility.	Contraction (c.c. per gram-molecule).
Lithium	$9{\cdot}0 \times 10^{-6}$	17·6
Sodium	15·6	21·5
Potassium	31·7	33·1
Rubidium	40·0	36·8
Cæsium	61·0	53·6

Not all examples will give such unequivocal evidence of the effect of chemical affinity in determining the atomic volumes of liquids and solids, because the effects of chemical affinity will be modified or even overshadowed by the effects of cohesion. Both must always be present, and it may be difficult to discriminate between the two effects. Similarly, the heat of formation Q of a compound runs parallel with the free energy, and may be regarded as proportional to the work done by the affinity pressure between two elements. Similarly, when two elements unite, the contraction Δ is evidence of the affinity uniting the elements. The contraction Δ

is the difference between the molecular volume of the compound, and the sum of the atomic volumes of the component elements in a free state. The quotient of the volume contraction, Δ, by the heat of formation, Q, will give a measure of the average compressibility. In Table X, T. W. Richards showed that the compressibility effect with the alkali halides must be the same in each member of the series, and the values of Δ/Q for the different salts should fall in the same order of magnitude as the compressibilities of the free alkali metals if the hypothesis relating affinity pressure to compressibility be correct. This is actually the case.

Table X.—Compressibilities and Affinity Pressures of the Alkali Halides.

Salt.	Compressibility of metal.	Sum of atomic volumes.	Molecular volume.	Contraction Δ.	Heat of formation Q.	$\frac{\Delta}{Q}$
LiCl . .	$8{\cdot}8\times10^{6}$	37·7	20·9	16·8	383	4·4
NaCl . .	13·4	48·7	27·2	21·5	399	5·4
KCl . .	31·5	70·0	37·8	32·2	427	7·6
LiBr . .	8·8	38·8	25·2	13·0	334	3·9
NaBr . .	13·4	49·2	34·2	15·0	359	4·2
KBr . .	31·5	70·5	44·2	26·3	398	6·6
LiI . .	8·8	38·4	33·1	5·3	257	2·1
NaI . .	13·4	49·4	41·4	8·0	289	2·8
KI . .	31·5	70·7	53·8	16·9	335	5·1

In the light of T. W. Richards' hypothesis, we can also see that for H. Kopp's rule to be valid the internal pressures of all compounds at their boiling points should be the same—subject to small variations due to differences in molecular complexity. The intense intermolecular pressures under which the molecules exist modify the boiling points, the surface tensions, the viscosities, etc. The effects produced by cohesive and affinity pressures on atoms with an elastic compressible envelope, as postulated by T. W. Richards, show that the volume occupied by an atom in the free state cannot be the same as in the combined state, and that the volume of an atom in combination will vary with the nature and orientation of the other atoms with which it is combined.

H. Schröder[9] worked on the subject of atomic volumes simultaneously with H. Kopp; he accepted F. Ammermüller's conclusion that equal volumes of the two oxides of copper contain the same amounts of copper, and multiple amounts of oxygen, and assumed that in the two compounds with the atomic volumes: $Cu_2O=24{\cdot}36$; and $CuO=12{\cdot}35$ or $Cu_2O_2=24{\cdot}70$, the quantities of copper are the same, and that the volume of the copper is in each case the same. The volume occupied by the oxygen in cuprous oxide then stands to that in cupric oxide as 1 : 2. H. Schröder concluded with H. Kopp that the molecular volume of a compound is the sum of the volumes of the component atoms. The former considered that the atomic volume of a given element under similar structural conditions throughout all its compounds is variable—the latter assumed that under these conditions the atomic volume of an element is constant. The different atomic volumes which an element can assume in different compounds were regarded by H. Schröder to be simple multiples of a certain unit volume which he called the *stere*. The stere is not the same for all elements, but it varies within comparatively narrow limits. When two elements are combined, one of them assumes the unit volume of the other, so that the stere of one element dominates the volume of the compound, and the molecular volume of the compound may be represented as a simple multiple of the stere of one of the contained elements. For example, the stere of silver is 5·14, and the atomic value is twice this, namely, 10·28, so that metallic silver occupies 2 steres.

	Stere value.	Molecular volume. Calculated.	Molecular volume. Observed.
Silver oxide	$5·14 \times 6 =$	30·8	30·8
Silver chloride	$5·14 \times 5 =$	25·7	25·8
Silver bromide	$5·14 \times 6 =$	30·8	30·8
Silver iodide	$5·14 \times 8 =$	41·1	41·8

Hence, the atomic volume of oxygen is $\frac{1}{2}(6-2)=2$ silver steres; of chlorine, $5-2=3$ silver steres; of bromine, $6-2=4$ silver steres; and of iodine, $8-2=6$ silver steres. The general conclusion is that the volumes of equivalents of different elements are approximately equal, or stand in some simple relation with one another. This naturally raises the question whether there is any connection between the valency of the atoms and its effect on the molecular volume. In a general way, an increase in the valency of an atom is attended by an increase in the molecular volume, although, as W. Städel has shown, the molecular volume is influenced by all the atoms in the molecule. G. le Bas [10] compared the molecular volumes of eighteen hydrocarbons of the paraffin series at their melting points, and found that the quotient, obtained by dividing the molecular volume by the total number of valencies of the carbon and hydrogen atoms present, is a constant—very nearly 2·97. In illustration, the molecular volume of dodecane, $C_{12}H_{26}$, is 219·9; there are 12×4 carbon valencies, and 26 hydrogen valencies, or a total of 74 valencies; consequently $219·9 \div 74 = 2·971$. The constant 2·97 thus represents one unit of valency in these compounds.

I. Traube [11] has investigated molecular volumes from a novel point of view. He takes the specific gravity at ordinary temperatures—usually about 15°—and he also allows for the association of the substance. I. Traube defines the *molecular solution volume*, V_m, of a substance in water by the relation

$$\text{Molecular solution volume, } V_m = \frac{M+A}{D_s} - \frac{A}{D_w}$$

where M denotes the molecular weight of the dissolved substance, D_s and D_w are the specific gravities respectively of the solution and of water, and A denotes the number of grams of water in which a gram-molecule of the substance is dissolved. If v denotes the ordinary molecular volume, defined by M/D, the difference $v-V_m$ denotes the contraction which occurs in the process of solution, and is called the *molecular contraction*, and it is found that if ionization and association effects are eliminated, the molecular contraction has the constant value $v-V_m=13·5$ c.c. per gram-molecule.

If ionization occurs, the number of ions which in their action are equivalent to non-ionized molecules must be taken into consideration. If α denotes the degree of ionization of a solute decomposed into n ions, then, in place of 13·5 c.c., the molecular contraction $=13·5\{1+(n-1)\alpha\}$. If association occurs, the association factor must be considered. The association factor is a number which represents how many times the molecular weight of a substance is greater than corresponds with the simple gaseous molecule. In place of 13·5 c.c. the molecular contraction is $13·5/\beta$ c.c. per gram-molecule.

The molecular solution volume can be calculated from the volume constants of the constituent elements according to H. Kopp's additive rule, and the introduction of a correction factor. I. Traube found that this correction factor is a constant 12·4 c.c., so that if $n_1, n_2, \ldots$ denotes the respective number of atoms of atomic volume $A_1, A_2, \ldots$; and $\Sigma nA = n_1A_1 + n_2A_2 + \ldots$

$$\text{Molecular solution volume, } V_m = \Sigma nA + 12·4$$

The term ΣnA also includes a correction term for multiple bonds, etc.

By empirical calculation from the observed molecular volumes, I. Traube has computed the solution volume constants in c.c. per gram-atom for different radicles. He obtains: C, 9·9; H, 3·1; F, 5·5; Cl, 13·2; Br, 17·7; I, 21·4; CN, 13·2; Na, 3·1; N^{III}, 1·5;

N^{V}, 10·7; P^{III}, 17; P^{V}, 28·5; double bonds, −1·7; triple bonds, −3·4; Hydroxylic oxygen (OH), 2·3; Hydrosulphylic sulphur (HS), 15·5. Oxygen atoms united to carbon by a double bond, 5·5; sulphur atoms united to carbon by a double bond, 15·5; oxygen atoms in a carbonyl group, or united to a carbon atom with a hydroxyl group attached to it, 0·4. The observed density of ether, $(C_2H_5)_2O$, is 0·7201 at 15°; the molecular weight is 74. Compare the observed and calculated molecular volume. The observed value is $74/0{\cdot}7201=102{\cdot}7$; the calculated value is $(4\times9{\cdot}9)+(10\times3{\cdot}1)+5{\cdot}5+25{\cdot}9=102{\cdot}0$.

If as before v denotes the molecular volume, and if there is no ionization, $v-V_m=13{\cdot}5/A$, then $v=\Sigma nV+12{\cdot}4+13{\cdot}5/\beta$, where the association factor β is usually nearly unity—*e.g.* with phosphorus trichloride, and carbon and silicon tetrachlorides, β=unity; for benzene, $\beta=1{\cdot}18$; for toluene, 1·08, etc.—but with water $\beta=3{\cdot}06$; formic acid, 1·8; acetic acid, 1·56; methyl alcohol, 1·79; ethyl alcohol, 1·67, etc. When β is unity $V_m=\Sigma nA+12{\cdot}4$; and

$$\text{Molecular volume, } v=\Sigma nA+25{\cdot}9$$

meaning, according to I. Traube, that "in the formation of any molecule from its atoms there is always a dilation; the molecular dilation is the same or nearly the same for all substances; it is independent of the chemical nature of the substance and can be only slightly modified by constitution; and at 15°, the molecular solution volume in aqueous solution is 12·4 c.c. per gram-molecule, and the molecular volume 25·9 c.c. per gram-molecule." Given the molecular volume it is possible to calculate the association factor which may or may not agree with that deduced by other methods.

I. Traube regards ΣnA as the sum of the spaces occupied by the matter of the atoms of a molecule. While the internal or nuclear volume of a molecule is the space actually filled by the mass of the atom, the external volume is the nuclear volume increased by the volume of a shell of combined æther. The external atomic volume corresponds with the magnitude b of J. D. van der Waals' equation, and is 3·5 to 4 times as large as the internal or nuclear volume. The difference $V_m-\Sigma nA$ gives what I. Traube calls the **molecular co-volume**—symbolized Co_v. The co-volume is a magnitude dependent on the temperature; for 15°, the molecular co-volume is 25·9 c.c., and at θ°, the molecular co-volume is $Co_{v_0}(1+0{\cdot}00367\theta)$, or the

$$\text{Molecular co-volume, } Co_v=24{\cdot}5(1+0{\cdot}00367\theta)$$

very nearly. There is a close formal analogy between the temperature effect of the co-volume and the volume of gas. Since, for every newly formed gram-molecule there is an expansion equal to the co-volume, and for every molecule which disappears there is a corresponding contraction, I. Traube concluded: "In a reaction between homogeneous liquids, the co-volumes of the initial and final products of the reaction stand in a simple rational ratio"—this is J. A. C. Charles' law applied to liquids. Since also I. Traube assumed that the molecular volume is the sum of the true molecular volume and the co-volume, Avogadro's rule applied to liquids becomes "with the same conditions of temperature and pressure, the co-volumes, or the volumes in which the molecules move, are all equally great."

I. Traube's method can be employed for calculating the molecular volume, and also the molecular weight M of an unknown substance of known specific gravity D. In this case, since $v=M/D$, the chemical formula which gives the closest value to

$$\frac{M}{D}-\Sigma nA=25{\cdot}9$$

is the desired chemical formula. Many examples will be found in H. Biltz's *Die Praxis der Molekulargewichtsbestimmung* (Berlin, 1898; Easton, Pa., 1899).

The observed specific gravity of tetrachloroethane is 1·6258 (15°), the empirical formula by analysis is $CHCl_2$. Hence, if the formula $CHCl_2$ obtains, the ratio $M/D=51{\cdot}6$ and $\Sigma nA=39{\cdot}4$, or $M/D-\Sigma nA=12{\cdot}2$; if the formula be $C_2H_2Cl_4$, $M/D-\Sigma nA=103{\cdot}2-78{\cdot}8$

$=24{\cdot}4$; and if the formula be $C_3H_3Cl_6$, $M/D-\Sigma nA=154{\cdot}8-118{\cdot}2=36{\cdot}6$. Here then 24·4 approximates closest to the theoretical co-volume 25·9, and the formula is accordingly $C_2H_2Cl_4$.

According to I. Traube, the **atomic co-volume** is the difference between the internal and external atomic volumes; and it represents the volume of the combined æther. I. Traube further postulates that the atomic co-volume is occupied by the valency electrons, *i.e.* the electrons which endow the atom with valency; for, unlike the molecular co-volume, the atomic co-volume varies in size and is proportional to the nuclear volume and the valency of the atom. I. Traube employed molecular refraction as a measure of the nuclear volumes of the atoms in a compound and found that the molecular refractive power, MR, of a saturated compound is proportional to the total number of valencies, n, of the component atoms. The value of the quotient MR/n for a large number of compounds deviates but little from the mean 0·787. I. Traube calls 0·787 the *refraction stere*—in illustration, the molecular refraction of alcohol, C_2H_5OH, is 12·71, and n is $8+5+2+1=16$; and $12{\cdot}71\div16=0{\cdot}794$. The nuclear volumes of the atoms in a molecule are therefore proportional to the valencies of the atoms.

W. C. Roberts-Austen[12] suggested that the remarkable influence of traces of elements on masses of metals is proportional to the atomic volumes of the contaminant. He showed that the metals or metalloids near the troughs of L. Meyer's periodic curve, Fig. 4, Cap. VI, do not diminish the tensile strength of gold; and that the metals which render gold fragile occupy high positions on the curve. Hence he argues:

> There is some relation between the influence exerted by the metallic and other impurities and either their atomic weights or their atomic volumes. It seems hardly probable that it is due to atomic weight, because copper, with an atomic weight of 63·2, has nearly the same influence on the tenacity of pure gold as rhodium, with an atomic weight of 104, or as aluminium, the atomic weight of which is 27·0. It will be evident from the following table, which embodies the results of the author's experiments, that metals which diminish the tenacity and extensibility of gold have high atomic volumes, while those which increase those properties have either the same atomic volume as gold, or a lower one. Further, silver has the same atomic volume as gold, 10·2, and its presence in small quantities has very little influence, one way or the other, on the tenacity or extensibility of gold.

It is suggested that the atoms with a small atomic volume can fill up interstitial spaces which would otherwise remain void and this without disturbing the disposition of the other atoms, while atoms with a large atomic volume act prejudicially by driving the atoms further asunder. The following experiment by E. Warburg and F. Tegetmeier illustrates a porosity in solids which will permit the passage of elements with a small atomic volume, but strain off those with a larger atomic volume.

> A cell with a glass partition with sodium amalgam about the anode and mercury about the cathode was heated to between 100° and 200°—when the glass became slightly conducting. In about 30 hrs. an appreciable quantity of sodium had passed from the glass into the mercury. The glass remained transparent, for the sodium lost by the glass was replaced by that from the mercury amalgam. W. C. Roberts-Austen showed that in the electrolysis of the glass, the passage of the sodium follows the ordinary law of electrolysis. If lithium amalgam be used, the glass becomes opaque, and then lithium accumulates in the mercury. The glass loses no potassium, but 7·8 per cent. of sodium, and gains 4·3 per cent. of lithium. With potassium amalgam, the potassium does not replace the sodium lost by the glass. It is suggested that the lithium atoms with an atomic volume 15·98 can replace sodium atoms with an atomic volume 16·04, while potassium atoms with an atomic volume 24 are too large to take the place of the smaller sodium atoms. The glass diaphragm has thus been said to act as a mechanical sifter for the potassium atoms.

The simple relation between atomic volumes and tenacity is no doubt modified when compounds are formed. F. Osmond also showed that elements with a smaller atomic volume than iron retard the transformation of β to α iron, while elements with a larger atomic volume than iron either have no influence upon the transition temperature or else raise that temperature.

Several investigators have traced the influence of the atomic volume of a metal on the mechanical properties ; for example, A. Wertheim and H. Tomlinson have shown that there is a relation between the atomic volume and elasticity ; W. Sutherland, between the atomic volume and rigidity ; R. A. Fessenden, between atomic volume and cohesion ; and H. Crompton, between the latent heat of fusion and the molecular volume of a compound. H. Crompton also showed that the molecular heat of fusion L; the absolute fusion temperatures T; and the valencies n of the elements, are so related that L/Tn is a constant; and that a similar rule holds for compounds. From I. Traube's relation between valency and atomic volume, it therefore follows that the latent heats of fusion are a function of the molecular volumes, or of the sum of the atomic volumes. Hence also the latent heat of fusion must be a function of the sum of the valencies of the atoms in a molecule.

W. Barlow and W. J. Pope [13] assume that each atom of a crystalline compound occupies a definite space or sphere of influence, so that each atom has its own polyhedral cell or domain throughout which its influence is predominant; that the space occupied by a substance is partitioned into atomic domains of definite volume; that the mode of arrangement of such atoms determines the shape of the molecule ; that the atoms are held in place in stable equilibrium by the balancing of interatomic attractive and repulsive forces ; that the atoms are incompressible but deformable; that the atoms are closely packed by the squeezing together of the spheres so that the interstices are filled, while the volumes of the polyhedral forms which the atoms assume remain constant ; and that the homogeneous structure of a crystal is obtained by a symmetrical arrangement of the atomic spheres of influence. It is further shown that any symmetrical and homogeneous aggregate of closely packed atomic spheres, can be divided into space units which represent in composition and configuration the chemical molecule ; and that the dimensions of each of these units will be in accord with the crystal form of the compound. As G. D. Liveing (1891) remarked, "The problem is then reduced to finding how to pack the greatest number of equal spherical balls into a given space." When two or more arrangements, equally closely packed, are possible, each may occur and polymorphism will result.

W. Barlow and W. J. Pope assume that the relative volumes of the atoms of a compound—the atomic domains—are proportional to their valencies, so that the valency of an atom expresses the relative atomic volume ; or *the valency of an atom is proportional to the space occupied by that atom in a crystalline compound*—**valency volume**. For example, in benzene, the volume of one carbon atom is four times that of four hydrogen atoms because the valency of carbon is four, and of hydrogen one. The atomic volume of the same element or radicle may be different in different bodies. For example, A. E. H. Tutton has shown that the potassium and cæsium sulphates

	Molecular volume,	Axial ratios, $a : b : c =$
K_2SO_4	94·91	0·5727 : 1 : 0·7418
Cs_2SO_4	84·58	0·5712 : 1 : 0·7531

so that the substitution of an atom of cæsium for potassium lowers the molecular volume while the configuration of the molecules as shown by the axial ratios $a : b : c$ remains virtually unchanged. The cæsium atom enters the molecule in a definite position, and therefore it does not seem possible for the configuration of the molecule to remain constant unless the sulphuric acid group increases in the same ratio. This shows that the absolute atomic volume of an element may vary in different chemical bodies, though the valency volume, the ratio of the volume of any constituent to the volume of the whole molecule, may remain constant.

W. Barlow and W. J. Pope build up structures representing various chemical molecules by closely packing deformable spheres in a homogeneous symmetrical arrangement, and they deduce the dimensions of the crystalline form of each substance. For example, they show that with equal spheres the dimensions of the aggregate will have holohedral cubic or hexagonal symmetry, and the axial ratio $a : c$ with the latter must be either $a : c = 1 : 0{\cdot}8165$ or $a : c = 1 : 1{\cdot}4142$. Hence, in substances built up with atomic domains of equal size—elements, and binary compounds of elements with the same valency—the crystalline forms must be either cubic or hexagonal. Of the forty elements whose crystals have been examined, half are cubic, and one-third are hexagonal with axial ratios in accord with the theoretical requirements. The remaining six are either pseudo-cubic or pseudo-hexagonal, and their exceptional behaviour is explained by assuming that the atomic spheres are packed in groups or aggregates so that some of the spheres are differently situated in a close-packed homogeneous assemblage. Again, with the binary compounds of the elements, J. W. Retgers found 88 per cent. of the known forms are either cubic or hexagonal, and nearly all of these are composed of elements of equal valency. For example :

Beryllium oxide, BeO .	$a : c = 1 : 1{\cdot}6305$	Zinc sulphide, ZnS . .	$a : c = 1 : 1{\cdot}8175$
Zinc oxide, ZnO . .	$1 : 1{\cdot}6077$	Cadmium sulphide, CdS .	$1 : 1{\cdot}8109$

In some cases in place of holohedral symmetry, these binary compounds exhibit hemihedrism or tetartohedrism, a state of things which occurs with symmetrical arrangements of two kinds of spheres of slightly different size.

The geometrical laws which govern the replacement of spheres in a closely packed assemblage by others of different size run parallel with the chemical laws which determine the relations between the valencies of the elements which can replace one another in a chemical compound. It is said that all cases of substitution can be reduced to one of two types : (i) those in which the sum of the valencies of the substituting and substituted atoms or groups is constant—*e.g.* the substitution of hydrogen by chlorine ; and (ii) those in which the sum of their valencies differ —*e.g.* the substitution of hydrogen by methyl.

In substitutions of the first type, virtually no change occurs in the configuration of the molecule. This is taken to be exemplified by B. Gossner's study of the rhombic chloro- and bromo-ethanes—Table XI. :

TABLE XI.

	Molecular volume.	Valency volume.	Axial ratios $a : b : c$.	Equivalence parameters $x : y : z$.
$Cl_3C.CCl_3$ . .	113·34	14	0·5677 : 1 : 0·3160	2·4260 : 4·2733 : 1·3503
$Cl_3C.CBr_2Cl$ . .	116·72	14	0·5612 : 1 : 0·3171	2·4047 : 4·2849 : 1·3587
$Cl_2BrC.CBrCl_2$.	120·16	14	0·5646 : 1 : 0·3192	2·4090 : 4·2669 : 1·3620
$Br_3C.CBr_3$ . .	131·83	14	0·5639 : 1 : 0·3142	2·4197 : 4·2911 : 1·3483
$HBr_2C.CBr_3$ . .	126·46	14	0·5650 : 1 : 0·3118	2·4294 : 4·2995 : 1·3406

The equivalence parameters x, y, z here represent the three dimensions of the molecular volume reduced to a volume proportional to the valency volume. The constancy of the values x, y, z is taken to mean that while the absolute volumes of the molecules vary, the configuration of the molecules undergoes no change. This means that the ratio of the volumes of substituting and substituted atoms to the volume of the whole molecule is constant. If it were not so, the configuration of the molecule would change. Hence, the relative volumes of hydrogen, bromine, and chlorine are proportional to their valencies.

With substitutions of the second type, the dimensions of the molecule do change, and the change is proportional to that of the valency of the atoms or radicles concerned. For example, with the minerals, chondrodite, humite, clinohumite, and forsterite, studied by S. L. Penfield and W. T. H. Howe—Table XII, T. V. Barker emphasized the fact that prolectite has not been analyzed, and that W. Barlow and W. J. Pope credit the mineral with the composition indicated in the table solely because its axial ratio has the value there indicated.

TABLE XII.

	Valency volume *w*.	$a:b:c.$	$x:y:z.$
Forsterite, Mg_2SiO_4 . . .	16	0·9296 : 1 : 2·4492	2·4492 : 2·2769 : 2·8691
Prolectite, $MgSiO_4.2Mg(F, OH)$.	22	1·0803 : 1 : 2·3877	2·3877 : 2·2102 : 4·1689
Chondrodite, $Mg_3(SiO_4)_2.2Mg(F, OH)$	38	1·0863 : 1 : 3·1447	2·4294 : 2·2333 : 7·0199
Humite, $Mg_5(SiO_4)_3.2Mg(F, OH)$.	54	1·0802 : 1 : 4·4033	2·4279 : 2·2475 : 9·8965
Clinohumite, $Mg_7(SiO_4)_4.2Mg(F,OH)$	70	1·0803 : 1 : 5·6588	2·4347 : 2·2769 : 12·8691

The minerals differ by the constant increment of the group Mg_2SiO_4, which corresponds with forsterite, which has the $a : b$ ratio common to the whole series, while the $c : b$ ratio closely expresses the successive increments of the c-axis. This indicates that possibly the structural units of chondrodite, humite, and clinohumite are nothing more or less than the structural unit of prolectite on which have been superposed one, two, and three structural units of forsterite. The Mg_2SiO_4 group enters the molecule in the z direction, since the values of x and y remain nearly constant. Hence, say W. Barlow and W. J. Pope, the volume of the molecule is proportional to z; but the ratio of the valency-volume $w : z$ is nearly constant, so that the volume is proportional to the valency; consequently, it follows that the axial ratios $a : b : c$, and the equivalence parameters $x : y : z$, can be predicted for some member of a series when these values for other members are known. T. V. Barker has shown that the close correspondence between fact and theory is due to the closeness with which the hypothetical valency volumes satisfy the conditions : volume of Mg_2SiO_4 : volume of $Mg(F,OH)_2 = 2 : 1$, and that the particular volumes arbitrarily selected by W. Barlow and W. J. Pope present one out of an infinite number of such solutions. Furthermore, when the minerals are arranged in accord with chemical composition, the order is not that of the accepted axial ratios, but forsterite, clinohumite, humite, chondrodite, and prolectite. There is very little difference in composition between clinohumite and forsterite, even the end-member prolectite differs from forsterite only by the amount of $Mg(F,OH)_2$. The group, indeed, is to be regarded as a series of varieties of forsterite with variable amounts of $Mg(F,OH)_2$, until further investigation has established the individuality of the mineral species.

It has been noticed that water of crystallization causes the expansion of the molecule mainly in one direction, showing that the water of crystallization probably enters the crystal structure in layers. With double salts there is usually a simple numerical relation between the valency values of the components which results geometrically from the packing. Thus, with potash alum, $K_2SO_4.Al_2(SO_4)_3.24H_2O$, the valencies of the component parts are in the ratio 14 : 36 : 96, which is nearly 1 : 3 : 8.

In a close-packed assemblage of spheres, certain groups of spheres may be situated so that they can be moved without affecting the arrangement of the others, and other spheres can be fitted into the resulting cavities so as to reproduce the original arrangement. Equivalent atoms or groups of atoms can replace others of the same volume without change of structure since, by hypothesis, valency is proportional to the relative volumes. Stable systems of related substitution products lead to likeness in crystal form—isomorphism. Equivalent atoms, though nearly equal, may differ slightly in volume, for A. E. H. Tutton, in his work on the alkali sulphates and selenates, obtained the following results, indicated in Table XIII:

TABLE XIII.

	Molecular volume.	Valency volume.	$x:y:z$.
K_2SO_4	64·91	12	2·2109 : 2·1977 : 2·8463
Rb_2SO_4	73·34	12	2·2049 : 2·1899 : 2·8648
Cs_2SO_4	84·58	12	2·2003 : 2·1826 : 2·8777
K_2SeO_4.	71·67	12	2·2207 : 2·2083 : 2·8204
Rb_2SeO_4	79·94	12	2·2147 : 2·1957 : 2·8412
Cs_2SeO_4	91·09	12	2·2112 : 2·1900 : 2·8524

The difference in the values of x, y, z indicate slight differences in the configuration of the molecules, corresponding with slight differences in the volumes of the atoms of potassium, rubidium, and cæsium. The atomic volumes of elements in the same group of the periodic classification probably increase slightly with increasing atomic weight. This principle gives an explanation of; (1) The difference in the crystal forms of the acids and many of their salts—*e.g.* H_2SO_4 and K_2SO_4—by the difference in the atomic volumes of hydrogen and potassium. (2) The isomorphism of salts of different acids—plagioclase felspars, $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$. Here NaSi- and CaAl-groups have the same molecular volume and hence can replace one another. (3) The isomorphism of complex bodies not observed in simple bodies. (4) The variation in the form of the crystal when replacing atoms with the same valency-volume but different in form—*e.g.* the substitution of a NO_2-group by a methyl or CH_3-group.

If like spheres are removed homogeneously from an assemblage of molecules and replaced by larger spheres or groups of spheres the walls of the cavity will gape. Close packing can be restored by inserting new spheres in the gap so produced, and the volume of the gap will be equal to the difference in volume of replaced and replacing spheres. If v be the volume of spheres replaced, the volume of replacing spheres to produce close packing will be v; $v+1+1$ or $v+2$; $v+2+2$ or $v+4$; and generally $v+2n$; that is, the volume of replacing spheres differ by intervals of 2. Chemically this means that the valencies of multivalent elements differ constantly by intervals of 2. The change in valency by intervals of 2 involves no variation in the actual volume of the atom. Thus, cæsium can combine with iodine to form CsI, CsI_3, CsI_5, CsI_7, and CsI_9.

In general, if the volume m be replaced by a volume $n+m$, an additional volume n must be added to conserve the marshalling—thus, if a univalent hydrogen atom be replaced by a quadrivalent carbon atom, an additional three valencies are required. Again, in replacing an H-atom by an oxygen atom in ethane, the further addition of an atom of unit valency is required to produce C_2H_5OH. Again, in three molecules of benzene, three hydrogen atoms may be substituted by a nitrogen atom to form triphenylamine, $(C_6H_5)_3N$, but if a carbon atom takes the place of three hydrogen atoms an additional hydrogen atom is required to form triphenylmethane, $(C_6H_5)_3CH$. The apparent isomorphism of salts like sodium nitrate, $NaNO_3$, and calcium carbonate, $CaCO_3$, is likewise explained by the volume-valency hypothesis.

The hypothesis that each valency in a given compound has the same volume is not generally accepted. T. W. Richards, for instance, argues that the relationship between benzene and tetrabromobenzene lands its supporters in an impossible position since it requires the subsidiary assumption that all the remaining carbon and hydrogen atoms in benzene should nearly double their volume when four atoms of bromine are substituted for hydrogen. It is more in accord with H. Kopp's observations that the atomic volume of hydrogen in combination is much larger than that of free hydrogen. In the nitro-dihalogeno-benzenes, observed by E. Repossi, the introduction of chlorine causes a marked shortening of the *b*-axis; and in the rhombic chloro- and bromo-ethanes, observed by B. Gossner, the symmetrical substitution of chlorine lengthens the *a*-axis in relation to the *b*-axis, and the unsymmetrical substitution of the same element shorten the *a*-axis. In these and many other examples there are real differences in the molecular volume and crystalline form; but the greatest variation occurs with the molecular volume, probably because a change in volume produces only the cube root of its proportional effect when applied in any one axial direction. The atomic volumes of chlorine and bromine respectively at —33·5° and 63°—which are like fractions of their boiling points—are 21·8 and 25·5 respectively. Although the atomic volumes change when these elements enter into combination, under similar conditions, the chlorine would be expected to occupy less space than bromine, and this is what is actually observed. It is urged that the method of equivalence parameters employed for testing the hypothesis of valency-volume is a mathematical device which has the effect of reducing widely deviating data to apparent harmony; and of hiding differences in crystal forms. The observed data are the axial ratios $a:b:c$. According to W. Barlow and W. J. Pope, the molecular volumes of liquids of normal paraffins calculated on the basis that one volume of carbon is equal to four volumes of hydrogen ($H=2·97$ c.c.; $C=11·88$ c.c.) are in close agreement; but T. W. Richards showed that the agreement is quite as good when calculated on other hypotheses, say, when the atomic volume of carbon is twice that of hydrogen.

T. V. Barker has shown that on the volume-valency hypothesis the atomic units in potassium chloride are approximately the same, as they are likewise in potassium iodide; consequently, since the atomic volumes of these two salts are respectively 37·49 and 53·06, the atomic volumes of the potassium atoms in these salts are respectively 18·74 and 26·53. There is every reason to believe that the atomic volume of an element in the free state may be much greater than when it is combined, so that there is no inherent objection to the hypothesis that the atomic volume of an element varies a little in its different forms of combination. Again, T. V. Barker has shown that the molecular volumes of potassium and ammonium iodides are respectively 53·06 and 59·62. On the volume-valency hypothesis, "the iodine atom in potassium iodide has a volume equal to 26·53, but in the ammonium compound the iodine can only have one-eighth the volume of the molecule, since the total valency-volume is eight—that is, volume of the iodine equals 7·45. It must be assumed that when potassium is substituted by ammonium the iodine atom experiences a shrinkage equal to about five-sevenths of its volume in the potassium compound. Is it likely that this is really the case? It must be remembered that a comparison is not being made between the atomic volumes of an element in the free and combined conditions, but rather its atomic volume in two compounds which have an extraordinarily close chemical relationship." A. E. H. Tutton adds that to explain the incontrovertibly proved iso-structure of ammonium and rubidium sulphates, where there are 24 valency-volumes in the former cases and only 12 in the latter, it is necessary to assume arbitrarily that the actual spheres of atomic influence in the former are on a smaller scale—one-half indeed—than in the latter in order to afford in the total the same volume. The congruency of the monoclinic ammonium and rubidium nickel sulphates or selenates shows that the replacement of two atoms of univalent rubidium by eight atoms of univalent hydrogen and two atoms of ter- or quinque-valent nitrogen, produces no opening up of the structure. This fact, says A. E. H. Tutton, is in entire antagonism with the hypothesis of valency-volume of W. Barlow and W. J. Pope.

T. V. Barker concludes from his study of the valency-volume theory that so far "the theory has received no general crystallographic support." A. Ogg and F. L. Hopwood also concluded from the X-ray spectrometric examination of the ammonium and alkali metal sulphates, that the replacement of eight potassium atoms by forty atoms of the four NH_4-radicles produces so little difference from what the replacement by eight rubidium atoms produces on the dimensions of the elementary cell, as to furnish " conclusive evidence against the general truth of the theory of crystal structure based on the closest packing of the constituent atoms or their spheres of influence."

W. J. Sollas[14] assumed that, with the haloids of the alkali metals, the structural unit is an aggregate of four molecules. He further assumes generally that the structural units are proportional to the atomic volumes, not of the free elements, but of the elements in the compounds concerned; nor is the sum of the atomic volumes equal to the molecular volume, for an allowance is made for interstitial space. W. J. Sollas also assumed that the structural units are loosely packed; he builds up structures with his units which give results in harmony with the observed geometrical forms of the crystals and with some of their physical properties. He has applied the hypothesis to the alkali halides, silver iodide, titanium dioxide, and cassiterite. T. V. Barker adds that loose packing is equivalent to assuming that some of the atoms have a greater volume than is initially supposed, and with sufficiently loose packing, it does not seem difficult to obtain any structure whatever irrespective of the atomic volumes.

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CHAPTER VI

THE CLASSIFICATION OF THE ELEMENTS

§ 1. The Classification of the Elements

> Most of our systems of classification are artificial and without distinct lines of demarcation. Being based upon limited knowledge, they have been formed upon apparent rather than upon real similarities and differences; and they are to our minds but artificial aids, like crutches to cripples.—G. GORE (1878).

THE classification of the elements has long been an attractive subject. It is only by the aid of classification that the mind of man is able to cope with the multitudinous facts presented by nature. In the words of F. Bowen (1866) [1]:

> The first necessity which is imposed upon us by the constitution of the mind itself, is to break up the infinite wealth of Nature into groups and classes of things with reference to their resemblances and affinities, and thus to enlarge the grasp of our mental faculties, even at the expense of sacrificing the minuteness of information which can be acquired only by studying objects in detail.

The primary object of classification is to arrange the facts so that we can acquire the greatest possible command over them with the least possible effort. This is accomplished by arranging the facts in a systematic way. In all systems of classification, the elements are assembled in a few groups or classes so that the members of each group possess in common the greatest possible number of important attributes; and the attempt is made to collect together in one group the elements which are alike in general properties, and to separate those which are unlike. No one has succeeded in devising an unimpeachable system of classification for the chemical elements, in which each element has only one peculiar place—when the *criterium* of the classification is chemical behaviour. It is invariably found that some elements are entitled with equal or almost equal consistency to a place in more than one group. In the ideal system of classification, each class will be clearly and sharply distinguished from every other class by some essential property or properties which can be accurately defined, and readily recognized, and which are common to the individual members of the class. In all the systems hitherto proposed the different classes are more or less affiliated one to another, and J. P. Cooke [2] has emphasized the fact that

> Nature seems to abhor abrupt transitions, and shades off her bounding lines. Many of the elements, while they manifestly belong to one series, have properties which ally them to another.

The alchemists divided the metals into two classes, the *perfect metals* and the *semi-metals*—the former included gold and silver; the latter copper, iron, lead, tin, and mercury. The former suffered no alteration when heated at the highest available temperatures; the base metals are changed under these conditions into primitive earths. The former were accordingly called *noble metals*, the latter *base metals*. At the beginning of the nineteenth century, J. J. Berzelius classified the elements into two groups, the *metals* and the *metalloids* (meaning *non-metals*). This simple division of the elements into two groups is confronted with many difficulties because some simple substances—like antimony and arsenic—have the general appearance of metals and yet behave chemically like the non-metals. These pseudo-metals exhibit characteristic properties of both classes. This simple dichotonous division leads to vagueness, ambiguity, and contradictions as soon as the attempt is made to formulate sharp clear-cut definitions of the metals and the non-metals. The attempt to group the elements by a code of definitions seems to be foredoomed to failure. There is a seductive simplicity about a definition which may be attractive, but it is artificial and often misleading. As T. Campanella (1590) expressed it: " Definition is the end and epilogue of science. It is not the beginning of our knowing, but only of our teaching."

The attempt has been made to mark the metals by a term ending in **um,** and the non-metals by a term ending in **en, ine,** or **on.** For example: *Metals*—Aluminium, barium, sodium, magnesium, calcium, ferrum (iron), hydrargyrum (mercury), etc. *Non-metals*—Boron, carbon, oxygen, silicon, chlorine, argon, neon, krypton, etc. The idea persists in many but not all the modern names of the elements. The time-honoured names, silver, gold, iron, copper, zinc, etc., have alternative Latinized equivalents—argentum, aurum, ferrum, etc.—from which their modern symbols are derived.

Philologists[3] tell us that the word *metallon* appeared in Greek literature about the time of Herodotus (*c.* 450 B.C.), and it is supposed to have been borrowed from some foreign language—possibly a Semitic word—since the Semites, represented by the Phœnicians, had mines in the island of Thasos—not of the Ægean. The Semitic meaning of the term was " to work iron like a smith," whereas the Greeks used it not for a metal but for a mine or for any kind of mineral, including salt, found in a mine. The resemblance of the Greek *μέταλλον*—a mine—to *μεταλλάω*—meaning " in quest of something "—is thought to be accidental.

With all its imperfections, J. J. Berzelius' subdivision of the elements into metals and non-metals is so convenient that it is in common use when great precision is not required. Very roughly, the properties of the metals can be contrasted with those of the non-metals as indicated in the subjoined scheme—Table I.

TABLE I.—THE PROPERTIES OF THE METALS AND NON-METALS CONTRASTED.

Metals.	Non-metals.
1. Form basic oxides.	1. Form acidic oxides.
2. Generally dissolve in mineral acids giving off hydrogen.	2. Do not usually dissolve easily in mineral acids.
3. Either form no compounds with hydrogen, or form unstable compounds—usually non-volatile.	3. Form stable compounds with hydrogen—these are usually volatile.
4. Solid at ordinary temperature (excepting mercury).	4. Gases, liquids, or solids at ordinary temperatures.
5. Usually volatilize only at high temperatures.	5. Excepting carbon, boron, and silicon, the non-metals are either gaseous or volatilize at low temperatures.
6. When in bulk the metals reflect light from polished or freshly cut surfaces.	6. Do not usually reflect light very well.
7. Specific gravity is generally high.	7. Specific gravity generally low.
8. Good conductors of heat and electricity. Electrical resistance usually increases with the rise of temperature.	8. Bad conductors of heat and electricity. Electrical resistance usually decreases with rise of temperature.
9. More or less malleable and ductile.	9. Malleability and ductility are not well defined.
10. Molecules usually monatomic in the vaporous state.	10. Molecules usually polyatomic in the vaporous or gaseous state.

If any particular property be selected as a criterion, it will be found that the different metals can be arranged in a series which passes imperceptibly into the non-metals without an abrupt change. P. P. von Weimarn,[4] indeed, has given evidence which makes it not improbable that the different metals can exist in both forms. Hence, the metallic or non-metallic nature is not an unchangeable characteristic of an element; the metallic property may predominate at a low temperature, the non-metallic at a high one. This does not mean that metals and non-metals are two distinct forms of matter like the three states of aggregation which all kinds of matter undergo when the conditions—particularly temperature—are favourable. To show how difficult it is to draw a hard-and-fast line of demarcation between metals and non-metals, the non-metals arsenic, antimony, and tellurium would be classed with the metals if we depended exclusively upon 6, 7, and 8; hence, some introduce a third division—the **metalloids**—to include the hybrids—almost analogous to the *bastard metals* of the alchemists—for elements which have properties characteristic of both the metals and the non-metals. The term metalloid is sometimes used synonymously with non-metals. The metals lithium, sodium, potassium, magnesium, and aluminium have a low specific gravity; and when potassium was discovered in 1807, some argued that it could not be a metal because it was light enough to float on water. The non-metals carbon, boron, and silicon are less volatile than most metals. The non-metal hydrogen is a good conductor of heat; and the non-metal graphitic carbon is a good conductor of heat and electricity. Hence the division of the elements into metals and non-metals is but a rough system of classification, arbitrarily adopted because it is convenient.

In A. L. Lavoisier's classification, in his *Traité élémentaire de chimie* (Paris, 1789), the elements were arranged in four classes:

> (1) Simple substances belonging to the three kingdoms which can be regarded as the elements of bodies—light, caloric, oxygen, nitrogen, hydrogen. (2) Simple non-metallic substances which are oxidizable and acidifiable—sulphur, phosphorus, carbon, muriatic radicle, fluoric radicle, boracic radicle. (3) Simple metallic substances, oxidizable and acidifiable—antimony, arsenic, bismuth, cobalt, copper, gold, iron, lead, manganese, mercury, molybdenum, nickel, platinum, silver, tin, tungsten, zinc. (4) Simple substances, salifiable and earthy—lime, magnesia, baryta, alumina, silica.

Lavoisier frequently expressed his desire to keep within the limits of experience, but that fact was not sufficient to prevent him from nursing the philosophical conception of a world made from a very small number of elements. He seems to have regarded light and heat as ponderable or material substances. Lavoisier's separation of simple substances into metals and non-metals is interesting.

A. F. de Fourcroy, in his *Système des connaissances chimiques* (Paris, 1801), divided the then known metals into five classes: The first class included brittle metals which form acids by combining with oxygen—arsenic, tungsten, molybdenum, and chromium; the second class included brittle metals which do not form acidifiable oxides—titanium, uranium, cobalt, nickel, manganese, bismuth, antimony, and tellurium. The third class included metals which showed signs of ductility and are oxidizable—zinc and mercury. The fourth class included ductile and easily oxidizable—tin, lead, iron, and copper. The fifth class included the ductile metals not oxidizable by fire—silver, gold, and platinum. The first three classes were called *demi-métaux*; the fourth class, *métaux imparfaits*; and the fifth class, *métaux parfaits*.

The elements have been classed into acidic and basic, or, what amounts to the same thing, into electro-negative and electro-positive elements—for example, J. J. Berzelius, in his *Lärbok i Kemien* (Upsala, 1818), where hydrogen with dual characteristics separated the electropositive and the electronegative groups from one another. The elements have also been classed according to their valency as A. Naquet did in his *Principes de chimie fondés sur les théories modernes* (Paris, 1864). The alchemists separated the metals into two groups—the base and the noble metals; and L. J. Thénard, in his *Traité de chimie élémentaire, théorique et pratique* (Paris, 1818), imbued with A. L. Lavoisier's views on oxidation, relegated the non-metals into one class, and classified the metals according to (i) their oxidizability when roasted in air; (ii) the stability of the oxides; and (iii) their behaviour when heated with steam. This system was modified by succeeding chemists and used by H. V. Regnault in his *Cours élémentaire de chimie* (Paris, 1853). It was soon afterwards abandoned because it failed to accommodate itself to new data and new knowledge.

J. B. A. Dumas, in his *Traité de chimie appliquée aux arts* (Paris, 1828), and later, in a *Mémoire sur les équivalents des corps simples* (1859),[5] arranged the non-metals in five groups or families. He founded his classification of the non-metallic elements on the character of the compounds which they formed with hydrogen, on the volume ratio of the two elements entering into combination, and on their mode of condensation.

I.—Hydrogène; II.—Fluor, chlore, brome, iode; III.—Oxygène, selenium, soufre, tellure; IV.—Azote, phosphore, arsenic; V.—Carbone, bore, silicium.

Hydrogen was supposed to be a metal. J. B. A. Dumas classed the metals, and in general those bodies which do not unite with hydrogen, from the character of the compounds they form with chlorine, and when possible, from the volume ratio of the two elements entering into combination, and from their mode of condensation. He further represented the atomic weights of the elements in a given family as the sum of a series $a+nd'+nd''+\ldots$ Thus, fluorine $=19$; chlorine $=19+16{\cdot}5=35{\cdot}5$; bromine$=19+2\times16{\cdot}5+28=80$; iodine$=19+2\times16{\cdot}5+2\times28+19=127$. Similarly with the other families.

J. B. A. Dumas further stated that the classification of the metals ought to be founded on the characteristic compounds which they form with chlorine; and, as a result of the further work of W. Odling,[6] L. Gmelin, etc., systems were devised in which family relationships were specially emphasized. Thus, W. Odling (1857) arranged the elements in 13 groups:

I.—Fluorine, chlorine, bromine, iodine. II.—Oxygen, sulphur, selenium, tellurium. III.—Nitrogen, phosphorus, arsenic, antimony, bismuth. IV.—Boron, silicon, titanium, tin. V.—Lithium, sodium, potassium. VI.—Calcium, strontium, barium. VII.—Magnesium, zinc, cadmium. VIII.—Beryllium, yttrium, thorium. IX.—Aluminium, zirconium, cerium, manium. X.—Chromium, manganese, iron, cobalt, nickel, copper. XI.—Molybdenum, vanadium, tungsten, tantalum. XII.—Mercury, lead, silver. XIII.—Palladium, platinum, gold.

In analytical chemistry, even to-day, the elements are conveniently classed according to their behaviour towards certain reagents which are conventionally taken as standards of reference. For instance:

Group I.—The addition of hydrochloric acid to a solution precipitates silver, mercurous, lead, and thallium chlorides; tungstic oxide; and possibly silicic acid and antimony oxychloride.

Group II.—The passage of hydrogen sulphide through the filtrate from the preceding group, acidified with hydrochloric acid, precipitates mercury(ic), lead, bismuth, copper, arsenic, antimony, tin, selenium, tellurium, gold, platinum, and molybdenum either as sulphides or as elements along with sulphur.

Group III.—The addition of ammonia, ammonium chloride, and ammonium sulphide to the filtrate from the preceding group precipitates sulphides or hydroxides of iron, nickel, cobalt, manganese, zinc, uranium, aluminium, chromium, titanium, beryllium, thallium, zirconium, and the elements of the rare earths.

Group IV.—The addition of ammonium carbonate and alcohol to the filtrate from the preceding group—after it has been evaporated to a small bulk—precipitates magnesium, barium, strontium, and calcium carbonates.

Group V.—The salts of the alkali metals—lithium, sodium, potassium, rubidium, and cæsium—remain in solution.

The groups are subdivided again and again until finally salts of individual elements remain.

In all these systems an element appears in more than one class; or elements with but few properties in common are grouped together; or elements otherwise related are separated into different classes. The properties of the elements used as the basis of classification may also vary with the conditions under which the properties are observed.

Were W. Odling's system to be revised in the light of existing knowledge, it would furnish the most convenient system of classifying the elements—*e.g.* some such system as that used in H. Moissan's *Traité de chimie minérale* (Paris, 1904); and also in L. Gmelin and K. Kraut's *Handbuch der anorganischen Chemie* (Heidelberg, 1907). It is usually supposed that the so-called periodic system (*vide infra*) is the best that can be done, but that is doubtful. Only those facts which are known can be classified; and the perfection of any system of classification must necessarily depend on the extent of our knowledge. The periodic system is usually adopted, not because it furnishes the best possible arrangement according to existing knowledge, but because it holds alluring promises for the future. According to G. Gore:

> The most perfectly philosophical classification of scientific truths can be made only when their most essential and fundamental characters are discovered, and they are probably those very characters which are the most difficult to find, and doubtless will be nearly the last to be discovered.

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§ 2. Triads, and the Law of Octaves

In all things there is order, harmony, and wisdom.—H. DAVY (1811).

Les propriétés des corps sont les propriétés des nombres.—A. E. B. DE CHANCOURTOIS (1862).

In all chemical changes one property at least remains unaltered, and the more popular systems of classification have been based on this property—the atomic weights of the elements. The early efforts in this direction were seriously hampered by the uncertainty in the numerical values of the atomic weights; but after chemists had cleared up the confusion associated with the atomic theory left by J. Dalton, and obtained a consistent system of atomic weights, the results were more promising. True enough, between 1816 and 1829, J. W. Döbereiner noticed some regularities in the atomic weights of certain related elements, and, in a paper, *Versuch zu einer Gruppierung der elementären Stoffe nach ihrer Analogie* (1829),[1] he showed that most of the chemically related elements either exhibited almost the same atomic weight—*e.g.* iron, cobalt, and nickel—or else showed a constant difference when arranged in sets of three. Thus, selecting one set from Döbereiner's list, and rounding off the modern atomic weights,

	Calcium.		Strontium.		Barium.
Atomic Weight . . .	40		87		137
Difference		47		50	

Döbereiner's idea was taken up by a number of chemists—J. B. A. Dumas (1858), J. B. P. Kremers (1852), J. H. Gladstone (1853), W. Odling (1857), and E. Lennsen (1857)—and J. P. Cooke (1854) showed that the triads are probably only parts of series, similar to the homologous series of organic chemistry, in which the differences between the molecular weights are a multiple of some whole number. He struck a fatal blow at the doctrine by pointing out that the triads broke up natural groups of the elements, so that instead of co-ordinating facts it tended in the opposite direction. J. P. Cooke (1854) further arranged the elements in six groups or series in which the members of each series followed a law of progression in which the variation of the atomic weights could be expressed by a simple algebraic formula.

In 1815, W. Prout[2] had suggested that the atomic weights of the elements were probably exact multiples of the atomic weight of hydrogen, but with increasing refinements in the methods of measurement, this suggestion did not fit with observations. In 1850, M. von Pettenkofer read a paper, *Ueber die regelmässigen Abstände der Æquivalentzahlen der sogenannten einfachen Radicale* (1850), before the Bavarian Academy of Sciences, in which he tried to show that similar elements formed an arithmetical series with the atomic weight of one of the elements as a whole number, and another integer added or subtracted to obtain the series. Thus the atomic weights of the three alkali metals then known were arranged as a series $7+2n8$, where $n=0, 1, 2 \ldots$ For example, $Li=7$; $Na=7+2\times8=23$; $K=7+2\times8+2\times8=39$; and he obtained analogous results with the alkaline earths, the chromium and sulphur groups, and the halogens. Most probably in ignorance of M. von Pettenkofer's series of 1850, modifications of analogous series were advocated by both J. P. Cooke (1854) and J. B. A. Dumas (1851), although the craze in quest of groups and triads, more or less independent and distinct from one another, seemed to divert attention from the establishment of a continuous system including all the elements, and many felt intuitively that the lists of **Döbereiner's triads** or **Pettenkofer's series** were but fragments of a more general law—for instance, A. Strecker in his *Theorien und Experimente zur Bestimmung der Atomgewichte der Elemente* (Braunschweig, 1859):

> It is scarcely reasonable to suppose that all the relations between the atomic weights of chemically related elements are merely due to chance. The discovery of the hidden meaning in these numerical relations must be left to the future.

And M. Faraday (1852):

> We seem here to have the dawning of a new light, indicative of the mutual convertibility of certain groups of elements, although under conditions which as yet are hidden from our scrutiny.

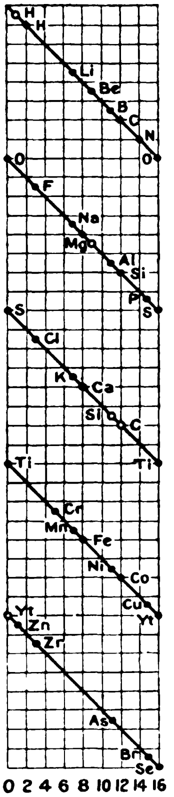

Fig. 1.—A. E. B. de Chancourtois' *Vis Tellurique.*

Some papers were published by A. E. B. de Chancourtois[3] between 1862 and 1863, in which it was proposed to classify the elements by their atomic weights. A. E. B. de Chancourtois divided the circular base of a cylinder into 16 parts, representing the atomic weight of oxygen; he then traced a helix inclined at an angle of 45°; and plotted the values of the atomic weights as *points caractéristiques* vertical to the axes of the cylinder so that one-sixteenth part of a complete rotation of the cylinder represented one unit. He called the helix so obtained the *vis tellurique*—the **telluric screw.** A portion of the telluric screw unrolled from the surface of the cylinder is illustrated in Fig. 1 as a plane surface. There is a tendency for analogous elements to fall on the same vertical line. The fundamental assumption involved in this scheme is that the atomic weights of the elements can be represented by whole numbers in accord with the formula $n+16m$, where m is an integer. Hence he assumed that the differences between the atomic weights ought to be constant. He tried to fill gaps in his list of elements by imagining new varieties of the known elements—such as actually occurs in the case of carbon—and these he called *caractères secondaires* represented in Fig. 1 by a circle. A. E. B. de Chancourtois' ideas were so much entangled with extraneous matters, and the truth was so much obscured by useless and faulty speculations, that his work lay buried for nearly thirty years, and it was only resurrected after Mendeléeff's system had become famous. There are also vague hints in N. H. Marne's *Ueber die Anzahl der Elemente* (Berlin, 1786), which, when read in the light of subsequent developments, have been taken as anticipations of the periodic law.

Again, between 1863 and 1866, J. A. R. Newlands [4] published a series of papers in which he arranged the elements in the ascending order of their atomic weights, and noticed that every succeeding eighth element was " a kind of repetition of the first." Thus, copying Newlands' first table as it appeared in his communication *On the law of octaves* (1865), where " the elements are arranged in the order of their equivalents, with a few transpositions, it will be observed that elements belonging to the same group usually appear on the same horizontal line."

TABLE II.—NEWLANDS' TABLE OF THE LAW OF OCTAVES (1865).

	No.		No.		No.		No.		No.		No.		No.		No.
H	1	F	8	Cl	15	Co, Ni	22	Br	29	Pd	36	I	42	Pt, Ir	50
Li	2	Na	9	K	16	Cu	23	Rb	30	Ag	37	Cs	44	Tl	53
Gl	3	Mg	10	Ca	17	Zn	25	Sr	31	Cd	38	Ba, V	45	Pb	54
B	4	Al	11	Cr	18	Y	24	Ce, La	33	U	40	Ta	46	Th	56
C	5	Si	12	Ti	19	In	26	Zr	32	Sn	39	W	47	Hg	52
N	6	P	13	Mn	20	As	27	Di, Mo	34	Sb	41	Nb	48	Bi	55
O	7	S	14	Fe	21	Se	28	Rh, Ru	35	Te	43	Au	49	Os	51

NOTE.—When two elements happen to have the same equivalent, both are designated by the same number.

It will be observed, said Newlands, " that the number of analogous elements generally differ by 7 or some multiple of seven ; in other words, members of the same group of elements stand to each other in the same relation as the extremities of one or more octaves in music. This peculiar relationship I propose to provisionally term **the law of octaves.**" Newlands noticed that elements belonging to the same group usually appeared in the same column, and he declared that all the numerical relations which had been observed among the atomic weights " including the well-known triads, are merely arithmetical results flowing from the existence of the law of octaves." Newlands' law of octaves did not attract much attention, probably because faulty atomic weights seriously interfered with arrangement ; and because the changes on triads and arithmetical series had been rung during the few preceding years with tiresome persistence.

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§ 3. The Periodic Law—D. I. Mendeléeff and L. Meyer

The periodic series is a brilliant and adequate means of producing an easily surveyed system of facts which by gradually becoming complete will take the place of an assemblage of the known facts.—E. MACH.

D. I. Mendeléeff and L. Meyer, quite independently and, so far as we can tell, quite in ignorance of Newlands' and Chancourtois' work, obtained a far clearer vision of the law of octaves about 1869. D. I. Mendeléeff published his *On the correlation of the properties and atomic weights of the elements*, in 1869, a year before L. Meyer. Mendeléeff said: "When I arranged the elements according to the magnitude of their atomic weights, beginning with the smallest, it became evident that there exists a kind of periodicity in their properties." Otherwise expressed, if the elements be arranged in the order of increasing atomic weights, the *properties* vary from member to member in a definite way, but return more or less nearly to the same value at fixed points in the series. D. I. Mendeléeff continued: "I designate by the name 'periodic law' the mutual relations between the properties of the elements and their atomic weights. These relations are applicable to all the elements, and have the nature of a periodic function." Expressed more concisely, **Mendeléeff's periodic law reads: The properties of the elements are a periodic function of their atomic weights.** A periodic function is one whose value repeats itself at regular intervals. The interval is called a "period." The ebb and flow of the tides, and the recurrence of the seasons are periodic phenomena.

Mendeléeff's table of the atomic weights was designed to tabulate the elements in such a way as to exhibit the greatest number of relationships; the early tables were rather imperfect on account of imperfections in the atomic weight data, and the paucity of our knowledge about the chemical characteristics of some of the elements. The original tables were afterwards amended and modified owing to improved data, and the discovery of new elements. The symbols of the elements with their atomic weights have been arranged on a helix, on a spiral, and in numerous other ways. Table III, not very different in style from one of Mendeléeff's first tables, is one of the simplest modes of arrangement, perhaps the best. The so-called *atomic numbers* of the elements are indicated in brackets. These constants will be discussed later. The fundamental principle of Mendeléeff's classification is that **the atomic weight of an element determines its position in the system.** When the elements are ranged in the order of their atomic weights, they form (i) definite families or groups of elements with allied properties; and (ii) series in which the properties of allied elements recur in definite periods. The nine vertical columns of the table are usually styled **groups**; and the twelve horizontal lines, **series** or **periods.** The properties of the elements and of their compounds are consequently studied from the point of view of this system of classification. The brief reviews of the family group given in this work will suffice to emphasize the relationships of the members of any given group. The **members of a group** have (1) general family properties like specific gravity, specific volume, laws of combination which (2) gradually vary from the first to the last number, so that the members of any particular group resemble one another more closely than do any of the other elements. (3) Each family group differs from the others, but the resemblances between the individual members of a family suggest that they have been internally constructed on the same plan. The **members of a series** have properties which (1) differ much from the first to the last member; and (2) each series is more or less a repetition of that which precedes. D. I. Mendeléeff emphasized the difference between the corresponding members of what he called the **odd series** and the **even series.** The members of the odd series show comparatively greater analogies with the corresponding members of the odd series than with the even series; and likewise the members of the even series have more

TABLE III.—THE PERIODIC SERIES OF THE ELEMENTS.

	Series	Group 0	Group I R_2O	Group II RO	Group III R_2O_3	Group IV RH_4 RO_2	Group V RH_3 R_2O_5	Group VI RH_2 RO_3	Group VII RH R_2O_7	Group VIII Transition elements RO_4
	1		H 1·008							
Short Period .	2	(2) He 3·99	(3) Li 6·94	(4) Be 9·1	(5) B 11·0	(6) C 12·00	(7) N 14·01	(8) O 16·00	(9) F 19·0	
Short Period .	3	(10) Ne 20·2	(11) Na 23·00	(12) Mg 24·32	(13) Al 27·1	(14) Si 28·3	(15) P 31·04	(16) S 32·07	(17) Cl 35·46	
Long Period .	4	(18) A 39·88	(19) K 39·1	(20) Ca 40·07	(21) Sc 44·1	(22) Ti 48·1	(23) V 51·0	(24) Cr 52·0	(25) Mn 54·93	(26) Fe 55·84 ; (27) Co 58·97 ; (28) Ni 58·68
	5		63·57 Cu (29)	65·37 Zn (30)	69·9 Ga (31)	72·5 Ge (32)	74·96 As (33)	79·2 Se (34)	79·92 Br (35)	
Long Period .	6	(36) Kr 82·92	(37) Rb 85·45	(38) Sr 87·63	(39) Yt 89·0	(40) Zr 90·6	(41) Nb 93·5	(42) Mo 96·0	(43) —	(44) Ru 101·7 ; (45) Rh 102·9 ; (46) Pd 106·7
	7		107·88 Ag (47)	112·40 Cd (48)	114·8 In (49)	119·0 Sn (50)	120·2 Sb (51)	127·5 Te (52)	126·92 I (53)	
Long Period .	8	(54) Xe 130·2	(55) Cs 132·81	(56) Ba 137·37	(57) La 139·0	(58) Ce 140·25	—	—	—	— — —
	9		—	—	Rare earths		—	—	—	
Long Period .	10	—	Rare earths			—	(73) Ta 181·0	(74) W 184·0	(75) —	(76) Os 190·9 ; (77) Ir 193·1 ; (78) Pt 195·2
	11		197·2 Au (79)	200·6 Hg (80)	204·0 Tl (81)	207·10 Pb (82)	208·0 Bi (83)	Po (84)	— (85)	
? Long Period.	12	(86) Nt 222·5	(87) —	(88) Ra 226·4	(89) Ac	(90) Th 232·4	(91) —	(92) U 238·5	—	

analogies with corresponding members of the even series than with the odd series. For example,

Group . . .	I	II	III	IV	V	VI	VII
4th series . .	*K*	*Ca*	—	*Ti*	*V*	*Cr*	*Mn*
5th series . .	Cu	Zn	—	—	As	Se	Br
6th series . .	*Rb*	*Sr*	—	*Zr*	*Nb*	*Mo*	—
7th series . .	Ag	Cd	In	Sn	Sb	Te	I

where the 4th and 6th series resemble one another more closely than do the 4th and 5th, or the 5th and 6th. Each **short period,** it will be observed, contains eight elements; and each **long period** either contains nineteen elements of which three are the so-called **transition elements,** or else it has provision made for nineteen elements. Hyphens are inserted in the spaces where the corresponding element is unknown. The elements in the first short period are sometimes called **group elements** or **bridge elements,** since they show a notable gradation of properties from one to the other, and serve as links or bridges between the different groups. The members of the next short period or series 3, are called **typical elements** because they have the typical properties and characteristics of the group, and show a rather wide divergence from neighbouring groups. After each typical element, the different groups diverge into two **sub-groups.**

The transitional elements.—It will be noticed that there is a distinct difference between the members of the odd and the even series. The even series, say the fourth and sixth, resemble one another more closely than the members of the odd series, say the fifth and seventh. The lower oxides of the last members of the even series resemble in many ways the first members of the odd series. Thus, the basic oxides of chromium and manganese are in many ways similar to the oxides of copper and zinc. Again, there are marked differences between the last members of the odd series (halogens) and the first members of the next even series (alkali metals). Those elements which cannot be placed in short periods fall in better with last members of the even series, and the first members of the odd series. Thus, iron, cobalt, and nickel fall between manganese and copper both with respect to chemical properties and atomic weights:

	Cr	Mn	Fe	Ni	Co	Cu	Zn
Atomic weight .	52	54·9	55·8	59·0	58·7	63·6	65·4
Specific gravity .	6·9	7·4	7·8	8·7	8·8	8·9	6·9
Atomic volume .	7·5	7·4	7·1	6·8	6·7	7·1	9·5

so also Ru—Rh—Pd → Ag come just after the sixth series, and Os--Ir—Pt → Au after the tenth series. The inert gases are considered to form a kind of transition between the last members of the odd series (halogens) and the first members of the even series (alkali metals), and consequently also, they only occur in the horizontal rows where transitional elements in the eight groups are absent.

The following arrangement, Fig. 2, modified from one by T. Bayley (1882),[1] emphasizes the relationship and yet the individuality of the sub-groups, the character of the transition elements, etc. *Protyle* represents an imaginary primordial element of elements, from which the ordinary elements are made; and by *extinct elements* are understood imaginary elements of high atomic weight which may have once been made from protyle, but which proved too unstable to endure under terrestrial conditions and broke down into simpler elements of smaller atomic weight.

T. Bayley's table emphasizes the fact that while the atomic weights of the elements progressively increase, their properties recur at definite intervals. No well-known elements are omitted from the scheme, and with three exceptions the order is that of the atomic weights, and the elements usually fall into virtually the same groups as would have been obtained had they been arranged according to their chemical behaviour. Otherwise expressed, there is one element for each place in the table, and each place in the table is intended for a definite chemical individual.

The valency of the elements shows a peculiar relation, for the maximum valency rises from 1 to 8 in passing along a given series from the first to the last group. Thus,

Group	I	II	III	IV	V	VI	VII	VIII
Oxide	K_2O	CaO	Al_2O_3	CO_2	P_2O_5	SO_3	Cl_2O_7	OsO_4
Valency	1	2	3	4	5	6	7	8

The curve, Fig. 3, is obtained by plotting as abscissæ the atomic weights of the elements, and for ordinates the higher oxides of the elements which correspond

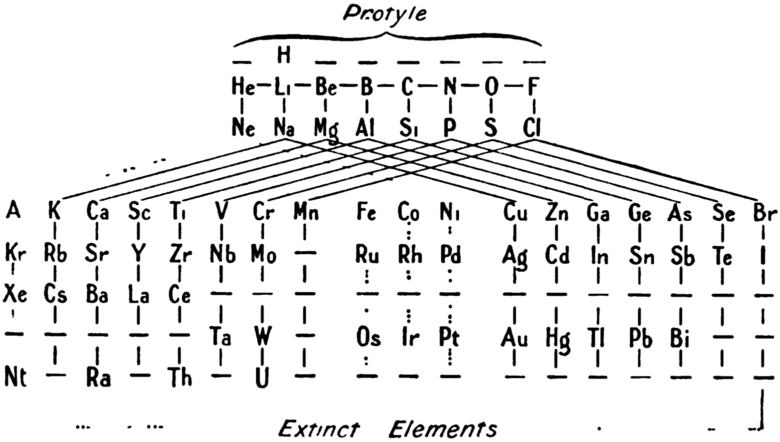

FIG 2.—T Bayley's Modification of the Periodic System.

to water and which can form hydrates with water, or unite together to form salts. There are several elements whose highest salt-forming oxide, corresponding with the family type, is not known, but, adds D. Carnegie [2]:

> Chemistry is by no means a completely worked-out science, wanting nothing, and the periodic law would be at fault did it fail to mirror forth such shortcomings and imperfections as still exist.

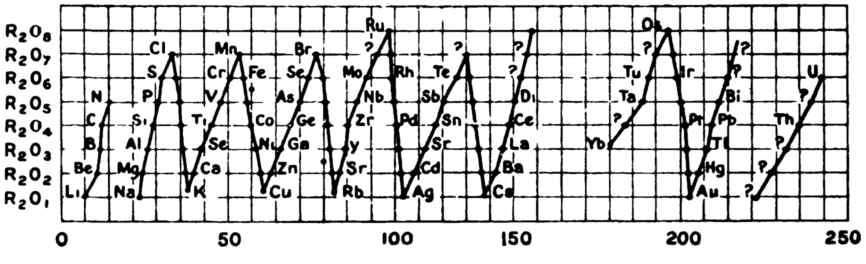

FIG. 3 —Periodic Curve of the Ideal Higher Oxides of the Elements

The periodicity of the curve, Fig. 3, is perhaps the most prominent feature. There is a blank for fluorine because it is not known to form any oxide ; there are also blanks in places supposed to correspond with unknown elements. The elements on the horizontal lines form families the members of which have many analogous properties. Elements with decided metallic characters collect towards the troughs of the wavy curve, and the non-metallic elements collect towards the crests. The basicity of the oxides decreases in passing upwards from trough to crest. Thus, lithium and sodium, and beryllium and magnesium oxides are strongly basic ; boron and aluminium oxides are but feebly basic, and they also show acidic properties ; carbon and silicon dioxides are distinctly acidic, not basic ; while the nitrogen, phosphorus, sulphur, and chlorine oxides are strongly acidic.

Again, the minimum valency rises from 1 to 4, and then falls to unity in passing through the different groups. Thus,

Group . .	I	II	III	IV	V	VI	VII
Compound . .	KH	CaH_2	(AlH_3)	CH_4	PH_3	SH_2	ClH
Valency . .	1	2	3	4	3	2	1

The maximum valencies of boron and aluminium may be quadri- not ter-valent, and if this suspicion proves well founded, these two elements will not fit the table. Note the increasing acidity of the hydrides of carbon, phosphorus, sulphur, and chlorine in passing from methane, CH_4, to hydrogen chloride, HCl. The properties of the hydrides of the elements in the first three groups are not so well known. Similar remarks apply to the halides, and in no case is a simple halide known which is higher in type than the maximum oxide indicated in the preceding scheme.

The quotient obtained by dividing the atomic weight of an element by its specific gravity in the solid condition is called the atomic volume of the element. Consequently, **the atomic volume represents the number of cubic centimetres occupied by an amount of the element equal to its atomic weight expressed in grams.** The magnitude of the atomic volume thus corresponds with the looseness of texture or porosity, so to speak, of the solid element. In 1870, in a paper, *Die Natur der chemischen Elemente als Function ihrer Atomgewichte*, Lothar Meyer[3] showed that when the atomic volumes of the elements are plotted with the atomic weights, a periodic curve showing a number of maximum and minimum points is obtained, as illustrated in Fig. 4. Certain portions of the curve are incomplete owing to the lack of data.

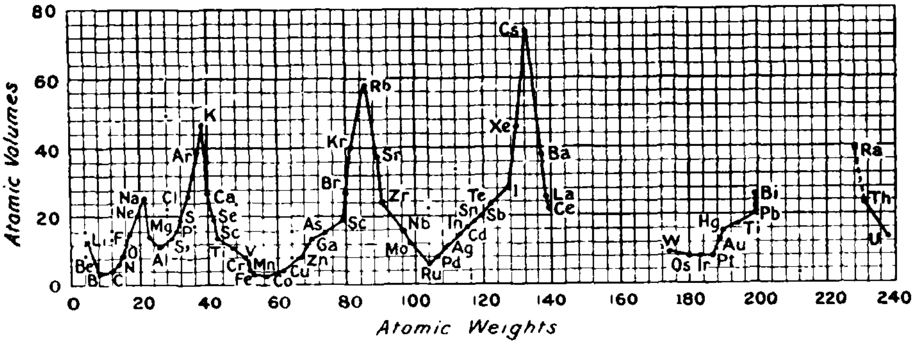

FIG. 4.—Relation between Atomic Volumes and Atomic Weights.

Most of the well-defined physical and chemical properties of the elements are periodic : for instance, specific gravity, atomic volume, melting point, hardness, malleability, ductility, compressibility, coefficient of expansion, thermal conductivity, latent heat of fusion, refraction equivalents for light, colour, electrical conductivity, magnetic power, etc. When the numerical values of these properties and the atomic weights of the elements are tabulated on squared paper, a curve is obtained which is broken up into periods as is the case with the atomic volumes —Fig. 4. The specific heats of the elements are unique in furnishing a non-periodic curve. According to Dulong and Petit's rule, if x denotes the specific heat of an element with an atomic weight y, at ordinary temperatures, we have $xy=6{\cdot}4$. This is obviously a hyperbolic curve as indicated in Fig. 5, and not a periodic curve like Fig. 4. J. Dewar's observations[4] of the specific heats of the elements at 50° K., or $-223°$, give a periodic curve running almost parallel with the atomic volume curve. Fig. 4.

There have been several attempts to represent the relation between the atomic weight of an element and the order in which it stands in the list of elements arranged in an ascending order of atomic weights, by algebraic formulæ. E. J. Mills[5] used $w=15(p-0{\cdot}9375^x)$, where the value of p ranges from 1 to 16, and x from 1 to 50. It is perhaps not surprising that the atomic weights can be represented by such a formula since the term 0·9375 approximates so closely to a whole number that any number can be expressed in decimals by this formula. J. H. Vincent represented the atomic weight of 58 elements by means of the formula $w=(n+2)^{1{\cdot}21}$, where n represents numbers rising by unity for each successive element from $n=3$ up to $n=60$. The results were good. J. B. Rydberg and F. M. Flavitzky used trigonometrical functions, and G. J. Stoney a logarithmic function to represent the magnitude as well as the periodicity of the atomic weights of the elements.

In 1870, H. Baumhauer[6] represented the relation between the elements graphically by means of a spiral; in 1876, L. Meyer used a helix after the manner of A. E. B. de Chancourtois (1862); and various other forms of periodic curve have been recommended by E. von Huth, W. Spring, J. E. Reynolds, W. Crookes, G. J. Stoney, S. Haughton, E. Loew, and others. The periodic law of D. I. Mendeléeff does not represent an uninterrupted function; it does not correspond with a continuous change of properties with a continuous variation of atomic weights. Mendeléeff therefore expressed himself against the attempt to represent the periodic relations of the elements by geometrical curves. In the Faraday lecture, 1889, D. I. Mendeléeff said:

> The periods of the elements have a character very different from those which are so simply represented by geometers. They correspond to points, to numbers, to sudden changes of the masses, and not to a continuous evolution. In these sudden changes destitute of intermediate steps or positions, in the absence of elements intermediate between, say, silver and cadmium, or aluminium and silicon, we must recognize a problem to which no direct application of the analysis of the infinitely small can be made. Therefore, neither the trigonometrical functions proposed by Rydberg and Flavitzky, nor the pendulum-oscillations suggested by Crookes, nor the cubical curves of the Rev. Mr. Haughton, which have been proposed for expressing the periodic law, from the nature of the case, can represent the periods of the chemical elements.

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§ 4. The Gaps in Mendeléeff's Tables of the Elements

The periodic law has given to chemistry the prophetic power long regarded as the peculiar dignity of its sister science astronomy.—H. C. BOLTON.

Both Meyer and Mendeléeff considered it necessary to leave gaps in their tables for undiscovered elements, and more particularly in order to keep certain related elements in the same vertical column. Mendeléeff boldly prophesied that the **missing elements** would be discovered later, and in some cases even predicted their properties in considerable detail. For instance, when Mendeléeff announced the law, there were two blank spaces in group III, the missing elements were called **eka-aluminium** and **eka-boron** respectively; and another space below titanium in group IV, represented a missing element which in this case was called **eka-silicon.** The hypothetical character of these elements was considered to be an inherent weakness of the law, but the weakness was turned to strength when gallium, scandium, and germanium appeared duly clothed with those very properties which fitted closely with Mendeléeff's audacious prognostications. This fit attracted

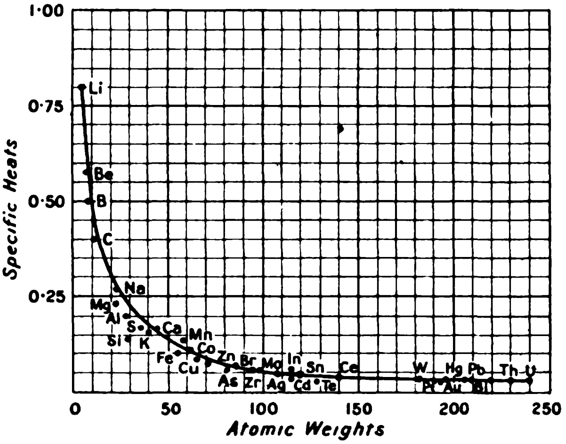

FIG. 5.—Curve showing the Relation between the Specific Heats and Atomic Weights of the Elements (0°).

TABLE IV.—COMPARISON OF PREDICTED AND OBSERVED PROPERTIES OF GERMANIUM.

Eka-silicon, Es (predicted in 1871).	Germanium, Ge (discovered in 1886).
Atomic weight, 72.	Atomic weight, 72·3.
Specific gravity, 5·5.	Specific gravity, 5·47.
Atomic volume, 13.	Atomic volume, 13·2.
Element will be dirty grey, and on calcination will give a white powder of EsO_2.	The element is greyish-white and on ignition furnishes a white oxide GeO_2.
Element will decompose steam with difficulty.	The element does not decompose water.
Acids will have a slight action, alkalies no pronounced action.	The element is not attacked by hydrochloric acid, but it is attacked by aqua regia. Solutions of KOH have no action, but it is oxidized by fused KOH.
The action of sodium on EsO_2 or on EsK_2F_6 will give the element.	Germanium is made by the reduction of GeO_2 with carbon, or of GeK_2F_6 with sodium.
The oxide EsO_2 will be refractory and have a sp.gr. 4·7. The basic properties of the oxide will be less marked than TiO_2 and SnO_2, but greater than SiO_2.	The oxide GeO_2 is refractory and has a sp.gr. 4·703. The basicity is very feeble.
Eka-silicon will form a hydroxide soluble in acids, and the solutions will readily decompose forming a metahydrate.	Acids do not precipitate the hydrate from dilute alkaline solutions, but from concentrated solutions, acids precipitate GeO_2 or a metahydrate.
The chloride $EsCl_4$ will be a liquid with a boiling point under 100° and a sp.gr. of 1·9 at 0°.	Germanium chloride, $GeCl_4$, boils at 86°, and has a sp.gr. at 18°, 1·887.
The fluoride EsF_4 will not be gaseous.	The fluoride $GeF_4.3H_2O$ is a white solid mass.
Eka-silicon will form a metallo-organic compound $Es(C_2H_5)_4$ boiling at 160°, and with a sp.gr. 0·96.	Germanium forms $Ge(C_2H_5)_4$, which boils at 160°, and has a specific gravity slightly less than water.

considerable attention, and served to strengthen the faith of chemists in the fundamental truth of the periodic law. In illustration, the predicted properties of eka-silicon and subsequently discovered properties of germanium are quoted side by side in Table IV.

The confirmations of Mendeléeff's predictions of the properties of eka-aluminium (gallium), and of eka-boron (scandium) were equally striking. This dramatic achievement focused attention on the generalization; but it is only fair to say that the predictions and their subsequent verification are not such positive proofs of the truth of the periodic law as some suppose. It is certainly wrong to say, as C. Winkler did, "it would be impossible to imagine a more striking *proof* of the doctrine of periodicity of the elements than that afforded by this embodiment of the hitherto hypothetical eka-silicon," because gaps appeared in some of the older systems of classification, and the properties of the missing members could have been predicted, and atomic weights estimated by analogy with the other members of the family, quite independently of the periodic law, and in some cases with better results.

§ 5. The Application of the Periodic Law

> A natural law only acquires scientific importance when it yields practical results, that is, when it leads to logical conclusions which elucidate phenomena hitherto unexplained, when it directs attention to occurrences till then unknown, and especially when it calls forth predictions which may be verified by experiment.—D. I. MENDELÉEFF.

D. I. Mendeléeff pointed out that the periodic law could be employed in: 1. The classification of the elements; 2. The estimation of the atomic weights of elements not fully investigated; 3. The prediction of the properties of hitherto unknown elements; and 4. The correction of atomic weights.

1. The classification of the elements.—T. H. Huxley (1864) has said: "By the classification of any series of objects, is meant the actual or ideal arrangement together of those which are like, and the separation of those which are unlike; the purpose of this arrangement being to facilitate the operations of the mind in clearly conceiving and retaining in the memory the characters of the objects in question." If a new element possesses one of the marked characteristics of a given class, it follows that it will probably possess the remaining characteristics. If a new element of the alkaline-earth family be discovered, a great many other properties could be inferred with a high degreee of probability of their being right. In fine, enthusiasts say that the periodic system is superior to all the older methods of classifying the elements, for the law makes it possible to build up a system of the greatest possible completeness free from much arbitrariness, and it furnishes strong circumstantial evidence of the correctness of the reasoning employed by Cannizzaro in deducing values for the atomic weights of the elements.

2. The estimation of the atomic weights of the elements.—On account of practical difficulties, it is not always possible to fix the atomic weight of some elements by vapour density determinations (Avogadro's rule), and by specific heat determinations (Dulong and Petit's rule), and the atomic weights of these elements were frequently assigned on somewhat uncertain grounds. According to C. L. Winkler, indium has the equivalent weight 37·8. The correct atomic weight must be some multiple of this, and for no special reason, the atomic weight was once taken to be $37{\cdot}8 \times 2 = 75{\cdot}6$. In that case, indium would fall between arsenic and selenium where it would be quite mis-matched. Mendeléeff proposed to make indium tervalent, like aluminium, so that the atomic weight became $37{\cdot}8 \times 3 = 113{\cdot}4$, and the element fell in the table between cadmium and tin where it fits very well. The subsequent determination of the specific heat of indium, 0·0577, corroborated the change made by Mendeléeff in the atomic weight from 75·6 to 113·4. Beryllium, uranium, and a number of the rare earths at one time did not fit very well into the table, but Mendeléeff's alteration of the supposed atomic weights to make these elements fit the table were subsequently justified by vapour density determinations of the volatile chlorides, or by specific heat determinations.

3. The prediction of the properties of hitherto undiscovered elements.—When an empty space occurs in Mendeléeff's table, it is assumed that an element will one day be discovered which will fill that place; and conversely, if a new element were found to correspond with a place in the table already filled, it would be suspected that the supposed element is not really elemental. In attempting to imitate Mendeléeff, and predict the properties of missing elements in the table, attention is paid to the composition and properties of the more important compounds—hydroxides, oxides, haloid salts, etc.—so as to bring out (1) the family characters of the group to which it belongs; (2) the character of the series to which it belongs; (3) its position in the series and group so that a comparison can be made with the properties of other known elements similarly situated in neighbouring groups or series; and (4) the relations of the particular group and series in which it occurs with other groups and series. In order to avoid introducing new names when speaking of unknown elements, represented by gaps in the table, Mendeléeff designated them by prefixing a Sanscrit numeral—*eka* (one), *dwi* (two), *tri* (three), etc.—to the names of the preceding analogous elements of the odd or even numbered series of the same group. Thus, the unknown elements of group I will be called eka-cæsium, and dwi-cæsium. Were strontium unknown, it would be called eka-calcium. In addition to the prediction of germanium, gallium, and scandium already discussed, Mendeléeff foretold the possible discovery of eka- and dwi-cæsium; of eka-niobium—En=146; of eka-tantalum—Et=235; of dwi-tellurium—Dt=212; and of the analogies of manganese: eka-manganese—Em=100; and tri-manganese—Tm=190.

The case of the so-called **inert gases** is of more recent date. The discovery of argon and helium could not have been predicted from Mendeléeff's periodic law, but after these elements had been discovered, and accommodated in the periodic table between the strongly acid halogen family and the strongly basic alkali metals, the probable existence of other similar inert gases was indicated. When an exhaustive search was made, krypton, neon, and xenon were discovered with properties and atomic weights which could have been predicted from the arrangement which was made for argon and helium in Mendeléeff's table.

4. The correction of the values of atomic weights.—If the atomic weight of an element does not fit with the regular course of, say, the atomic volume curve, Fig. 4, the atomic weight is probably in error. Thus, the atomic weights of platinum, iridium, and osmium at that time were probably too high, and subsequent determinations verified this inference. For example, the atomic weights of these elements were:

	Platinum.	Iridium.	Osmium.
In 1870 . . .	196·7	196·7	198·6
In 1919 . . .	195·2	193·1	190·9

§ 6. Some Defects in the Periodic Law

The scientific value of thoroughly sound hypotheses is enhanced daily both by known facts that they are continually assimilating, and new facts that they are continually revealing.—J. WARD (1899).

There are some **misfits** in the Mendeléeff's table as we have it to-day, owing to the fact that at least three pairs of elements would be mis-matched if they were simply classed according to their atomic weights: argon (39·88) and potassium (39·10); cobalt (58·97) and nickel (58·68); and tellurium (127·5) and iodine (126·92).

G. Krüss and F. W. Schmidt (1889)[1] attributed the difficulty with **cobalt and nickel** to the presence of a hitherto undiscovered element in nickel which they named *gnomium*. This explanation, however, had to be discarded. It did not survive the ordeal remorselessly applied to conjectures of this kind. No gnomium has yet been found. Again, the case of **iodine and tellurium** has been studied with relentless vigour stimulated largely by D. I. Mendeléeff's prediction: "The atomic weight of tellurium *must* be between 123 and 126, and cannot be 128." Iodine most certainly belongs to the same group as the other halogens, and tellurium undoubtedly belongs to the selenium group; these elements are accordingly placed among their own family relations in spite of the fact that if their atomic weights were alone considered tellurium would be ranked with the halogens, and iodine with selenium. B. Brauner (1889) suggested that ordinary tellurium is a complex containing α- and β-tellurium; and it was inferred that true tellurium—say α-Te—has an atomic weight 125, and that the other form of this element has a higher atomic weight, and will find a place in the periodic system in the valency below tellurium. D. I. Mendeléeff called this undiscovered element *dwi-tellurium*, Dt, and he sketched some of its physical and chemical properties; but tellurium, said G. Wyrouboff, has been tortured in every conceivable manner: it has been melted, sublimed, oxidized, hydrogenized, phenylated, dissolved, crystallized, fractioned, and precipitated; yet nothing but failure has followed all attempts to get an atomic weight lower than iodine or to fraction the element into two others. Nothing has developed which would warrant a belief in Mendeléeff's "must." Hence, in spite of the fact that "the laws of nature admit of no exception," faith in the law has led chemists to allocate these discordant elements according to their chemical properties and not according to their atomic weights. To put the matter bluntly, the procedure runs: It is necessary either to reject the periodic law or to reject the number 127·5 for tellurium; the periodic law cannot be rejected because it is the very embodiment of truth, nay, truth itself; *ergo*, in spite of all evidence to the contrary, the number 127·5 must be wrong. Bode's law of astronomy successfully *predicted* the asteroids and allocated their proper place in the solar system; but the subsequent discovery of Neptune did not agree with Bode's law. The law was accordingly abandoned and it is now regarded as a curiosity. Mendeléeff's law may have to go the same way. B. Brauner's assumption that tellurium is a mixture of true tellurium with a higher homologue, may be a good working hypothesis for stimulating experiments on this element, but to maintain the thesis against all evidence to the contrary "may afford an easier way out of the difficulty than by working steadily at the cause of the discrepancy, but it affords at best a feeble and undignified cover for one's retreat." This method must be dubbed unscientific, but the circumstantial evidence justifies the procedure in the expectation that a consistent system will ultimately grow from the truth and error engrafted into the "law." It is not very probable that the principle underlying the periodic law will be abandoned because it is founded on a vast assemblage of facts of different kinds; and because it seems to be plastic enough to fulfil subsequent requirements. The central problem in inorganic chemistry, said W Ramsay (1904), is to answer the question: **Why this incomplete concordance?**

Allocation of hydrogen.—The location of hydrogen in the table, as already indicated, is difficult, because hydrogen seems to be without companions. It is univalent, and thus falls either with the alkali metals (D. I. Mendeléeff, 1869; G. Martin, 1901) or with the halogens (O. Mason, 1896; W. Crookes, 1898; W. Ramsay, 1901). Although D. I. Mendeléeff[2] rather inclined to the belief that hydrogen occupies an "isolated independent position," he said that in virtue of "its salt-like oxide H_2O, and the salts H, it must stand in the first group;" that "the nearest analogue to hydrogen is sodium which also stands in an odd series of the first group;" and that "the more remote analogues of hydrogen are copper, silver, and gold." The attempts to displace hydrogen from its position at the head of the alkali metal group, and to place it with the halogens have not been very successful, but in either case many of the arguments appear rather strained and far-fetched; they run *pro et con.* somewhat as follows:

(1) Unlike hydrogen, the monad alkali metals appear to be monatomic, but hydrogen too is probably monatomic at a high enough temperature.

(2) If placed at the head of the halogen table, hydrogen is in close contiguity with the other gaseous elements, but the extreme mobility and lightness of the hydrogen molecules may be a powerful factor in determining its gaseity; after all gaseity is a mere accident of temperature.

(3) Hydrogen is electropositive like the alkali metals, but it is not now considered to be a metal; hydrogen does not exhibit the metallic properties characteristic of the family of alkali metals, and towards lithium it behaves like nitrogen, oxygen, and the halogens in forming a hydride. This argument is of little weight when no objection is raised to the allocation of nitrogen and bismuth; or of carbon and lead in the one family group.

(4) The difference between two consecutive elements usually ranges between 15 and 20, and this agrees better with superposing hydrogen above fluorine than above lithium (7); as G. Martin (1901) has pointed out this argument simply depends on the arbitrary selection of subtraction as a criterion; if division be selected, quite a different conclusion is obtained. Thus, progressing upwards from potassium, the ratio K : Na = 1·7; Na : Li = 3·3; and, following the same rule, Li : H = 6·9, which is near to the observed value.

(5) If hydrogen be placed above lithium, six gaps for undiscovered elements are crowded in between hydrogen and helium, or helium must come in an unnatural intermediate position, say, above carbon or nitrogen. In view of the gaps in the old periodic tables which were subsequently filled, there is, however, no particular objection to the assumption that these undiscovered elements have a real existence even if they have not yet been discovered.

(6) The mutual replacement of hydrogen and the metals which has led to the acids being regarded as salts of hydrogen, establishes a clear analogy between hydrogen and the alkali metals; against this it must be remembered that there is an equally striking analogy between hydrogen and the halogens, for these elements can mutually replace one another in many organic compounds with no more effect on the general properties of the resulting compounds than is produced by the substitution of one halogen with another. This argument loses much weight if it be remembered that the behaviour of a compound is determined by its constitution rather than by the chemical nature of the atoms themselves, and that "the most diverse radicles may displace other radicles in a compound and perform a similar function to that of the displaced radicles without materially affecting the fundamental characteristics of the body into which they have entered."

(7) If the behaviour of the halogens towards oxygen be selected as a criterion, the diminishing stability of the oxygen compounds with diminishing atomic weight culminates in fluorine. No stable oxides are known, hydrogen oxide is a very stable compound, totally unlike the halogen oxides. The halogens in their known oxides have a maximum valency of seven, while the maximum valency of hydrogen is one.

(8) Then again, there is a great contrast between the stable hydrogen compounds with the halogens, and the instability of the hydrides of the alkali metals. In a rough sort of way the former property suggests dissimilarity; the latter, similarity. Hence also B. Brauner (1901) asks: How can such a positive element as hydrogen stand at the head of such negative elements as the halogens? The elements at the head of a sub-group are always more negative and less positive than the lower members of that sub-group.

Accordingly, it will be evident that the position of hydrogen has not been definitely settled, and that *hydrogen appears to be a rogue element quite out of place in the general scheme.* Some suppose that hydrogen is a member of an extinct or yet undiscovered series of independent elements, but whether hydrogen is the *alpha* or the *omega* is indeterminate because it would be eligible for a place either in group I or group VII according to the properties selected for comparison. The supposed first member of the series is called "proto-fluorine"; so also the elements "proto-beryllium" and "proto-boron" have been invented, the former with an atomic weight 1·33, and the latter, 2. All this, however, is mere speculation.

Allocation of the rare earths.—This also presents some difficulties. Most of the rare earths can be distributed about the table according to their atomic weights, or they can be relegated to a class by themselves. B. Brauner (1902), who has made a special study of the rare earths, considers that they should all be grouped together with cerium between barium and tantalum so that "Ce, 140·25" in the table stands for: Ce, 140·25; Pr, 140·6; Nd, 144·3; Sa, 150·4; Eu, 152; Gd, 157·3; Tb, 159·2; Dy, 162·5; Er, 167·7; Tm, 168·5; Yb, 172·0 . . . This has been called the **asteroid theory of the rare earths.** The properties of the rare earths, however, are not well enough known to give us much confidence in the various proposals which have been made for dealing with them; and consequently, Mendeléeff considered that the installation of these elements should be deferred; a similar remark applies to the radioactive elements. Here F. Soddy and A. Fleck (1913)[3] assume:

> All members occupying the same place in the periodic system are chemically identical with one another, and are not separable from one another by chemical process, although their atomic weights may vary over several units.

The rare earths do not fall all in the same group in this sense because several of the members fit well enough into the table, thus, ytterbium—Yb, 172—fits into group III, series 10, etc. The so-called isotopic elements will be discussed later.

If the properties of the elements are dependent on their atomic weights the existence of two elements with different properties and approximately the same atomic weights should be impossible. Hence the difficulty with elements like cobalt and nickel; ruthenium and rhodium, etc. The peculiarities of these elements would never have been suspected from the periodic law. It might also be added that some experiments with the radioactive elements have led to the inference that "different elements not necessarily of identical atomic weight, do occupy the same place in the table, and that when this occurs, these elements possess an identical chemical nature." The evidence as to the identity of chemical properties is not very strong when it is remembered how very few chemical tests have been made owing to the small amount of available material. Not very long ago praseodymium and neodymium were considered to have identical chemical properties.

Twin elements.—R. Lorenz[4] has shown that certain elements have atomic weights which approach each other in pairs, and which differ from each other by at most 1·4 units; and he applies the term **twin elements** to pairs of elements whose atomic weights approach one another very closely—within 1·4—of one another. For example:

	Diff.		Diff.
Boron-carbon	1·009	Nickel-cobalt	0·660
Sodium-magnesium	1·322	Selenium-bromine	0·893
Aluminium-silicon	1·320	Palladium-silver	1·238
Phosphorus-sulphur	1·033	Tin-antimony	1·190
Potassium-calcium	0·864	Iodine-tellurium	0·736
Vanadium-chromium	0·940	Tantalum-tungsten	1·200
Manganese-iron	0·910	Lead-bismuth	1·099

The elements usually show many similarities in their chemical behaviour, and their separation presents some difficulties. Most of the twin-elements usually follow one another in immediate succession, so that the atomic weight of a member of one pair differs from that of the corresponding member of the next pair by approximately 4 or a multiple of 4, *e.g.* Na and Al, 4·022; Mg and Si, 4·02; Al and P, 3·95; Si and S, 3·663; etc. Lorenz shows that elements which do not form twin pairs may follow this rule if they be regarded as representing twin pairs with other unknown elements—the exceptions are H, Be, N, Zn, Ga, Rb, Y, Zr, Nb, In, Cs, Ba, Ir, Au, and some rare earths elements.

Some elements are allocated places in the table according to their atomic weights in opposition to their chemical properties. For instance, copper, silver, and gold fall into one group with the alkali metals. The tervalency of gold appears to be unconformable with the valency of its companions although in its present position the series $PtCl_4$, $AuCl_3$, $HgCl_2$, and TlCl is suggestive. Beryllium is peculiarly placed from this point of view. Thallium is very like lead, but its sulphate and some other salts are quite different from lead salts. At least three pairs of elements have been placed according to their properties irrespective of their atomic weights, as indicated by the misfits mentioned in the preceding section. Again, the so-called type-elements, Li, Be, B, C, N, O, F, which stand at the heads of the family groups—the vertical columns of Mendeléeff's table—usually have properties quite at variance with the other members of the family. In 1870, Mendeléeff attributed this to their low atomic weight, for he said :

> The elements of the first two series have the least atomic weights, and in consequence of this very circumstance, although they bear the general properties of the group, they still show many peculiar and independent properties.

The difficulty still remains, for these elements have not yet been altogether reconciled to the groups to which they should be closely analogous. The test of any given classification of the elements arises when the arguments why a given element should be included rather in one class than in another are reviewed. For instance, in spite of the unique properties of fluorine or of lithium, could the former be included in any group other than the halogens, or lithium in any group other than the alkali metals ? The answer is in the negative.

Some elements which appear to be chemically similar are separated in the table. For example, copper and mercury ; silver and thallium ; barium and lead ; etc. The position of these elements in the table gives no hint of these characteristics. Still, it might be argued that these elements exhibit many essential differences. Thus, the physical properties of the cupric and mercuric chlorides and sulphates show great contrasts. The stability of cuprous and mercurous chlorides is also very different. Lead and barium dioxides appear to have a different constitution. The unstable thallium sesquioxide, Tl_2O_3, corresponds with the other —more stable—sesquioxides in the group, but there are many important points of resemblance between thallium and the alkali metals, and between silver and lead. The extension of the periodic law to include compounds as well as elements is not always satisfactory. Many examples will appear when the different family groups are reviewed ; and J. Locke (1898) [5] inquires : Why should the relations between magnesium and zinc be emphasized and the closer relation between magnesium and manganese be ignored as if the explanation were not conditioned by an equally important law of nature ? The worship of the periodic law as a fetish may stimulate the pursuit of remote analogies in one direction, and close the door to the search for closer analogies in other directions.

Multivalent elements.—According to Mendeléeff, when an element like copper forms two series of compounds in one of which it has the same valency as its neighbour in a horizontal row, the compounds of the neighbouring elements are similar. This is confirmed by the close resemblance between the bivalent compounds of copper and zinc ; but, on the other hand, the close proximity of scandium to titanium does not seem to confer on tervalent titanium compounds any of the characteristic properties of scandium. Hence, Mendeléeff's classification does not make clear the fact that *heterologous elements*—*i.e.* elements belonging to different groups in the periodic table—may give analogous compounds when in the same form of combination below their highest valency—*e.g.* silver and thallous chlorides. The compounds of ferric iron resemble those of tervalent aluminium and chromium, while those of ferrous iron are like those of bivalent zinc and magnesium. Again, the cuprous and cupric compounds have little more in common than has hydrogen sulphide and sulphuric acid—each pair of compounds has the same element—copper in the one case, sulphur in the other. Still further, the compounds of bivalent vanadium resemble those of magnesium ; tervalent vanadium, those of aluminium ; quadrivalent vanadium, those of silicon ; and quinquivalent vanadium, those of phosphorus. Hence, J. Locke (1898) and G. A. Barbieri (1914) recommended that the compounds of an element with different valencies be regarded as belonging to so many different elements. Ferric and ferrous iron are just as distinct primary forms of matter as electricity and heat are forms of energy, and the one can be converted into the other, or into metallic iron. When a ferric salt is reduced to a ferrous salt, or into metallic iron, the form of matter analogous to tervalent iron has ceased to exist.

The higher oxides.—G. Wyrouboff represents the actual state of our knowledge of the higher oxides of the elements by a chart constructed like the ideal curve, Fig. 3. The selection of the characteristic oxides by Mendeléeff (Fig. 3) is quite arbitrary, there appears to be no guiding principle. Sometimes it is the lower oxide which is selected—*e.g.* BaO in place of BaO_2; sometimes a higher—*e.g.* Mn_2O_7 in place of MnO_2, MnO, etc. Sometimes it is the more stable oxide—*e.g.* BaO and not BaO_2; and sometimes it is the less stable one—*e.g.* Cu_2O, not CuO. The curve of the actual oxides will doubtless be modified by future researches, but it is far less regular and has more the character of a zig-zag line. No longer can the higher oxides ranged along the same horizontal line be said to have any relation with their chemical analogies; the best established of which may disappear; and harmonious order is replaced by *la plus absolue anarchie.* Against these views it has been urged that Mendeléeff purposed selecting the highest *salt-forming oxide* in his table, and that he did not regard such oxides as K_2O_2, BaO_2 as salt-forming oxides.[6] If he distinctly specified the salt-forming oxides, it is urged that the generalization cannot be impugned by the consideration of another class of oxides altogether. Mendeléeff claims that the true peroxides, BaO_2, Cr_2O_7, TiO_2, H_2O_2, cannot form corresponding salts, whereas PbO_2 and Bi_2O_5 are distinctly salt-forming oxides in that the one corresponds with the plumbates, and the other with the bismuthates. However, the existence of the persulphates, pertungstates, and permolybdates does not harmonize with D. I. Mendeléeff's views. The explanation of D. I. Mendeléeff, moreover, does not account for copper—cuprous oxide, Cu_2O, should be the maximum salt-forming oxide of this element, whereas cupric oxide, CuO, is the commoner salt-forming oxide.

G. Wyrouboff, in a paper, *Sur la classification périodique des éléments* (1896),[7] has the idea that the periodic system is a very interesting and highly ingenious table of the analogies and the dissimilarities of the simple bodies—a mere *catalogue raisonné* of the elements; and further, allowing Mendeléeff's *dictum*—the laws of nature admit of no exception—the periodic law must be accepted or rejected as a whole; there are numerous cases where the periodic law conflicts with facts; *ergo*, the law ought to be rejected. G. Wyrouboff adds that the periodic classification is a sterile combination of numbers; it is an ingenious combination of observations arbitrarily selected; and one of those vague formulæ which satisfies subjective conceptions, without corresponding with any objective reality. His proposal to reject the periodic law is somewhat precipitate, for we do not feel quite satisfied that the supposed misfits are not due to defective knowledge. Some can see a distinction between failure and incomplete success. Although a single contradictory fact is fatal to a hypothesis, the hypothesis is not to be rejected on the first *primâ facie* conflict with reality. This does not justify the relegation of inconsequent facts into obscurity, but rather indicates the need for keeping them in a conspicuous position. The law may have to be ultimately abandoned; it is only excessive zeal which could say *qu'aucun argument chimique ne pouvait prévaloir contre la loi périodique.* What M. Faraday[8] said a century ago (1819) applies to-day:

> Much as the present stage of knowledge owes to the tendency of the human mind to methodize, and therefore to facilitate its labours, still it may complain that in some directions it has been opposed and held down to error by it. All method is artificial and all arrangement arbitrary. The distinction we make between classes, both of thoughts and things, are distinctions of our own; and though we mean to found them on nature, we are never certain we have actually done so. That which appears to us a very marked distinctive character may be really of very subordinate importance, and where we can perceive nothing but analogies and resemblances, may be concealed nature's greatest distinctions.

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CHAPTER VII

HYDROGEN

§ 1. The Occurrence of Hydrogen in particular and of the Elements in general

> It can be said that hydrogen is more widely distributed in the universe than any other element, since its presence has been recognized spectroscopically in all the heavenly bodies.—E. BAUR (1907).

THE element hydrogen occurs free in nature in comparatively small quantities. Free hydrogen has been detected in the gaseous exhalations from volcanoes and fumaroles. Thus R. Bunsen,[1] in 1853, found 25·14 per cent. of hydrogen, along with carbon dioxide and hydrogen sulphide, in the gases from the Reykjalidh fumaroles in Iceland; H. Moissan (1902) reported 8·12 per cent. of free hydrogen in the gases from Monte Pelée (Martinique), where the disastrous eruption of 1902 occurred; A. L. Day and E. S. Shepherd found 10·2 per cent. of hydrogen in the gases from the crater at Kilauea, Hawaii, in 1912; and F. Fouqué, 29·43 per cent. in the gases from Santorini (Ægean Sea).

TABLE I.—COMPOSITION OF SOME NATURAL GASES.

	Reykjalidh, Iceland.	Monte Pelée, Martinique.	Kilauea, Hawaii.	Santorini, Ægean Sea.	Stassfurt Mines.
Hydrogen	25·14	8·12	10·2	29·43	93·050
Oxygen	—	13·67	—	0·32	0·185
Nitrogen	0·72	54·94	11·8	32·97	5·804
Carbon dioxide	50·60	15·38	73·9	36·42	0·180
Carbon monoxide	—	1·60	4·0	—	—
Sulphur dioxide	—	—	—	—	—
Hydrogen sulphide	24·12	—	—	—	—
Ethane	—	5·46	—	0·86	0·778

Hydrogen has also been detected in natural gas. The presence of hydrogen in these gases has been denied, although many published analyses include free hydrogen [2]—for instance, S. P. Sadtler reported 4·79 to 22·50 per cent. of hydrogen in the gases from the petroleum springs of Pennsylvania; C. C. Howard found an average of 1·76 per cent. of hydrogen in natural gas from Indiana and Ohio; E. H. S. Bailey found none in the gas from Kansas, and F. C. Phillips none in the gas from Vancouver; free hydrogen has been found among the gaseous inclusions in the anhydrite or salt deposits of Stassfurt, Leopoldshall, and Wieliczka; H. Precht's analysis is given in Table I. Confirmatory observations have been made by H. Rose, H. Precht, E. Reichardt, E. Erdmann, etc.[3] Occluded gases containing free hydrogen have been obtained from granites and other rocks.[4] Thus, W. A. Tilden found:

	H_2	N_2	CO_2	CO	CH_4
Granite (Skye)	61·68	5·13	23·60	6·45	3·02
Gabbro (Cornwall)	88·42	1·90	5·50	2·16	2·03
Pyroxene, Gneiss (Ceylon)	12·49	1·16	77·72	8·06	0·56
Gneiss (Seringapatam)	61·93	0·56	31·62	5·36	0·51
Basalt (Antrim)	36·15	1·61	32·08	20·08	10·00

A. Gautier obtained 134·61 c.c. of hydrogen from 100 grams of granitic rock. A small part of the gases existing in rocks is entrapped in minute cavities and pores. Some suppose that the larger part is occluded in the mineral much as palladium can occlude hydrogen, while others assume that the gases are not free in the minerals but are liberated through chemical reactions when the mineral is heated in vacuo —*e.g.* methane comes from organic matter present; carbon oxides from carbonates; nitrogen from nitrides; and hydrogen from the decomposition of steam by iron or its oxides or salts. Free hydrogen has also been found in the occluded gases of meteorites—in quantities varying from 0·2 to nearly 50 c.c. per gram of solid. T. Graham obtained 16·53 c.c. of gas from 5·78 c.c. of the Lenarto meteoric iron, and the gas contained 85·68 per cent. of hydrogen by volume; 9·86 of nitrogen; 4·46 of carbon dioxide; and no carbon dioxide. The meteorite contained 90·88 per cent. of iron; 8·45 of nickel; 0·66 of cobalt; and 0·002 of copper. A. W. Wright's analyses of the gases occluded in iron and stoney meteorites gave

	CO_2	CO	CH_4	H_2	N_2
Iron type . .	8·6–14·4	12·5–67·7	—	18·2–76·8	1·5–5·1
Stone type . .	35·4–81·0	1·7–4·4	0·0–3·6	13·1–57·9	1·7–3·5

W. Ramsay and M. W. Travers found a gram of a sample of meteoric iron from Toluca contained 2·8 c.c. of occluded hydrogen; from Charcas (Mexico), 0·28 c.c.; and from Rancho de la Pila (Mexico), 0·57 c.c. W. E. Hidden, W. M. Flight, J. Dewar and G. Ansdall, M. W. Travers, J. W. Mallet, etc., have also found hydrogen in meteorites. Hydrogen has also been reported by J. Parry, and A. Pictet and L. Ramseyer as occluded in cast iron, steel, coke, and coal.

Although hydrogen is being constantly liberated from the earth's solid crust, the proportion actually found in the atmosphere at sea level is very small; at higher altitudes, the proportion is probably greater, but the atmosphere is there so attenuated that the actual amount is very small. J. H. Jeans estimates that the number of molecules of hydrogen per c.c. at a height h kilometres, is

	$h=0$	$h=20$	$h=80$	$h=160$	$h=800$
Hydrogen . .	10×10^{13}	8×10^{13}	43×10^{12}	182×10^{11}	3×10^{10}
Nitrogen . .	78×10^{17}	43×10^{16}	520×10^{11}	35×10^{7}	0
Oxygen . .	21×10^{17}	7×10^{16}	25×10^{11}	3×10^{6}	0

F. C. Phillips[5] could detect no hydrogen at a height of 7000 feet above sea level, but owing to exhalations from natural gas and the decay of organic matter, he believes it will be found at still higher levels; H. and E. Erdmann found it at a height of 800 metres. J. L. Gay Lussac could find none in air collected at an altitude of 6,636 metres during his balloon ascent in 1804. The estimates which have been made of the amounts of free hydrogen in the atmosphere are somewhat discrepant. J. B. A. Dumas and J. B. J. D. Boussingault's analyses of air in 1841, indicated the presence of hydrogen, but they thought the gas must be present in air in the form of methane, CH_4. In 1898, A. Gautier calculated that 100 litres of air contain from 11 to 18 c.c. of hydrogen; and, in 1900, G. D. Liveing and J. Dewar found hydrogen and helium to be always present in the more volatile portions obtained by the fractional distillation of liquid air. Lord Rayleigh's estimate, from spectroscopic observations, is about one-sixth of that of A. Gautier; and A. Leduc's observations on the density of air also indicate that A. Gautier's estimate is too high. G. Claude found air to contain less than 0·00001 part of free hydrogen.

Spectroscopic observations[6] of the sun's chromosphere show what appear to be stupendous red flames of incandescent hydrogen with calcium and a few other elements in some cases towering over 300,000 miles (M. Fenyi, 1892) into space, and 100,000 miles in width (C. A. Young, 1872)—thousands of times larger than the earth on which we live. These prominences, as they are called, have been observed to shoot nearly half a million miles within 10 minutes of time. Spectroscopic observations also show that hydrogen is present in nebulæ and certain stars.

Combined hydrogen is common. Water contains one-ninth of its weight of hydrogen. We really know nothing about the hydrogen as it is combined with oxygen in water. The fact is that when water is decomposed under certain conditions, this proportion of hydrogen is obtained. It is the *façon parler* to say that the compound *contains* the element, or that the element *occurs* in or is *present* in the compound, when the element can be obtained from the compound by suitable methods of decomposition. The occurrence of an element, refers not only to the conditions under which the free element may be found, but also to those natural compounds which contain the element united with other elements. Hydrogen occurs combined not only with oxygen as water, but also with sulphur as sulphuretted hydrogen; with chlorine as hydrochloric acid; with nitrogen as ammonia; and more rarely combined with phosphorus, iodine, bromine, and carbon. It is one of the chief constituents of animal and vegetable tissue. Hydrogen also is present in nearly all organic compounds, in all acids, and in many gases—the hydrocarbons (petroleums), hydrogen sulphide, etc.

A. Gautier (1901) attributes the formation of free hydrogen in nature, (1) to the decomposition of water at a red-heat by ferrous salts, etc.; (2) to the decomposition by heat of hydrocarbons formed from natural carbides; and (3) to the decomposition of such compounds as iron nitride by steam—$2NFe_3+6H_2O=2NH_3+6FeO+3H_2$, a reaction observed when a crystalline iron nitride from Etna lava is treated with water.

Quantitative distribution of the elements.—By comparing a large number of analyses of rocks, etc., F. W. Clarke (1916)[7] has tried to estimate the percentage composition, by weight, of the earth's crust (½ mile deep) together with the ocean and the atmosphere. His result is:

	Per cent.		Per cent.		Per cent.
Oxygen	50·02	Magnesium	2·08	Barium	0·08
Silicon	25·08	Hydrogen	0·95	Manganese	0·08
Aluminium	7·30	Titanium	0·43	Strontium	0·02
Iron	4·18	Chlorine	0·20	Nitrogen	0·03
Calcium	3·22	Carbon	0·18	Fluorine	0·10
Sodium	2·36	Phosphorus	0·11	Bromine	0·008
Potassium	2·28	Sulphur	0·11	All other elements	0·41

He also emphasizes the fact that in the solid crust, the lighter elements predominate over the heavier, so that the abundant elements all have an atomic weight less than 56. The heavier metals occur only in trivial amounts. The mean density of the earth—5·4–5·6—however, is about double that of the average of the surface rocks. This has led to the assumption that the heavier elements are concentrated in the interior—a supposition, says F. W. Clarke, which is possibly true, but unprovable.

If we try to get an estimate of the *relative* number of atoms of the different *kinds* of elements distributed in the half-mile crust, the ocean and the atmosphere, Clarke's numbers must be divided by the corresponding atomic weights of the elements. We thus obtain for **the percentage number of atoms in the half-mile crust:**

Oxygen	53·81	Sodium	1·72	Potassium	1·02
Hydrogen	16·30	Magnesium	1·61	Carbon	0·27
Silicon	15·87	Calcium	1·40	Titanium	0·16
Aluminium	4·68	Iron	1·29	Chlorine	0·11

This gives a better idea of the relative distribution of the elements from the chemical point of view than the actual weights in the preceding list.

The occurrence of the elements and the periodic law.—D. I. Mendeléeff[8] has drawn attention to the fact that *the elements which occur most abundantly on the earth's surface have small atomic weights*; the converse does not necessarily apply, for some elements with small atomic weights—*e.g.* lithium (7), beryllium (9), and boron (11) —are by no means abundant. There are some exceptions to D. I. Mendeléeff's rule; strontium, for instance, appears to be less abundant than barium. The elements in the groups of Mendeléeff's table often occur more abundantly in passing from the first to the second member, and afterwards decrease with increasing atomic weight—*e.g.* the alkali family; the tetrad group; etc. J. H. Gladstone argued that the average vapour density of the elements which are plentiful is less than that of the elements which are common; and with those which are common, it is less than with the rare elements; and with the rare elements less than with the very rare elements. Consequently, says J. H. Gladstone, as the earth cooled from the vaporous state, those elements having the least vapour density must have tended to remain near the surface, while those with a high vapour density accumulated more towards the centre, and therefore occur most rarely on the surface crust.

In a paper *On the periodic law, and the occurrence of the elements in nature* (1884), T. Carnelley has made a special study of the occurrence of the elements from the point of view of the periodic law. He shows that with the exception of carbon, nitrogen, oxygen, sodium, magnesium, aluminium, and silicon, the elements belonging to the odd series of Mendeléeff's table are, as a rule, easily reduced to the free state, while those elements belonging to the even series are usually reduced with difficulty. The exceptional elements correspond with the exceptional character of the atomic volume curve—Fig. 4, Cap. VI—where the curve instead of continuing to fall as it reaches carbon, begins to rise until it comes to sodium. The ready reducibility of the elements of the odd series corresponds with their common occurrence in the free state. Excepting carbon, nitrogen, oxygen, and group VIII, *the elements belonging to the even series do not occur in the free state, whereas elements belonging to the odd series generally, and sometimes frequently, occur free.* The following elements of the odd series, for instance, are frequently found in a free state: copper, silver, gold, mercury, arsenic, antimony, bismuth, sulphur, selenium, tellurium, lead, and tin, while gallium, indium, and thallium are so sparsely distributed that not enough is known to justify a definite statement about them. The four halogens—fluorine, chlorine, bromine, and iodine—zinc, and phosphorus are the only notable exceptions because sodium, magnesium, aluminium, and silicon have already been accounted for, and the exceptions, carbon, nitrogen, and oxygen, in the even series also belong to the peculiar part of the atomic curve. The elements of group VIII all occur native, and this tendency is the more marked the greater the atomic weight. The four halogens are the most electro-negative of the elements, and they occur in nature united with the most electro-positive elements, and excepting a few secondary products—oxychlorides and sulphochlorides—are never found in combination with oxygen or sulphur.

T. Carnelley further shows that excepting the halogens and the members of group VIII, *the elements belonging to the odd series of Mendeléeff's Table rarely occur in nature as oxides, but usually occur as sulphides (or double sulphides), selenides, tellurides, or arsenides*—*i.e.* in combination with negative elements belonging to an odd series. In illustration, the following elements of the odd series commonly occur as sulphides, selenides, tellurides, or arsenides—copper, silver, zinc, cadmium. mercury, gallium, indium, thallium, lead, antimony, sulphur, selenium, and tellurium. On the other hand, arsenic, bismuth, and tin are generally found in this form; while gold, sodium, magnesium, aluminium, silicon, and phosphorus rarely if ever occur so combined. *The tendency of the members of the odd series in any particular group to occur in nature as sulphides increases, and the tendency to occur as oxides or double oxides diminishes as the atomic weight increases.* For example, in group II, magnesium nearly always occurs as double oxide (carbonate, silicate, etc.); zinc occurs commonly as sulphide, sometimes as oxide; cadmium, found as sulphide, never as oxide; and mercury as sulphide, or metal, never as oxide. In group IV, silicon occurs always as oxide or double oxide (silicates); tin, almost always as oxide, sometimes as sulphide; and lead generally as sulphide, rarely as oxide. Similarly with the other groups.

On the other hand, *elements belonging to the even series usually occur as oxides or double oxides—silicates, carbonates, sulphates, aluminates, etc.*—*i.e.* in combination with an element belonging to an even series. In illustration, the following elements of the even series commonly occur as oxides or double oxides—lithium, potassium, rubidium, cæsium, beryllium, calcium, strontium, barium, boron, scandium, yttrium, lanthanum, ytterbium, carbon, titanium, zirconium, cerium, thallium, vanadium, niobium, didymium, tantalum, chromium, terbium, tungsten, and manganese. Molybdenum and manganese (rarely) occur as sulphides. Nitrogen (in the nitrates) and molybdenum frequently occur as oxides or double oxides.

Excepting iron, nickel, and cobalt the elements of group VIII rarely occur in a combined state. Iron usually occurs as oxide, frequently as sulphide; cobalt usually as sulphide or arsenide, and sometimes as oxide; while nickel almost always resembles the elements of the even series, cobalt the elements of the odd series. Hence the three triads of elements in group VIII show a gradual passage from the even to the odd series.

T. Carnelley summarizes the facts: *Elements standing on the falling portions of the curve of atomic volumes are reducible with difficulty, and never occur in a free state in nature or in combination as sulphides, but always in combination with oxygen, forming oxides or double oxides—e.g. silicates, sulphates, carbonates, etc. Elements on the rising portions of the curve are easily reducible, and almost always occur more or less in the free state in nature, and also in combination with sulphur, but rarely with oxygen.* It is possible that the exceptions are apparent, not real, and that with increasing knowledge the anomalies will disappear, for the coincidences are too many, and the exceptions too few, to lead to any conclusion other than that the relative abundance of the elements is somehow connected with their position in the periodic classification.

W. D. Harkins[9] has noticed that when the elements are arranged in the order of their atomic numbers, the even numbered elements are in every case more abundant in meteorites than the adjacent odd numbered elements; similar remarks apply to the earth's lithosphere. In all cases also the elements of low atomic number and low atomic weight occur much more abundantly than elements with a high atomic weight.

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§ 2. The Preparation and Purification of Hydrogen

The progress of aeronautics, and the use of hydrogen for the so-called hardening or hydrogenation of oils, and the synthesis of ammonia, has incited industrial chemists to improve the existing processes and to develop new methods for preparing this gas. The use of hydrogen for the inflation of balloons was proposed by J. A. C. Charles in 1783, soon after H. Cavendish's work on inflammable air ; and the first balloon sent up from British soil on November 25, 1793, was inflated with hydrogen. The lifting power of hydrogen is about 1·2 kilograms per cubic metre, or about 68½ lbs. per 1000 c. ft.

If the molecular weight M (hydrogen=2) of a gas be expressed in ozs., a gram-molecule of the gas will occupy nearly 22·3 c. ft., at n.p.t.; an ounce of the gas will thus occupy 22·3/M c. ft., and a pound of the gas will occupy nearly 357/M. c. ft., or a cubic foot of the gas will weigh M/357, or 0·0028M lb. Again, the lifting power of a given volume, v, of any gas is equal to the difference between the weight of the gas and the weight of an equal volume of air at the same temperature and pressure. The lifting power of a gas of molecular weight M at sea level is therefore 0·0028v (28·98—M) lbs., so that the lifting power of 500,000 c. ft. of hydrogen at n.p.t. is nearly 38,000 lbs. If a gas had a lifting power greater than hydrogen its molecular weight would be less than 2, and in the extreme case, a gas with a vanishingly small atomic weight would have a lifting power about 7½ times that of hydrogen.

The gas for dirigible balloons must be free from such impurities as are liable to attack the fabric of the balloon ; and for military purposes as small a plant and as small a weight of material as is practicable must be employed. Cost is not then of prime importance. In addition hydrogen is also used as a combustible in special cases—*e.g.* the oxyhydrogen blowpipe ; for the manufacture of quartz glass ; the synthesis of gems—*e.g.* rubies and sapphires ; in the melting of platinum ; and in the autogenous welding of steel, iron, copper, and various alloys. It is also used mixed with nitrogen as an inert atmosphere in the manufacture of tungsten filaments for lamps, and in fusing tungsten powder into rods.[1]

Some processes for the preparation of hydrogen have been previously discussed. The more important methods which have been suggested for preparing hydrogen are based upon the electrolysis of water, the decomposition of water by chemical reactions, the action of metals on dilute acids, the decomposition of metal hydrides, the action of metals and alloys on alkaline lye, the decomposition of hydrocarbons, and the formation of hydrogen as a product of secondary importance—*i.e.* as a by-product—in processes pursued for other substances called the primary or main products of the reaction.

(1) *The electrolysis of aqueous solutions.*—Highly purified water is a poor conductor of electricity, but if the water be made slightly acid or alkaline it can be readily electrolyzed. Hydrogen gas is liberated at the cathode, oxygen at the anode. In addition to the work of decomposition, a certain proportion of current is expended in warming up the liquid, so that the total energy expended is the sum of that

absorbed as heat and that which does chemical work. The heating effect is proportional to the resistance, R ohms, and to the square of the current, C amps. The total electrical energy of the current—C amps. and E volts—is CE watts; the chemical work done by the current is $CE-C^2R$, and this is approximately 69 Cals. per gram-molecule of water. One coulomb of current decomposes 0·0933 mgrm of water; and gives 0·0829 mgrm. or 0·058 c.c. of oxygen; 0·01034 mgrm. or 0·1150 c.c. of hydrogen; that is, 0·0933 mgrm or 0·1725 c.c. of mixed gases. Otherwise expressed, one ampere hour of current decomposes 0·3351 grm. of water liberating 0·298 grm. or 207·2 c.c. of oxygen; 0·0373 grm. or 414·4 c.c. of hydrogen; or 0·3353 grm. or 621·6 c.c. of mixed gases. With an intensity of 1·5 volts, virtually no current passes through the electrolyte, because at least that potential is required to start the electrolysis and provide the energy for the decomposition. With a rather higher voltage, a current passes through the electrolyte, but no visible evolution of gas occurs with electrodes of the usual size until the solution is saturated with hydrogen and oxygen gases. A solution of one part of sulphuric acid with ten of water, in an electrolytic cell fitted with platinum electrodes, is readily broken down by a current with an intensity of not less than 1·7 volts; sodium hydroxide solutions have a similar minimum voltage of 1·69 volts, and potassium hydroxide, 1·67 volts. The electrolysis proceeds with a copious evolution of gas when a current with an intensity of 2 or 3 volts is used.

The strong tendency towards oxidation at the anode and towards reduction at the cathode renders the electrodes particularly liable to attack during the electrolysis. Graphite or carbon anodes suffer some oxidation; platinum and gold anodes are not attacked; and lead anodes are superficially oxidized, but the film of lead dioxide seems to protect the metal from further attack. Gold cathodes are not perceptibly attacked; platinum cathodes slowly blacken, probably owing to the absorption of hydrogen and its subsequent decomposition whereby a film of platinum-black is formed; and lead cathodes slowly blacken and disintegrate superficially so that powdered lead collects on the floor of the cell. The action is probably similar to that with platinum. Iron makes a good cathode with alkaline solutions. The electrodes, of course, must also resist the chemical action of the acid or alkaline electrolyte. If the cathode can unite with an alkali metal, or occlude or dissolve hydrogen gas, it is liable to disintegrate rapidly, presumably because of the successive formation of an alloy and its decomposition by the water of the electrolyte.

The proportion of gases liberated during the electrolysis of water is always less than the theoretical amount, and the volume of oxygen less than half that of hydrogen. Temporary losses at the beginning of the electrolysis may occur through the absorption of hydrogen at the cathode, or of oxygen by the superficial oxidation of the anode. These losses, however, cease when the cathode is saturated, and when a continuous protective coat of oxide is formed on the anode. There is a certain loss caused by the recombination of hydrogen and oxygen dissolved in the electrolyte to form water. The dissolved hydrogen unites with oxygen at the anode; and the dissolved oxygen with the hydrogen at the cathode. The diminution in the volumes of the two gases is in the same proportion as they are evolved. If the electrolysis proceeds while the system is under pressure, more amperes will be transmitted for the same applied voltage, or the same number of amperes can be passed with a smaller applied voltage. In this case, the output of gas per ampere hour decreases, and the heating effect is diminished, because, under pressure, (i) more hydrogen and oxygen dissolve in the electrolyte and this increases the amount of recombination; and (ii) the conductivity of the solution is increased while the resistance and consequently also the heating effect is decreased.

In the electrolysis of dilute sulphuric acid, oxygen may be lost owing to the formation of *persulphuric acid* or persulphates. The amount so lost depends on the temperature, current density, and the concentration of the acid. Thus, O. Schönherr[2] found that at ordinary temperatures the percentage amounts of oxygen lost in the formation of persulphuric acid with acids of different concentrations—specific gravities—and different current densities—amperes per sq. metre—are :

Sp. gr. H_2SO_4 . .		1·15	1·20	1·25	1·30	1·35	1·40
Loss of oxygen	5 amps. .	—	—	—	1·18	3·9	23·0
	50 amps. .	—	4·4	29·3	47·2	60·5	67·7
	100 amps.	7·0	20·9	43·5	51·6	71·3	75·7

In commercial work the concentration of the acid and the current density are adjusted to fall well below the minimum here indicated. The persulphuric acid in solution may pass by diffusion or circulation to the cathode where it is reduced by the hydrogen back to sulphuric acid. Under these circumstances the net result is a loss of hydrogen and oxygen in the proportions in which they are liberated—the persulphuric acid acts as an intermediate compound. The higher the temperature the less the loss of oxygen by the formation of persulphuric acid, and running the cell warm is one of the best remedies. There may be losses of oxygen from the anodic formation of *hydrogen peroxide*. The conditions which particularly favour the formation of this compound—over 60 per cent. sulphuric acid—do not usually obtain in the electrolytic cells used for the generation of hydrogen and oxygen. There is also a tendency to form a little *ozone*, which decreases the total volume of oxygen given off—but the presence of ozone is often an advantage since the oxygen gas is then a more efficient oxidizing agent. The conditions which favour the formation of ozone are high current density ; highly concentrated sulphuric acid—say up to 50 per cent. ; and low temperatures. The amount of ozone formed is small when working with a low current density, very dilute acid, and warm solutions.

When but small quantities of electrolytic hydrogen are required in the laboratory the anode is formed by immersing the platinum wire in a mass of liquid zinc amalgam (Fig. 1) which absorbs the oxygen to form zinc oxide and finally zinc sulphate ; the cathode is a platinum plate. A current from an accumulator giving between 4 and 6 volts, suffices to work the cell charged with dilute acid (1 : 10)—the gas is comparatively pure. If alkali lye and nickel electrodes be used, the hydrogen will be contaminated with hydrocarbons derived from traces of carbides, etc., in the caustic alkali ; but, according to H. B. Baker (1902),[3] an aqueous solution of purified crystalline baryta gives a gas of the highest degree of purity. H. B. Baker used a platinum plate as cathode, and a platinum wire dipping in zinc amalgam for the anode. The zinc amalgam absorbs the oxygen. According to E. W. Morley, if the alkaline solution used in the electrolysis contains carbonates, hydrocarbons may be formed.

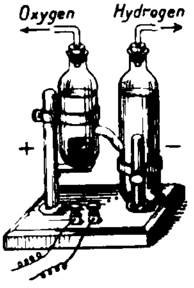

FIG. 1.—Preparation of Hydrogen on a small scale of electrolysis

On the industrial scale, a great many systems for the electrolysis of water have been designed and used ; many of these are described in V. Engelhardt's *Die Electrolyse des Wassers* (Halle a. S., 1902) and M. N. Schoop's *Die industrielle Electrolyse des Wassers* (Leipzig, 1901). In most of the arrangements, dilute sulphuric acid is electrolyzed between lead electrodes, or sodium hydroxide solutions between iron or nickel electrodes. The main practical difficulties are : (i) The slight attack of the electrodes by the electrolyte, and (ii) the necessity of preventing the admixture of the two gaseous products of the electrolysis without increasing the internal resistance of the cell too much by means of diaphragms, say asbestos. There are four leading types of cell : [4] (1) The filter-press type ; (2) the tank type : (3) the bell type ; and (4) the metal partition type.

O. Schmidt's **filter-press type** of cell is based on the fact that if a conducting material be placed between the anode and cathode of an electrolytic cell, the system behaves as if it were really two cells, because while hydrogen is liberated at the cathode and oxygen at the anode, oxygen is also liberated from the side of the diaphragm facing the original cathode and hydrogen from the side facing the original anode—provided the voltage drop between the original anode or cathode and the conducting partition is less than the minimum voltage required for electrolysis. The cell is made of recessed iron plates and they are clamped together with an intermediate partition with a rubber border and porous asbestos cloth in the centre. Hence, a series of each pair of plates forms one cell and two half cells. The iron plates are thus insulated from one another so that if the cells be filled with electrolyte, and the end plates be made respectively positive and negative poles, the current passes from pole to pole through the electrolyte and the iron plates. A series of these plates are clamped together as indicated in Fig. 2. The hydrogen and oxygen liberated at alternate sides of these plates pass through suitable passages into collecting pipes. The asbestos partitions prevent the mixing of the gas. The hydrogen is about 99 per cent. purity, the oxygen 75½ per cent.; about 5·9 c. ft. of hydrogen and 3 c. ft. of oxygen at mean temperature and pressure are collected per kilowatt hour; with a series of 40 plates, about 2·5 volts are absorbed in each cell and the current density about 2 amps. per sq. decimetre. The apparatus is compact, but the rubber joints of the diaphragm require close attention to prevent leakage.

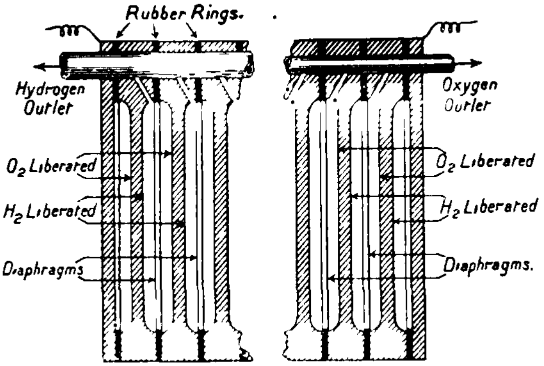

Fig. 2.—Diagrammatic Arrangement of O. Schmidt's Filter Cells.

The International Oxygen Co.'s **tank type** of cell has a mild steel tank fitted with an iron cylinder perforated with holes and hung from the cast-iron lid of the tank by means of a conducting rod. An asbestos curtain surrounds the inner cylinder. The lid of the tank is insulated from the outer walls and from the central rod. The cell is filled with a 10 per cent. solution of sodium hydroxide. The lid is also fitted with suitable outlet pipes so that during the electrolysis the hydrogen liberated from the walls of the tank and the oxygen liberated on the walls of the inner cylinder are collected in separate pipes. At 20°, and 29·92 in. pressure, 3·051 c. ft. of oxygen and 5·950 c. ft. of hydrogen were collected per kilowatt hour, and the purity of the hydrogen was 99·70 per cent., and of the oxygen, 98·34 per cent. In M. U. Schoop's **bell type** of cell, a perforated tube—made of iron if the electrolyte be alkaline, and of lead if the electrolyte be acid—is surrounded by a glass or porcelain tube as illustrated in Fig. 3. The electrodes are arranged in pairs as shown in the diagram. Two pairs are placed in each cell. One pair acts as anode, the other pair as cathode. The glass tubes collect the gases, and there is little risk of mixing the gases. In Schuckert's system, the electrodes are arranged so that the gas from each electrode collects in a separate cell. In P. Caruti's **diaphragm type** of cell, pierced metal diaphragms are employed. The electrolysis of brine solutions for caustic alkali and chlorine furnishes hydrogen as a by-product. The cost of the electrolytic process per 2000 cubic feet of hydrogen (and 1000 cubic feet of oxygen) is about 19*d.* on the assumption that the electrical energy costs ½*d.* per unit.

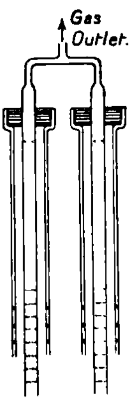

Fig 3.—Pair of M. U. Schoop's Electrodes

(2) *The decomposition of water.*—A large number of oxidizable substances can be employed for this purpose. In his *Essai de mécanique chimique fondée sur la*

thermochimie (Paris, 2. 521, 1879), M. Berthelot showed that in very many cases, the decomposition of water with the liberation of hydrogen can be effected by substances, which, in uniting with the oxygen of the water, give off more heat than occurs when hydrogen unites with the same proportion of oxygen. The results of the action of the alkali metals and the metals of the alkaline earths, previously indicated, are represented by the equations:

$$\begin{matrix}\text{Na}\\ \text{Na}\end{matrix}+\begin{matrix}\text{H}-\text{O}-\text{H}\\ \text{H}-\text{O}-\text{H}\end{matrix}=\begin{matrix}\text{Na}-\text{O}-\text{H}\\ \text{Na}-\text{O}-\text{H}\end{matrix}+\begin{matrix}\text{H}\\ \cdot\\ \text{H}\end{matrix};\ \text{and}\ \begin{matrix}\text{Ca}\\ \vdots\end{matrix}+\begin{matrix}\text{H}-\text{O}-\text{H}\\ \text{H}-\text{O}-\text{H}\end{matrix}=\begin{matrix}\text{H}\\ \cdot\\ \text{H}\end{matrix}+\text{Ca}<\begin{matrix}\text{O}-\text{H}\\ \text{O}-\text{H}\end{matrix}$$

In the former case, one atom of hydrogen in each molecule of water, H—O—H, is replaced by an atom of sodium whereby a solution of sodium hydroxide, Na—O—H, is formed; in the latter case, one atom of calcium replaces one atom of hydrogen in each of the atoms of water, and thus forms one molecule of calcium hydroxide, $Ca(OH)_2$. The reactions with the alkali metals are violent, but they are controlled by amalgamating the metals with mercury. An alloy of sodium with lead—called commercially *hydrone*—generates hydrogen when in contact with water.

According to H. Fleck and H. Basset,[5] amalgamated magnesium decomposes cold water, while the metal alone has no appreciable action on cold water. H. St. C. Deville could detect no appreciable action between aluminium and boiling water. J. B. Baille and C. Féry showed that if the aluminium be amalgamated, it is rapidly oxidized by boiling water: $2Al+6H_2O \rightarrow 2Al(OH)_3+3H_2$. In the commercial application of this process, it is not necessary to amalgamate the aluminium directly, since the metal reduces solutions of mercuric salts to the metallic state: $2Al+3HgCl_2 \rightarrow 2AlCl_3+3Hg$, and any excess of aluminium present is automatically amalgamated.

H. Wislicenus and L. Kaufmann prepare the amalgamated aluminium turnings, freed from oil by treatment with aqueous soda until a copious evolution of hydrogen has set in, by rinsing them once with water, and acting on the metal for one or two minutes with a half per cent. solution of mercuric chloride; the process is then repeated, and the metal finally well washed with water, alcohol, and ether, and kept under light petroleum ready for use. The last traces of water may, after a little while, cause a reaction vigorous enough to raise the petroleum to its boiling-point. This amalgamated aluminium decomposes water with violent evolution of hydrogen.

The aluminium should be free from copper. The alloy *duralumin* contains 94 per cent. of aluminium and 4 per cent. of copper, and it is but slightly attacked by boiling water even in the presence of a mercury salt. In M. Baupré's process an intimate mixture of aluminium powder, mercuric chloride, and potassium cyanide, which is quite stable in dry air, gives a close approximation to the theoretical yield of hydrogen when gradually added to water at about 70°. S. Uyeno's alloy of aluminium (78 to 98) with a small proportion of zinc (1·5 to 15) and tin (0·5 to 7·0 per cent.) cast into plates and then amalgamated with mercury, decomposes hot water. If a little potassium permanganate be added to boiling water, in which aluminium powder is suspended, there is a continuous evolution of hydrogen. If too much permanganate be present, the reaction is retarded. Chlorates, perchlorates, and nitrates do not act in place of the permanganate as catalytic agents. H. Fösterling and H. Philipps make a mixture of metallic sodium and aluminium silicide, Al_2Si_4, into briquettes, and preserve them in air- and water-tight boxes. In contact with water, a mixture of sodium silicate and aluminium hydroxide is formed, $Al_2Si_4+8Na+18H_2O=2Al(OH)_3+4Na_2SiO_3+15H_2$. The method has been called the *sical process*.

O. Prelinger[6] found that manganese decomposes cold water slowly, and hot water rapidly. According to J. A. Wanklyn and L. Carius, reduced iron does not decompose water at 50°, but it does decompose water at 100°, and E. Ramann obtained 12 c.c. of hydrogen by boiling water for an hour with 10 grms. of iron, reduced in hydrogen. It is not clear how much of this hydrogen was occluded in the metal. N. J. B. G. Guibourt found the reaction between iron and water is accelerated by salts of mercury, copper, and the less easily oxidizable metals. M. Lorin also found the reaction to be appreciable at 40° in the presence of ammonium salts. M. Meusnier and A. L. Lavoisier prepared hydrogen in 1784 by passing steam over red-hot iron; and the hydrogen used for inflating the first balloon sent up from French soil, in 1794, was prepared by this method. The metals chromium, nickel, and cobalt act similarly. The reaction with steam and iron is usually represented by the equation: $3Fe+4H_2O=Fe_3O_4+4H_2$. It is not clear, however, what particular mixture of iron oxides is actually formed, for the observed results would accord with the formation of ferrous oxide, FeO, on the back reaction, so that for equilibrium: $3FeO+H_2O \rightleftharpoons Fe_3O_4+H_2$. M. Gillard (1850)[7] used the iron-steam process industrially; and he reduced the spent oxide with carbon monoxide and hydrogen derived from the action of steam on heated carbon. The process was soon abandoned as commercially unsatisfactory.

Porous briquettes—made from spent pyrites, obtained as a by-product in the manufacture of sulphuric acid, and clay—have been used as a source of the iron. The oxide of iron can be reduced to the metal and used over and over again by heating the oxidized briquettes with a reducing agent—*e.g.* water gas, coal gas, or producer gas. C. Jacoby used a mixture of finely divided iron with twice its weight of a hydroxide of calcium, barium, or strontium calcined to dull redness. In the modification called A. Messerschmitt's *iron contact method*, the red-hot iron in a shaft retort, resembling a gas producer, is sprayed with a jet of steam, and the iron oxide is reduced by a stream of water gas, producer gas, or coal gas. There are two types of plant, the so-called single retort and the multiple retort processes. The process is efficient and cheap when the right kind of iron is employed. Spongy iron acts more efficiently, presumably because it presents a larger surface for a given amount of iron. J. Jacob heated iron by part of the hydrogen produced in the reaction. A great many patents have been obtained for modifications of this process. The gas employed for the reduction must be free from certain impurities which gradually reduce the activity of the iron, by forming a layer of impurities (siliceous dust, sulphides, etc.) on the surface of the metal. In practice, the iron lasts from eight to thirty days, but it may be more or less revivified by periodically heating it in a stream of air.

A. Messerschmitt[8] used natural ores of manganese, or manganese and iron with the idea of lowering the reaction temperatures; O. Dieffenbach and W. Moldenhauer used alloys of iron with manganese, chromium, tungsten, titanium, aluminium, and related elements, as well as briquetted mixtures of the oxides; the Badische Anilin und Soda Fabrik used iron oxide fused with refractory oxides—zirconia, magnesia, or silicates; C. F. Jaubert used briquettes of iron oxide with fireclay, pumice, or magnesia, together with a small amount of manganese, chromium, copper, or lead oxide. Using lime purifiers to remove hydrogen sulphide and carbon dioxide a gas of 99·75 per cent. purity can be obtained by this process. The efficiency of the process rapidly deteriorates, and the maintenance of the temperature of the reaction consumes much of the hydrogen.

F. Bergius[9] argues that liquids are more reactive than gases, and that the liquid state can be maintained from the boiling point to the critical temperature if a sufficient pressure be used, and he has patented a process for the preparation of hydrogen by the action of liquid water on iron. It was found that the gas was of 99·95 per cent. purity because liquid water does not attack the dangerous impurities —sulphur and carbides—of iron so readily as steam. The speed of the reaction is accelerated in the presence of sodium chloride, ferrous chloride, and copper—*e.g.* at 300°, 230 c.c. of hydrogen per hour were obtained with pure water and iron; 1390 c.c. per hour if ferrous chloride be present; and 1930 c.c. per hour if in addition some copper be present. The yield of hydrogen per hour in the last case was nearly doubled by raising the temperature of the reaction from 300° to 340°. The hydrogen can be charged directly into cylinders without further compression. A pressure apparatus of 10 gallons capacity produced 3000 c. ft. of hydrogen per day.

The metalloids boron, silicon, and carbon can deoxidize steam. H. Moissan[10] says amorphous boron begins to act at a red heat and the reaction then proceeds with incandescence: E. Vigouroux found amorphous silicon begins to react at a red heat, and crystalline silicon at a rather higher temperature. Steam is also decomposed in its passage over red-hot coke; hydrogen and carbon monoxide, CO, are the main products of the reaction: $C+H_2O=CO+H_2$. The mixture of gaseous products by this reaction is called *water gas*. There is also a side reaction: $C+2H_2O=CO_2+2H_2$, and according to O. Dieffenbach and W. Moldenhauer,[11] the latter reaction occurs if the coke be saturated with 10 per cent. potassium carbonate, and when the coke is also mixed with five times its weight of lime, the carbon dioxide is absorbed by the lime if the temperature of the reaction be between 550° and 750°. F. Bergius also claims that the carbon dioxide reaction alone occurs if the water be maintained in the liquid state by pressure at 340°, and if one per cent. of thallium chloride be mixed with the coke. The carbon dioxide is then removed by lime. The Badische Anilin und Soda Fabrik worked with finely-divided iron as catalyst between 400° and 500°, and from 4 to 40 atm. pressure; J. L. Buchanan and E. B. Maxted used a catalyst of finely-divided iron and copper for the same purpose.

According to J. J. Coquillion water vapour and carbon monoxide are decomposed in the presence of red-hot platinum, forming carbon dioxide and hydrogen; L. Macquenne says that the transformation is complete in 25–30 hrs. in the presence of platinum sponge. The reaction is of the balanced type: $CO+H_2O\rightleftharpoons CO_2+H_2$. O. Hahn found the equilibrium condition to be $p_{H_2}p_{CO_2}K=p_{H_2O}p_{CO}$, where the equilibrium constant K has the value 0·05 at 400°; 0·1 at 500°; 0·3 at 600°; 0·6 at 700°; and 0·9 at 800°. Hence, low temperatures favour the formation of hydrogen, but, at the same time, lead to slow reactions. Consequently, the successful production of hydrogen from water gas requires the use of catalytic agents to accelerate the reaction at as low a temperature as possible. L. Mond and C. Langer patented the use of nickel at 350°–400°, or of cobalt at 400°–450° as catalysts; C. Ellis and B. E. Eldred used iron, nickel, or manganese; W. Näher and K. Müller, rhodium or palladium asbestos; L. Vignon, iron or platinum; and H. S. Elsworthy, iron or nickel.

Another problem is to separate the hydrogen from the carbon monoxide, when the first reaction predominates. There have been several proposals; among others: (1) B. C. Sykes and S. Blamires, J. Pullmann and H. S. Elsworthy, and A. Longsdon recommend removing the hydrogen by driving the gas under pressure through porous tubes. The hydrogen and methane diffuse through the walls of the tubes faster than the carbon monoxide. A. Jouve and G. Gautier (1906)[12] reduced the percentage amount of carbon monoxide from 45 to 8 per cent. by passing water gas through a porous partition through which the hydrogen diffuses far more rapidly than the carbon monoxide. (2) C. von Linde, A. Frank, and N. Caro (1906) subject the water gas to a preliminary cooling with liquid air whereby the carbon monoxide and dioxide are liquefied, the hydrogen remains as a gas. When the liquid by-product is allowed to gasify, it can be burnt as a fuel gas. (3) A. Frank (1906) passed the dried mixture over calcium carbide, CaC_2, at a temperature exceeding 300°. The carbon monoxide and dioxide form calcium oxide and carbonate, and free carbon—any nitrogen present forms calcium cyanamide. In the former case, $CaC_2+CO\rightarrow CaO+3C$; and in the latter case, $CaC_2+N_2=CaCN_2+C$. (4) When a mixture of steam and carbon monoxide is passed over lime at about 500°, the carbon monoxide is oxidized and an equal volume of hydrogen is evolved: $CaO+H_2O+CO\rightarrow CaCO_3+H_2$. According to M. G. Levi and A. Piva the reaction occurs in two stages: $CaO+H_2O+2CO=(H.COO)_2Ca$—calcium formate; and $(HCOO)_2Ca=CaCO_3+CO+H_2$. Hence, if water gas—say, a mixture of equal volumes of hydrogen and carbon monoxide—be passed over lime under these conditions, hydrogen will be substituted in place of the carbon monoxide. (5) E. K. Rideal and H. S. Taylor[13] have shown that even in the presence of large quantities of hydrogen, carbon monoxide can be oxidized to the dioxide in the presence of suitable catalysts—a mixture of iron and chromium oxides to which small quantities of ceria and thoria have been added. This catalyst completely oxidizes carbon monoxide between 200° and 300°, but does not attack hydrogen. The problem of removing a relatively large proportion of carbon dioxide by lime is a serious one. The basal patent is by C. M. T. du Motay (1880), and the Greisheim Elektron Co. added 5 per cent. of iron powder to act as a catalyst. This action was studied by W. E. Engels.

In the so-called *auto-combustion* processes of G. F. Jaubert,[14] a combustible substance and an oxidizing agent are kindled in the presence of water. The combustion once started continues and the water is decomposed. In one case, a mixture of lime and ferrosilicon at a high temperature is exposed to steam, and a little gunpowder is used to start the reaction: $3FeSi_6+40H_2O=Fe_3O_4+18SiO_2+40H_2$. In another, a mixture of iron filings, potassium perchlorate, and hydrated lime, or a mixture of ferrosilicon, litharge, and soda lime, is used. Here the reducing agent decomposes the water in the hydrated body.

J. E. G. Lahousse (1905)[15] recommended the decomposition of steam by passing it over red-hot barium sulphide, BaS, which is thereby oxidized to barium sulphate, $BaSO_4$, thus, in symbols, $BaS+4H_2O=BaSO_4+4H_2$. The sulphate can be reduced back to the sulphide by heating it with coal or producer gas: $BaSO_4+2C=2CO_2+BaS$. In the analogous process by G. Teissier and P. Chaillaux, barium sulphate is heated with manganous oxide: $BaSO_4+4MnO\rightarrow BaS+4MnO_2$; and the product raised to a white heat: $BaS+4MnO_2\rightarrow BaS+4MnO+2O_2$. When the reactions complete, steam under pressure is passed over the mixture and hydrogen is set free: $BaS+MnO+4H_2O\rightarrow BaSO_4+MnO+4H_2$. The solid products of the reactions are then ready to be employed in a fresh cycle.

(3) *The action of metals on dilute acids.*—The usual laboratory method of preparation is to act upon zinc with dilute sulphuric acid (1 : 8) or hydrochloric acid (1 : 2) as already described. Aluminium, magnesium, or iron may be substituted for the zinc. The reaction is symbolized: $M''+H_2SO_4=MSO_4+H_2$, or $M''+2HCl=MCl_2+H_2$, where M'' represents a gram-atom of the bivalent metals. The process of chemical change results in the substitution of two atoms of hydrogen in the acid by an equivalent bivalent atom. According to E. W. Morley, the purest redistilled zinc contains a little absorbed carbon monoxide which ultimately finds it way into the hydrogen gas prepared from the zinc. The impurities in the commercial metals—carbon, sulphur, silicon, phosphorus, antimony, and arsenic—form the corresponding gaseous hydrides. Sulphuric acid may contain: (i) sulphur dioxide which is evolved as such or partly reduced to hydrogen sulphide; (ii) nitrogen compounds which form nitrogen and nitrous oxides; (iii) arsenic and selenium, which form the corresponding hydrides. Hydrochloric acid made from sulphuric acid may also contain these same impurities. If the zinc and acid are pure, the resulting hydrogen has a high degree of purity, but it is evolved so slowly as to make the process of little practical use.[16] N. A. E. Millon noticed that the speed of evolution is much accelerated if a little platinic chloride be added to the hydrochloric acid. The platinic chloride is decomposed, and platinum metal is deposited on the zinc so as to form a kind of voltaic couple. A similar result was obtained by J. C. d'Almeida with platinum wire or finely divided platinum in contact with zinc, and C. Gourdon found that in these cases the hydrogen is given off quickly at the surface of the platinum—not the zinc. A similar effect is obtained with a small quantity of a salt of copper, silver, gold, tin, antimony, bismuth, nickel, cobalt, or one of the less oxidizable metals. The reaction between zinc and sulphuric acid was reported by F. Selmi to be accelerated by the presence of sulphates of manganese, magnesium, or iron, but to be retarded by sulphates of potassium, sodium, or aluminium.

Iron is little used in the preparation of hydrogen for laboratory purposes since the gas is contaminated with hydrocarbon gases derived from the carbides in the iron. These impurities give the hydrogen an unpleasant odour. In stationary military camps, hydrogen is sometimes made in this manner, but the main objection is the enormous quantity of metal and acid needed for filling an airship or balloon of but moderate size—say, 250,000 or 500,000 cubic feet capacity. In the former case, about 18 tons of iron and 31 tons of acid are needed for an inflation. The captive balloon at the 1878 Paris Exhibition had a capacity of about 883,000 c. ft. and it is said to have required 190 tons of sulphuric acid and 80 tons of iron for an inflation. This method of making hydrogen for inflating balloons is reported to have been used in 1861 in the American Civil War. Unless specially treated, the impurities in the hydrogen produced by this process are liable to rot the fabric of balloons and airships. L. V. Pratis and P. Marengo patented a process for the purification of the gas by first scrubbing it with water; and then passing it through a solution of a lead salt. Several other methods of cleaning the gas have been patented. F. Konther patented a process for recovering the acid in the preparation of hydrogen by the action of hydrochloric acid on iron; he heated the ferrous chloride to a high temperature with steam: $3FeCl_2+4H_2O \rightarrow Fe_3O_4+6HCl+H_2$.

G. V. Barton patented the recovery of the zinc sulphate produced as a by-product when zinc is used in place of iron, by treating the solution with sodium carbonate or hydrocarbonate, and igniting the precipitated zinc carbonate to form zinc oxide —the zinc white used as a pigment by paint-makers. J. Wannschaff and J. Savelsberg [17] proposed to make hydrogen and zinc oxide by the action of zinc chloride solutions on waste zinc.

(4) *The decomposition of metal hydrides.*—The hydrides of the alkali and alkaline earth metals readily decompose water at ordinary temperatures liberating hydrogen and forming the corresponding metal hydroxide: $CaH_2+2H_2O \rightarrow Ca(OH)_2+2H_2$. The commercial powder *hydrolith*—devised by G. F. Jaubert [18]—contains 90 per cent. of calcium hydride, and it gives off hydrogen by mere contact with water. A kilogram of the solid gives about a cubic metre of hydrogen. It has been used by the French army for filling observation balloons. The process is rather expensive though very convenient. In the commercial process for making calcium hydride, CaH_2, a little nitride, Ca_3N_2, is formed at the same time, and this reacts with water producing ammonia: $Ca_3N_2+6H_2O=3Ca(OH)_2+2NH_3$. The ammonia, being very soluble in water, is readily removed by scrubbing the gas with water. The lightness—low specific gravity—of lithium hydride, Li_2H, or Li_4H_2, has led to its being suggested as a means of restoring hydrogen to an airship should there be a serious loss of this gas from any cause. 27·76 lbs. of lithium hydride and 66·6 lbs. of water give 1000 c. ft. of hydrogen at about 5° and 760 mm. This amount of hydrogen would have a buoyancy of 74·06 lbs., and if the products of the reaction were dropped overboard, every 94·36 lbs. of materials would increase the buoyancy of the airship 168·42 lbs. The cost of lithium hydride is, however, too great for the general realization of this proposal.

(5) *The action of metals and alloys on alkaline lye.*—Hydrogen gas can be obtained by warming tin, aluminium, or zinc with a dilute solution of sodium hydroxide (50 grms. of the hydroxide per 500 c.c. of water). If the metals are free from carbon, the resulting gas is fairly pure. J. P. Cooke and T. W. Richards (1888) [19] used this process in some atomic weight determinations and purified the gas by passing it over solid potassium hydroxide, calcium chloride, concentrated sulphuric acid, and phosphorus pentoxide. When aluminium is used, the method is sometimes called the *hydrik or aluminal process.* We are told that the Russians prepared hydrogen for their war balloons in Manchuria during the Russian-Japanese war, 1904–5, in this way. The reactions with aluminium and zinc are respectively represented:

$$2Al'''+\left\{\begin{matrix}NaOH\\NaOH\\NaOH\end{matrix}\right.=2Al\begin{matrix}\diagup ONa\\ -ONa\\ \diagdown ONa\end{matrix}+3H_2\text{ ; and }Zn''+\left\{\begin{matrix}NaOH\\NaOH\end{matrix}\right.=Zn<\begin{matrix}ONa\\ONa\end{matrix}+H_2$$

Here it will be observed that one hydrogen atom in each molecule of sodium hydroxide is replaced by the respective elements—three by the tervalent aluminium, and two by the bivalent zinc; sodium aluminate, $Al(ONa)_3$, is a by-product in the former process; and sodium zincate, $Zn(ONa)_2$, in the latter case. With tin, sodium stannate, $Sn(ONa)_4$, is formed. We see, therefore, that under the stated conditions, an atom of sodium or potassium can displace only *one* of the two hydrogen atoms in the water molecule—H_2O; and that tin, zinc, or aluminium can displace the other hydrogen atom.

According to H. Williams (1881),[20] zinc dust heated with water alone gives hydrogen gas. Water alone, however, does not appreciably decompose boiling water; but, as shown by W. Wilson, decomposition does occur if copper turnings are also present. L. Meyer and T. Leykauf observed the evolution of hydrogen during the action of zinc and water on crystals of copper sulphate; the action in these cases is similar to that of the zinc-copper couple. H. Schwarz obtained hydrogen by heating a mixture of zinc dust and calcium hydroxide, and the process was patented by W. Majert and G. Richter for the generation of hydrogen in the field or the inflation of observation balloons. Hydrogen may be prepared by heating slaked lime with coal—C. M. Tessie du Motay and C. R. Marechal (1868)—$C+2Ca(OH)_2=CaO+CaCO_3+2H_2$.

Under the name of the *silicol process* the preparation of hydrogen by the action of sodium hydroxide on the element silicon has been recommended by Siemens and Schuckert (1911), and on the cheaper ferrosilicon—called *silicol*—or other silicon alloys by G. F. Jaubert (1908).[21]

An intimate mixture of powdered sodium hydroxide and ferrosilicon when moistened with water gives off hydrogen rapidly, and becomes incandescent. When ferrosilicon is added to a cold solution of sodium hydroxide, the metal is not rapidly attacked, but owing to the heat of the reaction, the temperature of the liquid gradually rises as ferrosilicon is added, and then reaches a stage—about 80°—where the ferrosilicon is instantly attacked. Consequently, if ferrosilicon is added faster than it is attacked by the caustic lye, when the temperature has risen to the critical stage the accumulated ferrosilicon may be instantly attacked causing an explosive pressure of gas in the gas generator. The reaction is not a simple oxidation of the water by the silicon: $Si+2H_2O=SiO_2+2H_2$, followed by the formation of sodium silicate: $SiO_2+2NaOH=Na_2SiO_3+H_2O$, so that the composite equation is symbolized: $Si+2NaOH+H_2O=Na_2SiO_3+2H_2$, since, instead of 2·86 parts of sodium hydroxide being required for one part of silicon, the ratio is less, 1 : 1·7. This shows that a richer silicate is simultaneously formed, possibly by the action of the simple sodium silicate on the silicon: say, $Si+Na_2SiO_3+2H_2O=Na_2Si_2O_5+2H_2$, where the composite reaction is symbolized: $2Si+2NaOH+3H_2O=Na_2Si_2O_5+4H_2$. This requires a ratio of silicon to sodium hydroxide of 1 : 1·43. The ratio 1 : 1·72 is the one usually recommended. With a 10 per cent. sodium hydroxide and 92 per cent. silicol solution P. L. Teed found at 15° and 30 in. barometric pressure:

Weight ratio, Si : NaOH	1 : 0·745	1 : 1·065	1 : 1·480	1 : 3·200
Hydrogen per lb. of silicol	13·62	14·30	15·36	16·80 c. ft.

With 30 per cent. sodium hydroxide solution with the ratio by weight Si : NaOH =1 : 0·852, 1 : 2·13 and 1 : 3·19, the respective yields of gas were 19·35, 23·90, and 23·58 c. ft.; while with 40 per cent. sodium hydroxide, and a weight ratio of Si : NaOH of 1 : 1·58 and 1 : 3·19, the respective yields of hydrogen were 24·10 and 24·50 c. ft. Hence, a 40 per cent. solution of sodium hydroxide with a ratio by weight of Si : NaOH of 1 : 1·6 would appear to be best, but if the solution be too concentrated, it becomes so viscous or even solid during the action that the plant is difficult to clean; if the solution be too dilute, the frothing is troublesome. A little mineral grease is sometimes used with the soda lye to prevent frothing. The usual solution employed contains about 25 per cent. of sodium hydroxide, and the ratio of Si : NaOH by weight nearly 1 : 1·72. With the 25 per cent. caustic lye and a wide generator there is no difficulty with frothing when no grease is used.

Plants are in use generating 1500 to 6000 c. ft. per hour by the silicol process. It furnishes 2500 c. ft. of gas per hour. The sodium hydroxide is dissolved in water in a tank, and run into a generator fitted with a stirrer run by a benzene motor.

The silicol in the container is fed into the generator by an automatic feed also operated by the benzene motor. The hydrogen then passes into the condenser or scrubber, where it is cooled and freed from steam. The heat generated during the action reaction raises the temperature in the generator above 100°, sometimes to 120°. Thermometers inserted in the generator enable the temperature to be observed and if necessary controlled. An excessive pressure due to the rapid generation of hydrogen is prevented by suitable seals. Precautions are of course taken to prevent the generation of an explosive mixture of hydrogen and air—usually before the caustic lye is run into the generator—by allowing hydrogen from the gas-holder to blow back hydrogen equivalent to four times the volume of the plant. When the generation of gas from a given charge has ceased, the sodium silicate solution and sludge are run from the generator by a trapped discharge pipe ; the generator is washed out with water and is ready for another charge. Low-grade ferrosilicon is not economical because it does not give equivalent yields of hydrogen. At least 80 per cent. ferrosilicon is needed to give satisfactory yields :

Silicol	50	70	85	90	per cent. Si
Yield	12½	27¼	91	97	per cent. of theory

An 84 per cent. ferrosilicon has iron 6·9 per cent., aluminium 5·3 per cent., and carbon 0·2 per cent. The sodium carbonate impurity in the caustic lye and the iron of the ferrosilicon are found unaltered in the sludge. The sludge contains 37 per cent. of silica ; 6 per cent. sodium carbonate ; 20 per cent. of soda calculated as Na_2O ; about 10 per cent. of matter insoluble in water and the remainder is water. The ferrosilicon gives a 90 per cent. yield of hydrogen, the loss being mainly due to the protective action of impurities, leakages, and the solubility of hydrogen in the water used in the scrubber. The gas has from 99 to 99·9 per cent. purity and is virtually free from arsine and phosphine, for less than 0·01 per cent. of these gases are present; the acetylene amounts to about 0·005 per cent. The main impurity is air. This process gives a large hydrogen production from an inexpensive plant ; but the cost of the reagents is high. The process is therefore advantageous where large quantities of hydrogen are periodically required, but not where there is a continuous demand.

Slaked lime substituted in place of sodium hydroxide gives very poor yields of hydrogen, but a mixture of the two gives better results than with sodium hydroxide alone. The sodium silicate formed in the first stage of the reaction between the silicon and sodium hydroxide is probably converted into the hydroxide again : $Na_2SiO_3+Ca(OH)_2=2NaOH+CaSiO_3$. A mixture, devised by G. F. Jaubert (1910), containing 25 parts of 90–95 per cent. ferrosilicon or manganosilicon, 60 of sodium hydroxide, and 20 slaked lime, is commercially known as *hydrogenite*. It is sold compressed in cakes contained in metal cartridges to protect the mixture from moisture, and when ignited—by forcing a hot ball or wire into the briquette—forms sodium and calcium silicates with the evolution of hydrogen. A kilogram of the powder gives from 270 to 370 litres of hydrogen.

(6) *The decomposition of hydrocarbons.*—When hydrocarbon gases are heated to about 1000°, they dissociate forming lamp-black, hydrocarbons, and hydrogen. In 1911, R. Pictet [22] patented a process for heating a mixture of water and hydrocarbon vapour—*e.g.* petroleum—whereby a mixture of hydrogen with some carbon monoxide is formed. The proportion of the latter depends on the proportion of water present in the original mixture. The Carbonium Co. at Friedrichshafen, the headquarters of the Zeppelin airships, has obtained hydrogen by decomposing acetylene, C_2H_2, prepared from water and calcium carbide, by electric sparks or by explosion; preferably, according to J. Machtoff, under a pressure of 4 to 6 atmospheres, $C_2H_2=2C+H_2$. The carbon wins a high price as a high-grade lamp-black. In F. G. L. Rincker and L. Wolter's process the gas produced by the distillation of crude tar, oil, or other hydrocarbon is passed through hot coke or charcoal. The 6 to 8 per cent. of carbon monoxide and hydrogen sulphide in the washed gas is partly removed by hot soda lime. The Badische Anilin und Soda Fabrik suggest

reducing the temperature of decomposition by the use of a refractory oxide like magnesia impregnated with nickel oxide for reducing the temperature of decomposition; O. Dieffenbach and W. Moldenhauer, the use of wire gauze of nickel, cobalt, platinum, etc., with short contact and sudden cooling of the products so as to avoid the reduction of carbon dioxide to the monoxide; and the Berlin Anhaltische Maschinenbau, and C. Ellis, the use of coke as a contact catalyst.

7. *By-product hydrogen.*—Hydrogen is a by-product in the manufacture of chlorine by the electrolysis of aqueous solutions of alkali chlorides; $2NaCl+2H_2O=2NaOH+H_2+Cl_2$. Chlorine is given off at one electrode and hydrogen at the other. The sodium chloride is broken down by the electric current into sodium and chlorine; and the sodium, in contact with water, reacts as indicated in the equation: $2Na+2H_2O=2NaOH+H_2$. Hydrogen is also a by-product in the manufacture of oxalates from formates, which in turn are made by treating caustic potash with carbon monoxide (producer gas) under pressure: $KOH+CO=H.COOK$; and $2H.COOK=K_2C_2O_4+H_2$. L. Vignon (1911) showed that if carbon monoxide be passed over powdered calcium hydroxide at 300°, there is no action; at 400°, a mixture of hydrogen and hydrocarbons—chiefly methane, CH_4, and ethylene, C_2H_4—is evolved.[23] The proportion of hydrogen increases as the temperature rises until at 600° only hydrogen is formed: $CO+Ca(OH)_2=CaCO_3+H_2$. The formation of the hydrocarbons is probably preceded by the formation of calcium formate and oxalate as intermediary products of the reaction: $4CO+2Ca(OH)_2+CaO=3CaCO_3+CH_4$; and $4CO+4Ca(OH)_2+CaO=4CaCO_3+2H_2+C_2H_4$. A mixture of sodium formate and calcium oxide yields nearly pure hydrogen. Steam, carbon monoxide, and calcium hydroxide form calcium formate at 250°–300°; at 500°–600°, there is almost a quantitative yield of hydrogen; the presence of sodium hydroxide lowers the temperature of the reaction. In 1861, M. Berthelot noticed that when either the formates or the oxalates of the alkalies are heated with the alkali hydroxide, hydrogen is formed; and R. Pictet prepared hydrogen by heating sodium formate, H.COONa, with soda lime. The reaction is symbolized $H.COONa+NaOH\rightarrow Na_2CO_3+H_2$; similarly, with sodium oxalate, $(COONa)_2$, or potassium oxalate: $Na_2C_2O_4+2NaOH=2Na_2CO_3+H_2$. The reactions are not particularly convenient when compared with other methods of preparation, but E. H. Amagat used the process in his work on the effect of pressure on the volume of gases.

There are several other reactions in which hydrogen is formed. These reactions are of greater theoretical than practical interest. For example, A. Bruno[24] found that when iron filings are shaken with water saturated with carbon dioxide for 36–48 hrs., the carbon dioxide is replaced by hydrogen: $Fe+CO_2+H_2O=FeCO_3+H_2$. According to M. Lorin, most of the ammonium salts and the salts of the amine bases develop hydrogen when treated with zinc at ordinary temperatures, or better at 40°; iron acts more slowly. Ammonium nitrate is not applicable since it gives nitrous oxide at 50°; similar remarks probably apply to the nitrates of the amine bases. W. P. Winter regards the alleged evolution of hydrogen by the action of water on sodamide as probably due to the presence of some free sodium. A. Descamps found that potassium cobaltocyanide, K_4CoCy_6, decomposes water at ordinary temperatures giving off hydrogen and forming the cobalticyanide, K_3CoCy_6. M. Berthelot found that acidified solutions of chromous salts gradually decompose with the evolution of hydrogen; and R. Peters noted that the reaction is accelerated by the presence of platinum black. Hydrogen is given off by uranyl acetate in sunlight. A. Sieverts found that in aqueous solutions platinum, silver, and copper cause hypophosphorous and phosphorous acids to split off hydrogen, respectively forming phosphorous and phosphoric acids: $H_3PO_2+H_2O=H_3PO_3+H_2$; and $H_3PO_3+H_2O=H_3PO_4+H_2$. Hydrogen is often evolved when organic compounds —*e.g.* oleic acid—are fused with alkalies. Hot soda-lime converts alcohol into acetic acid with the evolution of hydrogen: $C_2H_5OH+NaOH=CH_3COONa+2H_2$; formaldehyde, H.COH, gives off hydrogen in the presence of cuprous oxide and alkali: $H.COH+NaOH=H.COONa+H_2$; and also with sodium peroxide:

$2HCOH+Na_2O_2=2HCOONa+H_2$. M. Kernbaum found water can be decomposed by sunlight in accord with the equation: $2H_2O=H_2O_2+H_2$, and by exposure to ultra-violet light; and A. Dobierne observed a similar reaction with radium rays. W. Loeb detected hydrogen among the products obtained when the electric arc is formed under water.

According to G. Pollacci, W. Palladin, and J. Stoklasa and W. Zdobnicky, the gases obtained as exhalations from the green parts of plants contain some hydrogen,[25] and F. Selmi found that hydrogen is liberated by fungi and moulds—arsenic, antimony, and sulphur are converted by the same organisms into the corresponding hydrides. S. Kostytscheff found the gas formed in the respiratory gases of some seed plants. H. Tappeiner found that the gas is formed in the fermentation of cellulose, and in the decay of certain organic bodies. C. Oppenheimer and A. Krogh detected hydrogen among the intestinal gases of many animals.

The purification of hydrogen gas.—Most of the methods of preparing hydrogen furnish a gas contaminated with impurities which can generally be removed by treating the gas with suitable reagents. The nature of the impurities depends upon the character of the materials employed in the preparation of the gas. Air is one of the commonest of impurities, and it comes from the air dissolved in the liquids used in the preparation of the gas; from the air originally present in the apparatus; and by leakage through rubber and other joints. This impurity can be considerably reduced by using liquids previously boiled; and mercury sealed glass joints for the apparatus. Oxygen may also be derived from the potassium permanganate solution sometimes used for washing the gas. According to H. Debray,[26] traces of oxygen can be removed by passing the hydrogen gas over red-hot copper, over spongy platinum, melted sodium, or through a solution of chromous chloride, but the nitrogen from the air is not removed by this treatment. According to E. W. Morley,[27] from 0·01 to 0·001 per cent. of nitrogen in the gas can be recognized spectroscopically.

The hydrocarbon gases in hydrogen are derived from carbonaceous impurities in the metals and acid. E. W. Morley states that the electrolysis of dilute alkali hydroxides, or dilute hydrochloric acid, may furnish a gas contaminated with traces of carbon compounds. When the alkali contains carbonates, or the acid organic matter, M. Berthelot says that hydrogen prepared from the metals always contains carbon compounds. The electrolysis of water acidified with purified sulphuric acid is recommended by E. W. Morley[28] as the safest process to use for hydrogen of a high degree of purity, and M. Berthelot recommends washing the electrolytic hydrogen with potassium permanganate solution and scrubbing it with fused potassium hydroxide.

The metal used in preparing the gas may contain occluded carbon oxides, or sulphur, selenium, phosphorus, silicon, antimony, and arsenic, which contaminate the hydrogen with gaseous compounds. Sulphuric acid may also be reduced by hydrogen to sulphur dioxide or even to hydrogen sulphide.[29] The acids may also contain nitrogen, selenium, and arsenic compounds. Hydrocarbons can be removed by passing the gas through alcohol, or, according to J. W. Döbereiner and J. Stenhouse,[30] by passing the gas through a tube packed with recently ignited wood charcoal, or paraffin wax. M. Donovan recommends passing the gas through an oxidizing liquid—say fuming nitric acid followed by a solution of ferrous sulphate to absorb the nitrous fumes; E. Varenne and E. Hebre used a sulphuric acid solution of potassium dichromate followed by potassium hydroxide; and E. Schobig used potassium permanganate in a similar way. The sulphur, selenium, and silicon compounds are absorbed by passing the gas through a solution of potassium hydroxide; and the hydrides of arsenic, antimony, and phosphorus, according to A. Lionet,[31] are decomposed by passing the gas over red-hot copper turnings, but they are usually removed by passing the gas through solutions of the salts of metals—*e.g.* mercuric chloride, silver sulphate, lead nitrate—as indicated by J. B. A. Dumas in 1843; or else by passing the gas through a saturated solution of potassium permanganate, and then through a 5–10 per cent. solution of silver nitrate. According to H. Reckleben and G. Lockemann (1908), bromine, bleaching powder, and potassium hypochlorite are good absorbents for arsine ; the same gas is said to be removed by bubbling hydrogen through petroleum spirit cooled by liquid air at —110°, and H. K. Onnes recommends freezing out the various impurities from hydrogen by cooling it with liquid air. Carbon monoxide can be removed by passing the gas over heated soda lime : $2NaOH+CO \rightarrow Na_2CO_3+H_2$.

Hydrogen has been purified in special cases by passing it into a glass tube containing metallic palladium previously evacuated, and heated red-hot. The metal is allowed to cool in contact with the gas. The hydrogen is assumed to be alone absorbed by the metal ; and to be given off again when the tube containing the metal is heated. The tube containing the palladium is of course attached to the apparatus into which the hydrogen is to be introduced.

Drying gases.—In 1766, H. Cavendish dried gases by passing them through a tube containing a hygroscopic salt. Anhydrous calcium chloride and concentrated sulphuric acid are most commonly used as drying agents, and in special cases phosphorus pentoxide is employed. Several attempts have been made by R. Fresenius (1865),[32] E. W. Morley (1885), and G. P. Baxter and R. D. Warren (1911), to estimate the amount of moisture left in a gas after the desiccating agents have done their work. From these investigations it appears that the weight of residual water (grams) left in a litre of gas dried by different desiccating agents is as follows :

	Calcium chloride.	Zinc bromide.	Zinc chloride.	Calcium bromide.	Sulphuric acid (1·838).	Phosphorus pentoxide.
Moisture .	0·0021	0·0011	0·0008	0·0002	0·0000025	0·000000025 grm.

The phosphorus pentoxide should be freed from the lower oxides of phosphorus by distillation over platinized asbestos in a current of oxygen. Alumina dehydrated at a low temperature is said to be a little superior as a drying agent to sulphuric acid, and has the additional advantage that it can be revivified by reheating after it has done its work.

Storage.—The gas is compressed in steel cylinders called *bombs*—under a pressure of about 100–150 atmospheres. There has been a number of fatal accidents from the explosion of the cylinders. In most cases it is certain that an explosive mixture of hydrogen and oxygen has been introduced into the cylinder, or an oxygen cylinder still containing oxygen has been charged with hydrogen. The cylinders of hydrogen or the taps of hydrogen cylinders are often coloured red to lessen the risk of accidentally using a cylinder of hydrogen for one of oxygen. We are told that in the Boer War, the British transported hydrogen compressed in cylinders at about 200 atm. pressure, and that it required 50 horses to transport sufficient for a balloon 400 cubic metres capacity.

The cost of hydrogen per cubic metre prepared by the different processes, is, according to E. D. Ardery (1916)[33] : Steam on iron, 1·5*d.* ; distillation of crude oils and tar, 1·75*d.* ; ferrosilicon, 10*d.* ; water gas, 2·5*d.* ; iron and sulphuric acid, 12·5*d.* ; hydrogenite, 16*d.* ; hydrolith, 44*d.* to 50*d.* ; silicon and caustic soda, 53*d.*

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§ 3. Chemical Affinity

There are agents in nature able to make the particles of bodies stick together by very strong attractions. And it is the business of experimental philosophy to find them out.—ISAAC NEWTON.

All things act according to their nature. The atoms of the different elements join because they possess a tendency to combine with definite other atoms, and one affinity is overpowered by another stronger affinity so that atoms far from being pushed or passively pressed into combination, are themselves actively pushing.—P. CARUS (1913).

The cause of chemical action has mystified man from the earliest ages, and there is no prospect of an immediate solution. The crucibles, pelicans, and alembics of the working alchemists of the Middle Ages must have demonstrated every day in a thousand different forms that matter seems to be endowed with properties—or to possess a kind of *vis occulta*—in virtue of which two or more dissimilar substances, when brought into contact, give rise to other forms of matter possessing properties quite distinct from the original substances. The process of change is called a **chemical reaction.** At present, *chemical action can only be referred back to the presence of a selective force, indwelling in the different kinds of matter, which leads certain substances, under certain conditions, to undergo chemical change.* This selective force is called **chemical affinity.**

Nearly five centuries before Christ, Empedocles attributed the various changes which occur in the form of matter to the operation of two motive forces which he personified by assuming *love* to be a dynamic attractive force which induces the union of substances, while an analogous repulsive force, *hate*, effects their separation. Union was regarded as a marriage of the elements, decomposition a divorce ; love unites, hate scatters :

All through hate are split to shapes diverse ;
Each through love draws near and yearns for each. . . .

Aristotle (*c.* 320 B.C.) rightly maintained that Empedocles' two forces—harmony and discord ; love and hate ; attraction and repulsion—are two different aspects of one motive force, because the formation of a new combination must involve the disruption of a previous one, and the decomposition of one system must involve the production of another system.

Not very long after the time of Empedocles, Hippocrates postulated that when two substances unite to form a compound, they must possess one common principle or bond of kinship, for, said he : " like unites only with like." In later centuries, Hippocrates' maxim seems to have given rise to the idea that substances with kindred qualities react chemically ; the greater the resemblance between two specific forms of matter, the more likely are they to enter into combination, and the more stable the resulting product. It was argued that the metals are akin to mercury, and therefore " mercury devours the metals," or " the metals lick up the mercury," *æqualitas enim amicitiæ parens est ;* and the word affinity was coined near the end of the thirteenth century—in a work *De rebus metallicis* attributed rightly or wrongly to Albertus Magnus [1]—in order to connote the idea that the *affinitas* (relationship) between combining substances is the cause of their union. Sulphur burns the metals, said Albertus Magnus, because of the affinity it has for these substances—for the metals were themselves supposed to contain the common principle sulphur. J. J. Becher [2] expressed the same idea in 1669 when he stated that one substance *attrahet* another in virtue of its *affinitas*, and a *reactio* ensues ; the stronger the attraction, the more vigorous the reaction. J. Mayow [3] used the term affinity in the same sense in 1674. He said :

> Nitro-aerial spirit and sulphur are engaged in perpetual hostilities with one another . . . and each has a great affinity and relationship with salt, for these very active elements are being married to salt as to a fitting bride, and are fixed in its embrace.

J. Mayow also used the word *combinetur* or *combinentur* in speaking of the *congressus* of different substances. The necessary similitude, relationship, kinship, or family tie between reacting substances was taken for granted by J. C. Barchausen in his *Pyrosophia* (Lugduni Batavorum, 1698), and the then chemical world generally. Heretics, however, did insist that opposite natures are best suited for chemical union, and, following Empedocles, the principle was enforced by analogies drawn from the theory of marriage. For example, in his book *Elementa chemiæ* (Lugduni Batavorum, 1732), Hermann Boerhaave maintained that dissimilar substances show the greatest tendency to combine with one another, and he metaphorically compared affinity with love: *amicitiæ si amor dicendus copulæ cupido*—if love be called the desire for marriage; and in 1837, J. B. A. Dumas said that we must allow that there is some truth in this poetic comparison. A. F. de Fourcroy (1801)[4] also emphasized the fact that the concept of affinity is a generalization largely derived from observations made on reactions between bodies of dissimilar natures, or between unlike particles; and the existence of this force is regarded as one of the first principles of dynamical chemistry. There is, however, nothing to show that the force which binds two dissimilar atoms to say chlorine and hydrogen is intrinsically different from the force which binds a pair of hydrogen or a pair of chlorine atoms together.

Although unlike elements have a greater tendency to unite than like elements, F. W. Clarke[5] has shown that there appears to be a preference for neighbouring elements in the horizontal rows of the periodic table, rather than for those more remote. Thus, silicon follows its neighbour aluminium in the magnitude of its atomic weight, and the alumino-silicates form the most extensive class of stable minerals; similarly, phosphorus is nearer than arsenic to aluminium, and the aluminium phosphates are more common than the arsenates; while with copper nearer to arsenic than to phosphorus, the arsenates are more common than the phosphates. Another striking illustration is furnished by the compounds of oxygen, sulphur, selenium, and tellurium. The oxides or oxidized salts are the most common with the elements of low atomic weight; from manganese and iron, the sulphides are the most abundant; while selenium and tellurium are more often united with the metals with the larger atomic weights.

H. Boerhaave distinguished what he called *cohesion* between the parts of the *same* substance from the *affinity* between the parts of *different* substances. Boerhaave virtually used the term affinity to connote the tendency of different kinds of matter to unite with one another; and the term is therefore applied to that peculiar selective force or form of energy which is the origin of all chemical changes. This definition has nothing to say about the similarity or dissimilarity of the reacting substances, and it makes no reference to the very real difficulty in distinguishing clearly between chemical and physical changes. This definition has been repeated with superficial variations of phraseology by most writers.

Although the law of gravitation has been styled " the most extensive generalization to which the human intellect has ever attained," Isaac Newton did not unduly speculate on the cause, but he employed the term *gravitation* to signify, in general, any force by which bodies tend towards each other, whatsoever be the cause. He said:

> To show that I do not take gravity for an essential property of bodies, I have added one question concerning its cause, choosing to propose it by way of a question because I am not yet satisfied about it for want of experiments.

Newton applied the gravitation concept to atoms, and in this sense he was the founder of molecular as well as of celestial mechanics. The propensity of two bodies to react chemically was attributed to the attraction of the particles of the one for the particles of the other, pair by pair; and conversely, when a compound of two bodies is decomposed by a third body coming into the field of action, the particles of the intruding body were supposed to attract the one and repel the other constituent. The struggle between the three kinds of particles was supposed to be decided by the resultants of two pairs of forces. Shortly after Isaac Newton had published his views on chemical attraction, St. F. Geoffroy changed Newton's term *attraction* to *affinity*, and attempted to make a table in which the powers which different bodies possess of uniting with one another are represented by numbers.[6] The same concept, if not the name, was used by J. R. Glauber (1648), F. de la Böe Sylvius (1659), A. L. Lavoisier (1783),[7] and others. For instance, R. Boyle (1664) used the terms *coalition* and *association*[8] for the concept affinity. Both T. Bergmann and G. L. L. Buffon,[9] following Newton, tried the hypothesis that the forces between the constituent particles of a body are the same in kind as those which determine the relations of the heavenly bodies ; but both abandoned the idea as impracticable, because it was believed that the atoms are so close together that their shapes must interfere with the attractive force and make the theorems to be solved inextricably complex.

The idea that the atoms were retained each to each by hooks or other mechanical means is suggested in Lucretius' poem, and was adopted by N. Lemery.[10] R. J. Haüy supposed that different particles have different polygonal solid shapes which when chemically compounded pack themselves together like so many solid bricks.

There have been many attempts to evade the use of the word affinity, and as alternatives, the terms electric attraction, atomic gravitation, chemical activity, chemical avidity, chemical energy, chemism, etc., have been variously suggested ; but the original term chemical affinity is convenient, provided it be kept in its place —*in verbis non simus faciles*. To say that " oxygen unites with hydrogen because it has an affinity for it " explains nothing, but simply restates the fact in different words. Many examples of similar pseudo-explanations might be given : " Hydrogen burns because it is combustible," " morphine induces sleep because of its soporific qualities," " arsenic causes death because it is a poison," " potassium carbonate absorbs moisture from the air because it is deliquescent." Explanations and definitions of this kind are so rife that the fault has been given a name : *circulus in definiendo*. We quite recognize with Isaac Newton (1675) that " to tell us that every species of things is endowed with an occult specific quality by which it acts and produces manifest effects is to tell us nothing," yet is it hardly fair to say that the term chemical affinity is a veil which covers our ignorance in obscure language. What H. F. Link[11] wrote at the end of the eighteenth century—1795—might almost have been written to-day :

> Although the term affinity has sprung from the dark ages of chemistry, and appears at first glance to be mystical and unprofitable, yet, it is certain that since the causes of all chemical phenomena have been referred to one single cause, chemistry has made extraordinary progress for which it has to thank the definition—affinity is the cause of chemical action.

With this understanding, chemical affinity can be conveniently regarded as " the driving force of a chemical reaction." In 1887, W. E. Ayrton and J. Perry expressed the idea that

$$\text{Reaction velocity} = \frac{\text{Driving force}}{\text{Resistance}}$$

Consequently, if we could measure the **chemical resistance** offered by substances to undergo chemical change, it would be possible to get a definite and quantitative idea of chemical affinity from measurements on the velocity of a reaction. No real advance can be made in the study of chemical affinity until a method of measurement has been devised. As W. Whewell (1840) expressed it : " In all attempts to explain the processes of nature, the proper course is first to measure the facts with precision, and then to endeavour to understand their cause."

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§ 4. The Measurement of the Affinity between the Acids and the Metals

> I often say that if you can measure that of which you speak, and can express it by a number, you know something of your subject; but if you cannot measure it, your knowledge is meagre and unsatisfactory.—LORD KELVIN.

Towards the end of the eighteenth century, T. Bergmann found it necessary to issue a warning against "some chemists who consider thermometers and suchlike measuring instruments to be physical subtilties, superfluous and unnecessary in a chemical laboratory," and he further emphasized his belief in the importance of generally "so comparing an effect with its cause as to determine the exact quantitative relation between the two." At this day, the resources of the physical laboratory are commandeered by the chemist in his quest after the quantitative relations between causes and their effects.

Chemical reactions are not instantaneous processes, but are propagated with finite measurable velocities which may range from the explosion wave travelling through a mixture of hydrogen and oxygen at a speed not much less than 10,000 feet per second; or it may be so slow that years are needed to detect an appreciable change. It is assumed that every elementary atom and every molecule is charged with a definite amount of energy which is a measure and cause of its *chemical affinity*; chemical affinity is assumed to be the *driving force* of chemical reactions; and the *speed of chemical reactions*, other things being equal, is proportional to the driving force. It will be obvious that if a ball be sent rolling with a velocity of 20 cm. per second, the force applied to the ball will be twice as great as would be required to make the ball travel with a velocity of 10 cm. per second during the same time. Neglecting friction, the intensities of the two forces are proportional to the velocities which they impart to each unit of mass during the same time.

The relation between the speed of a chemical reaction and affinity.—In an important book, *Lehre von der Verwandtschaft* (Dresden, 28, 1777), C. F. Wenzel tried to determine the affinities of the metals for different acids by comparing the rates at which the metals liberate gas from acids of different concentration. He found that if an acid of a given concentration dissolves one unit of metal per hour, an acid of half that concentration will take two hours to dissolve the same amount of metal. The velocity of these reactions can be measured by finding the amount of gas liberated per minute, or the amount of acid or of metal consumed, say, every minute. Then, at any given moment:

$$\text{Velocity} = \frac{\text{Amount of gas liberated}}{\text{Time occupied}} = \frac{\text{Acid consumed}}{\text{Time occupied}}$$

The affinity of a metal for an acid depends on the concentration of the acid. In fine, **the velocity of the chemical action at any instant is proportional to the concentration of the reacting substances.** This is sometimes called **Wilhelmy's law,** because L. Wilhelmy (1850) [1] demonstrated the generalization by measurements on the speed of inversion of cane sugar. A comparison of the rate of dissolution of, say, magnesium in hydrochloric acid of different concentrations, $\frac{1}{10}N$, $\frac{1}{20}N$, and

$\frac{1}{50}N$, where N here denotes an equivalent weight of HCl per litre, brings out clearly the increase of speed with increasing concentration. The slopes of the curves in Fig. 4 are proportional to the speed of the attack..

If a solution be of such a concentration that it contains a gram-molecules of acid per unit volume, then at the end of a certain time t, x gram-molecules of the acid per unit volume will have been consumed, and the solution will contain $a-x$ gram-molecules of the acid per unit volume. Hence, the velocity of the reaction will gradually slacken down. At the beginning, the velocity V will be proportional to a; that is, $V=ka$, where k is a constant of proportion; and at the end of the time t, the velocity will be $V=k(a-x)$. Hence, in C. F. Wenzel's experiment, when $x=\frac{1}{2}a$, the reaction is only progressing half as fast as at the beginning when $x=0$. The speed of the reaction at different times is illustrated by the slope of the curve in Fig. 5, where the abscissa axis represents time, and the ordinate axis, the velocity expressed in any convenient units—say, volume of gas evolved per minute.

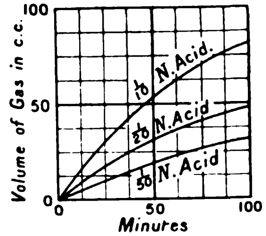

FIG. 4.—Dissolution of Magnesium in Hydrochloric Acid of Different Concentrations.

The velocity of a reaction is not always quickest at the start. When some reacting substances are brought into contact, a certain interval of time—called the **period of induction**—elapses before the reaction can proceed "full speed ahead." With zinc and dilute hydrochloric acid, for example, the dotted line, Fig. 5, shows how the speed gradually increases, reaches a maximum, and then gradually diminishes as described by Wilhelmy's law.[2] A similar period of induction has not been observed with magnesium. During the period of induction, therefore, some action takes place by which the resistance to combination is decreased, or a more favourable condition for combination is inaugurated.

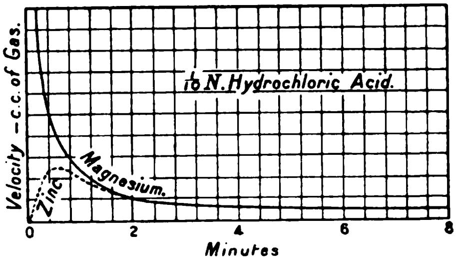

FIG. 5.—The Reduction in the Speed of Chemical Action with Time.

By measuring the rate at which hydrogen is liberated per minute per unit area of the different metals on the same sample of dilute acid, it is possible to get a rough idea of the relative affinities of the different metals for that particular acid. The comparison of the effect of dilute hydrochloric acid on zinc and magnesium—Fig. 6—shows that the dissolution of magnesium gives a steeper curve than does zinc. This means that magnesium dissolves faster than zinc. Experiments with other metals show that with dilute hydrochloric acid, starting with the most vigorous, this order is: Potassium, sodium, calcium, magnesium, zinc, and iron.

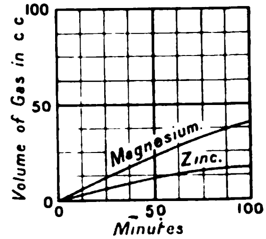

FIG. 6.—Dissolution of Zinc and Magnesium by Dilute Hydrochloric Acid.

The surface of the dissolving metal is supposed to be constant. As near as can be determined, the rate of attack, for any given concentration of acid, increases or decreases proportionately with the surface exposed to attack. Exact measurements are difficult because so many disturbing influences are at work—local rise of temperature; bubbles of gas protecting the surface of the metal from attack; variations in the surface of the metal during the action; etc. Still, the conclusion just indicated is in harmony with a great deal of work on a variety of other simple heterogeneous reactions. The generalization now under discussion is a special case of one still more general: **The speed of a heterogeneous reaction at any instant of time is directly proportional to the remoteness of the system from its equilibrium condition, and to the surface of contact of the reacting parts.** M. Wildermann (1899) has shown that this generalization is generally applicable to molecular reactions between two parts of a heterogeneous system—*e.g.* the evaporation of liquids, the condensation of vapours, the solidification and crystallization of liquids, etc. When zinc dissolves in acid, the rising bubbles of gas keep the liquid constantly agitated, bringing fresh acid to the zinc plate, but when a solid dissolves in a liquid, without disturbances of this kind, the rate of dissolution is nearly proportional to the rate at which the solid diffuses in the liquid; because the nearer the liquid is to the dissolving solid, the greater its concentration, and the layer of liquid in the immediate vicinity of the solid, is virtually a saturated solution.

By measuring the rates at which hydrogen is evolved with one metal and different acids of equivalent concentration, an idea of the relative affinity of the acids for the given metal can be obtained. For instance, acids containing 36·5 grms. of HCl (hydrochloric acid) per litre, 49 grms. of H_2SO_4 (sulphuric acid), and 60 grms. of CH_3COOH (acetic acid) per litre are chemically equivalent to one gram of hydrogen. When these three acids—in equivalent concentrations—react with magnesium ribbon (say, 0·05 grm.), the relative affinities appear to be in the order named:

Hydrochloric acid.	Sulphuric acid.	Acetic acid.
100	70	0·5

The first gives off most hydrogen in a given time, the latter least. Measurements of the volume of gas (reduced to n.p.t.) evolved by the action of normal hydrochloric and acetic acids upon magnesium gave results which furnished the curves shown in Fig. 7. The difference in the speeds of attack by the two acids is brought out clearly by the relative slopes of the two curves. The swifter the reaction the steeper the curve.

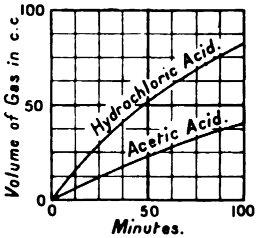

FIG. 7.—The Speed of the Dissolution of Magnesium by Hydrochloric and Acetic Acids.

The speed of the reaction of a given concentration of hydrochloric acid or sulphuric acid on iron or zinc was found by G. Lunge to be considerably reduced if the viscosity of the medium be augmented by admixture with glycerol, or gum arabic. It is assumed that the explanation is partly due to the more tardy liberation of the gas bubbles from the surface of the metal in the more viscous medium, and this prevents contact between the metal and the acid. That this is the whole explanation is regarded as improbable because a mixture of the acid with a little lamp-black (moistened with alcohol to make the acid "wet" it) also acts in an analogous manner.

Returning to the law symbolized in the equation $V=k(a-x)$, with an acid of unit concentration, it follows that the initial velocity $V=k$. And k has accordingly been called the **affinity constant** of the acid for the metal; k represents the speed of the reaction at the instant when the acid has unit concentration. The speed of a chemical reaction is usually, not always, augmented by raising the temperature. In illustration, with $\frac{1}{2}N$-sulphuric acid, a rise of temperature from 12·8° to 35° nearly doubled the speed of dissolution of zinc; and a rise from 12·8° to 55° nearly trebled the speed. The result of this discussion shows that **the velocity of a chemical reaction is proportional (1) to the "affinity constant" between the reacting substances, and (2) to the concentration of the reacting substance; while (3) the velocity of a chemical reaction is augmented by raising the temperature.**

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§ 5. Opposing Reactions. Guldberg and Waage's Law

Chemical action is reciprocal, and its effect is the result of a mutual tendency to combination.—C. L. BERTHOLLET (1803).

In an aggregate of molecules of any compound, there is an exchange constantly going on between the elements which are contained in it.—A. W. WILLIAMSON (1850).

Some of the earlier chemists [1]—*e.g.* St. F. Geoffroy (1718), and Torbern Bergmann, in his *De attractionibus electiviis* (Upsala, 1775)—argued that the result of a chemical change must be in favour of that substance with the stronger affinity. Accordingly St. F. Geoffroy compiled what he called *Tables des différents rapports observés en chimie entre différentes substances;* and T. Bergmann, **affinity tables** intended to show the order in which the different substances would displace one another from a given compound. It was argued that *if A displaces B from one compound, and B displaces C from another compound, the order of the affinity of these three substances is A, B, C.* It was clearly recognized that this method of work does not give a numerical measure of affinity, but it was thought that relative results were obtained. The suggestion is certainly a good trial hypothesis. Let us compare it with the facts.

We have seen that iron can displace hydrogen from its combination with oxygen; hence iron has a stronger affinity than hydrogen for oxygen. Similarly, we have seen that hydrogen can displace iron from its combination with oxygen; consequently, hydrogen has a stronger affinity than iron for oxygen. These two conclusions are contradictory; both cannot be true. Therefore, *the affinity hypothesis must be either false, or some powerful perturbing influence must be at work.*

In 1799, C. L. Berthollet [2] clearly recognized an important disturbing factor, and described it in an heretical but prophetic work entitled *Recherches sur les lois de l'affinité* (Paris, 1801). Berthollet noticed large quantities of *trona*—sodium carbonate—on the shores of the natron lakes of Egypt. He suggested that the sodium chloride brought down by the rivers was decomposed by the calcium carbonate present on the banks of these lakes:

$$CaCO_3+2NaCl=CaCl_2+Na_2CO_3$$

Berthollet knew, quite well, that this reaction is the reverse of that which usually obtained in the laboratory, for sodium carbonate, when added to calcium chloride, precipitates calcium carbonate:

$$Na_2CO_3+CaCl_2=CaCO_3+2NaCl$$

but, added Berthollet, the large masses of calcium carbonate on the banks of these lakes is able to " strengthen " the weak affinity of carbon dioxide for sodium, or of chlorine for calcium. Here Berthollet brings the disturbing factor into bold relief: **Chemical action is conditioned not only by affinity but by the relative concentrations of the reacting bodies—Berthollet's law.** Excessive concentration can compensate for a weakness of affinity. A chemical reaction can be reversed by changing the concentrations of the reacting bodies. We must apply Berthollet's hypothesis to the reaction under consideration—the action of iron on steam.

The reaction between iron and steam.—At the outset, it will be obvious that we have to deal with two opposing reactions: steam reacts with iron to produce iron oxide and hydrogen :

$$3Fe+4H_2O=Fe_3O_4+4H_2$$

and iron oxide and hydrogen react to produce steam and metallic iron :

$$Fe_3O_4+4H_2=3Fe+4H_2O$$

J. L. Gay Lussac and H. V. Regnault[3] showed that these opposite effects are not produced merely by a difference of temperature, for, at every degree of temperature from the dullest to the brightest red heat, the action takes place sometimes in one way and sometimes in the other. All depends on the relative proportions of hydrogen and water vapour which are present. If hydrogen be in excess, iron oxide is reduced and water vapour is formed ; while if the water vapour be in excess, the iron is oxidized and hydrogen is formed. In either case a mixture of water vapour and hydrogen is obtained. Reactions of this kind were regarded by the older chemists as an example of the conflict of affinities, and they grouped such reactions as a class exhibiting what they called *reciprocal affinity—affinitates reciprocæ.* C. M. Despretz found zinc, tin, cobalt, and nickel to act in the same manner as iron, and H. V. Regnault found uranium and cadmium to do the same.

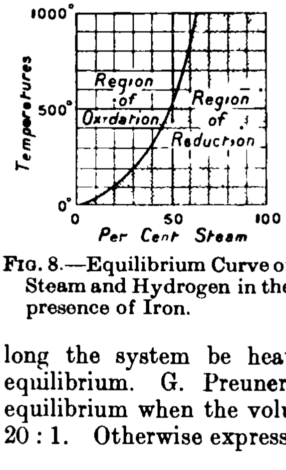

FIG. 8.—Equilibrium Curve of Steam and Hydrogen in the presence of Iron.

It is therefore clear that two antagonistic changes take place simultaneously in the system. The result of the change will be determined by the fleeter reaction. When steam is passed over red-hot iron, the hydrogen does not get much chance, it is carried away into the gas jar before it has had time to set up the reverse change. Similarly, when hydrogen is passed over red-hot iron oxide, the steam does not get a chance, for it is carried away from the reduced iron by the stream of hydrogen. In order to study the affinity relations between these different substances, they should be heated in closed vessels so that the products of the reaction are not whisked away from the seat of the reaction as soon as they are formed. The result is then very curious. It seems as if the reaction stops after a time. At any rate, if the temperature remains constant, no further change can be detected, however long the system be heated. In other words, the system assumes a state of equilibrium. G. Preuner's experiments show that at 200° the system is in equilibrium when the volume of the steam is to the volume of hydrogen nearly as 20 : 1. Otherwise expressed, for equilibrium at 200° :

$$\frac{\text{Volume of hydrogen}}{\text{Volume of steam}}=\frac{1}{20}$$

If a mixture of one volume of hydrogen and twenty volumes of steam be passed over iron filings or over iron oxide at 200°, no apparent change will occur, for the mixture, after passing through the tube at 200°, will have the same composition as when it entered, if no secondary actions occur. If more than this proportion of hydrogen be present at 200°, some iron oxide will be reduced until the equilibrium ratio is obtained. If the temperature be raised, the velocities of the two reactions are altered in such a way that at 440° the volume of steam will be to that of hydrogen nearly as 6 : 1, or as 1 : 0·17 ; and at 1500°, as 1 : 1. This means that if equal volumes of steam and hydrogen be passed over iron filings or iron oxide at 1500°, no change in the composition of the gaseous mixture will be perceptible. The results are summarized in Fig. 8. The curve showing the percentage amount of, say, steam in the system at different temperature divides the plane surface into two regions. If the state of the system be described by a point in the region of oxidation, iron will be oxidized; and conversely, if the state of the system be described by a point in the region of reduction, iron oxide will be reduced.

Chemical equilibrium is dynamic, not static.—Let us now try to picture what is taking place. Start with metallic iron and steam. At the outset when the reaction is just starting, the velocity of decomposition of the steam will be greatest because the system then contains the greatest amount of reacting substance, and because the velocity of chemical action is proportional to the concentration of the substances taking part in the reaction. From this moment, the velocity of the reaction gradually slows down as the concentration of the reacting steam becomes less and less. On the other hand, the velocity of the reverse action will be zero at the commencement, because none of the reacting hydrogen is then present. The speed of the reverse change will become faster and faster as the product of the first-named reaction—hydrogen—accumulates in the system. Ultimately, a point will be reached where the velocities of the two opposing reactions will be equal. The one will be balanced by the other. The reaction will appear to have stopped in spite of the fact that more or less of the original substance still remains untransformed. The system is then in a state of equilibrium. No further change will occur, however long the substances be heated under the same physical conditions of temperature, etc. Chemical changes of this kind are conveniently styled **opposing or balanced reactions,** according as it is wished to emphasize the fact that the one reaction is undoing the work of the other; or that the speeds of the opposing reactions are ultimately so nicely balanced that the composition of the system remains constant. The idea of a dynamic and not a static equilibrium is such reactions was emphasized by A. W. Williamson [4] about 1850, while studying the action of acids on alcohol. He said:

> An exchange is constantly going on between the elements of the molecules of a compound so that each atom of hydrogen in the molecules of HCl present in a drop of hydrochloric acid does not remain quietly in juxtaposition with the atom of chlorine with which it first united, but, on the contrary, is constantly changing places with the other atoms of hydrogen, or what is the same thing, changing its chlorine atom.

A. W. Williamson further adds that when a system appears to be *in equilibrio*, that condition "is only kept up by the number of exchanges in one direction being *absolutely* the same in each moment of time as those in the opposite direction." This is a very clear explanation of M. Lieben's contention that when substances are decomposed by heat and the products of decomposition are not removed as they are formed, the decomposition is never complete; and the small quantity of the original substance, which always remains undecomposed, produces a kind of "molecular equilibrium."

Terminology.—Reversed pointers "$\rightleftharpoons$" are conventionally used in place of the symbol "=" for opposing reactions, so as to indicate that two reactions are proceeding simultaneously "from right to left" and "from left to right." Accordingly, the reaction under consideration is symbolized: $3Fe+4H_2O\rightleftharpoons Fe_3O_4+4H_2$. Opposing reactions are also called **incomplete or reversible reactions** in contradistinction to **irreversible or complete reactions** typified by the action of zinc on sulphuric acid, where the reaction is completed in one direction and is not opposed by a counter reaction.

Concentration and active mass.—It is not difficult to see that the *absolute quantities* of steam, hydrogen, iron, and iron oxide, in the reaction under consideration, do not matter. The velocities of the two opposing reactions, and therefore **the distribution of the reacting substances, when in equilibrium, is determined by the relative concentrations of the changing substances.** This is conveniently expressed by the number of gram-molecules of each present in unit volume. Thus 18 grams of water—H_2O—per litre represents one gram-molecule; 36 grams of water per litre, two gram-molecules; etc. The concentration of a reacting substance is sometimes (inappropriately) called—after C. M. Guldberg and P. Waage (1864)—its **active mass** or—after C. L. Berthollet (1803)—its **chemical mass.** However, it is not mass but concentration which is the determining factor in chemical equilibria, and hence, C. N. Lewis (1907) proposed to substitute the term **activity** in place of active mass.

If the surface of the iron were doubled, it is true that twice as many molecules of the black oxide, Fe_3O_4, might be formed in a given time by the decomposition of the steam, but then twice as many molecules of Fe_3O_4 would be decomposed by the hydrogen in the same time. Hence, **the amount or the concentration of the solid in a gaseous reaction can have no appreciable influence on the equilibrium; although it may affect the speed at which the state of equilibrium is attained.** In studying equilibria in gases and liquids, anything which separates in the solid condition is often supposed to be thrown out of the reacting system because the state of equilibrium is independent of the concentration of the solid; and a liquid which separates when studying gaseous equilibria, is also supposed to be thrown out of the reacting system. The vapour pressure of water, for instance, in presence of its own liquid is independent of the *amount* of liquid water present. Suppose also that the back reaction between hydrogen and black oxide of iron, Fe_3O_4, at the temperature of the experiment furnishes black ferrous oxide, FeO, the reaction would then be symbolized:

$$3FeO+H_2O\rightleftharpoons Fe_3O_4+H_2$$

Determinations of the ratio $H_2O:H_2$ would not give any information as to the accuracy of the assumption. The principles of opposing reactions just outlined are summarized: **In a system of reacting bodies, the effect of each substance is proportional to its concentration, and the total effect is proportional to the product of the molecular concentrations of the reacting substances.** This is one statement of what is called **Guldberg and Waage's law of mass action,** because the ideas of Berthollet were expressed in this form by C. M. Guldberg and P. Waage in an important memoir, *Études sur les affinités chimiques* (Christiania, 1867), published first in Norwegian in 1864.[5]

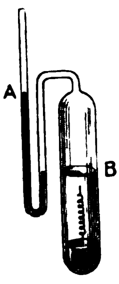

FIG. 9

L. P. Cailletet (1869) [6] has shown that when, say, sodium amalgam acts on water, the hydrogen exerts no back action because it passes away from the seat of the reaction as soon as it is formed. Suppose the reaction be conducted in a thick-walled vessel, *B*, in Fig. 9, capable of withstanding great pressure and fitted with a manometer, *A*, in order to measure the pressure of the hydrogen as it accumulates in the apparatus. The speed of the reaction gradually slackens and finally stops. With dilute sulphuric acid and zinc, this occurred when the hydrogen was exerting a pressure of nearly 20 atmospheres. The cessation of the reaction is not a mere mechanical effect because an equal pressure exerted by an indifferent gas will not do. The idea of preventing chemical action in this way is said to have been first tested by C. Babbage in 1813, for he confined concentrated hydrochloric acid in a hole 30 inches deep and 6 inches wide drilled in limestone rock (Chudley Rocks, Devon) and plugged up the hole. He thought the pressure of the developed gas would prevent the action of the acid on the limestone. No definite conclusion was drawn from the experiment.

Still further, as N. N. Beketoff (1864) has shown, if salts like zinc sulphate, copper acetate, silver sulphate, etc., be exposed to hydrogen under great pressures —over 100 atmospheres—the metal is precipitated and the acid is re-formed. Hence, the reaction $Zn+H_2SO_4=ZnSO_4+H_2$ is reversible when conducted in a closed vessel.

It might be added that in some cases the back reaction does not proceed along the same path as the forward reaction. Thus, hydrogen at 130 atmospheres pressure (70°) precipitates cuprous oxide from copper acetate, and at 150 atmospheres (120°) metallic copper. It might also be added that the work done by affinity during, say, the reaction between zinc and dilute acid, may be roughly regarded as proportional to the pressure exerted by the gas provided the reacting system suffers no change in volume. If v denotes the change in volume, and p the pressure registered by the manometer when the reaction just stops, the work W done by affinity at a constant temperature will be $W=pv$.

Chemical affinity.—To summarize the preceding discussion: chemical affinity is a convenient term for the driving force which causes certain substances to combine together and to remain united with one another. (1) Unlike gravitation, chemical affinity seems to act only when the reacting substances are in contact with one another; or, as it is sometimes expressed, "when the substance are brought within insensible distances of each other." (2) Unlike gravitation, chemical affinity is a selective force, and it seems to act more intensely the more unlike the substances are; or, as it is sometimes expressed, "Like reacts with the unlike." (3) The affinity of an element is not only definite as to the *kind*, but it is also definite as to the *quantity* of the elements which enter into combination. In this again it differs from gravitational attraction. The quantitative characteristics are described by the laws of chemical combination. (4) The strength of the affinity varies with changes in the conditions of temperature, pressure, light, etc. This has not been noticed with gravitational attraction. (5) The effects produced by chemical affinity are modified by the relative concentrations—active masses—of the reacting substances.

The ideas developed in this section were not so clear to the old workers, not even to Berthollet himself, for Berthollet appears to have confused the incompleteness of certain reactions with the law of multiple proportions. The confusion gave him some strong arguments in the celebrated Berthollet *v.* Proust Controversy. Proust did not know enough to clarify Berthollet's argument.

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§ 6. The Solubility of Hydrogen

Hydrogen is slightly soluble in water. About 1803, W. Henry[1] found that 100 c.c. of water absorb 1·56 c.c. of hydrogen; J. Dalton found 2·5 c.c.; and T. de Saussure, 4·55 cc. N. Paul noted that the solubility is augmented by pressure, so that 100 c.c. of water can be made to absorb about 33 c.c. of hydrogen. According to A. T. y Marti, water can be made by degrees to absorb more and more hydrogen, so that in two years water will take up not quite its own volume of the gas. It was suggested that *hydrogen suboxide*, H_4O, is formed, and C. J. B. Karsten even supposed this oxide to be formed by saturating cold water with hydrogen sulphide, and removing the sulphur by certain metals. There are no satisfastory reasons for supposing the existence of this oxide.

R. W. Bunsen (1855) [2] thought that the solubility of hydrogen in water is not affected by variations of temperature between 0° and 24°, so that between these temperatures one volume of water absorbs the equivalent of 0·0193 vol. of hydrogen; but his method of measurement was probably not sensitive enough to detect the difference, since W. Timofejeff and others have shown that there is quite an appreciable change between these temperatures. Let β denote the *absorption coefficient* used by R. W. Bunsen; it represents the volume of gas reduced to 0° and 760 mm. which is absorbed by one volume of the solvent when the pressure of the gas itself, without the partial pressure of the solvent, amounts to 760 mm.; and let β' denote the absorption coefficient when the total pressure of the gas and water vapour is the barometric pressure, 760 mm. The solubility of a gas—symbolized S—can also be represented as the volume of gas absorbed by unit volume of the solvent at the temperature of the experiment—consequently, the solubility S of a gas at $\theta°$ is $1+0{\cdot}003670\theta$ times the coefficient of absorption β, or $S=\beta(1+0{\cdot}003670\theta)$. The solubility can also be represented as the weight ω of gas in grams dissolved by 100 grams of the solvent at the temperature of the measurement and a total pressure 760 mm., where 760 mm. represents the partial pressure of the gas plus the partial pressure of the solvent.

The solubility of hydrogen in water.—The values of the constants β and ω for the solution of hydrogen in water between 0° and 24° are:

	0°	4°	8°	12°	16°	20°	24°
β .	0·02153	0·02079	0·02010	0·01947	0·01889	0·01837	0·01791
ω .	0·03192	0·03185	0·03179	0·03173	0·03167	0·03162	0·03157

and W. Timofejeff represents the coefficient of absorption β at a temperature θ over the range 0° to 26°, by $\beta=0{\cdot}0215286-0{\cdot}03196\theta+0{\cdot}0_517228\theta^2$. For the range from 25° to 100°, the four solubility coefficients are:

	25°	30°	40°	50°	60°	80°	100°
β .	0·0175	0·0170	0·0164	0·0161	0·0160	0·0160	0·0160
β' .	0·0171	0·0163	0·0153	0·0141	0·0129	0·0085	0·0000
S .	0·0156	0·0145	0·0140	0·0131	0·0125	0·0113	0·0107
ω .	0·03156	0·03147	0·03139	0·03129	0·03119	0·0470	0·0000

Although hydrogen, like other gases, decreases in solubility as the temperature rises, no definite law has been discovered for the phenomenon. According to C. Bohr and J. Bock the solubility of hydrogen decreases gradually with rise of temperature and from $S=0{\cdot}0203$ at 0° to $S=0{\cdot}0155$ at 90°, and then rises to 0·0166 at 100°. Helium is the only other gas which gives any indication of a reversal in the direction of the solubility curve. The formulæ representing the relation between the temperature θ and the solubility S, based on the series $S=a+b\theta+c\theta^2+\ldots$—where $a, b, c, \ldots$ are constants whose numerical values are derived from the observed data—are quite empirical. L. W. Winkler (1892) sought to prove that the percentage decrease in the absorption coefficient or solubility is nearly proportional to the cube root of the molecular weight of the gas in question. A comparison between the observed and calculated results for hydrogen, nitrogen, oxygen, carbon monoxide, and nitric oxide was satisfactory; but T. E. Thorpe and J. W. Rodger (1894) showed that L. W. Winkler's rule is not generally valid, though they found that for the same gas, the decrease in the coefficient of absorption for any interval of temperature is nearly proportional to the corresponding decrease in the viscosity coefficient of the solvent.

According to K. Angström,[3] the increase in the volume of the solvent which occurs during the solution of a gas is proportional to the amount of gas absorbed; and with

	Nitrogen.	Air.	Carbon monoxide.	Oxygen.	Hydrogen.	Carbon dioxide.
Dilation .	0·04294	0·04346	0·04418	0·04474	0·04204	0·0023

The increase in volume with hydrogen is 0·0016 for chloroform; 0·0017 for benzene; 0·0017 for methyl alcohol; 0·00152 for ethyl alcohol; and 0·00184 for ether

The dilation due to absorption was found to be independent of the nature of the liquid, and not in agreement with W. Ostwald's statement that "the volume of the absorbed gas is almost exactly reduced to the volume of its molecules."

The solubility of hydrogen in aqueous solutions of acid, bases, and salts.—A great many empirical observations have been made on the solubility of hydrogen in aqueous solution of acids, bases, and salts.[4] The values of S for *hydrochloric, nitric, sulphuric, acetic, chloroacetic,* and *propionic acids* at 25° are :

	HCl	HNO_3	$\frac{1}{2}H_2SO_4$	CH_3COOH	$CH_2ClCOOH$	C_2H_5COOH
$\frac{1}{2}N$-acid .	0·0186	0·0188	0·0185	0·0192 .	0·0189	0·0017
$4N$-acid .	0·0160	0·0160	0·0141	0·0186	0·0180($2N$)	0·0016($1\frac{1}{2}N$)

A. Christoff found the solubility of hydrogen in 95·6 per cent. sulphuric acid to be 0·01097 between 17° and 20° ; in 61·62 per cent. sulphuric acid, 0·007181 ; in 35·82 per cent, acid, 0·009544 ; and in pure water, 0·02077. The solubility S of hydrogen in a $\frac{1}{2}N$-solution of *potassium hydroxide* is 0·0167 ; and in a normal solution, 0·0142 ; for a $\frac{1}{2}N$-solution of *sodium hydroxide,* 0·0165 ; for a normal solution, 0·0139 ; and for a $4N$-solution, 0·0055. W. Knopp, H. von Euler, and others have suggested formulæ for representing the effect of a salt on the solubility of hydrogen in water.

The coefficient of absorption, β, of a 1·037 per cent. solution of *ammonium nitrate* at 20° is 0·01872, and for a 11·55 per cent. solution, 0·01647 ; for a 4·73 per cent. solution of *potassium nitrate* β=0·01683 (15°). and a 21·46 per cent. solution β=0·01180 (15°) ; a 5·57 per cent. solution of *sodium nitrate* has β=0·01603 (15°), and a 37·43 per cent. solution, β=0·00578 (15°). A 3·83 per cent. solution of *potassium chloride* has β=0·01667 (15°), and for a 22·92 per cent. solution, β=0·00892 (15°) ; with a 1·25 per cent. solution of *sodium chloride,* β=0·0191 (15°), 0·0177 (20°), and for a 23·84 per cent. solution, β=0·00595 (15°) ; a 3·48 per cent. solution of *lithium chloride* has β=0·01619 (15°), and a 14·63 per cent. solution, β=0·0099 (15°). For a 3·29 per cent. solution of *barium chloride,* β=0·0185 (15°), 0·0172 (20°) ; a 7 per cent. solution has β=0·0172 (15°), 0·0159 (20°) ; with a 3·47 per cent. solution of *calcium chloride,* β= 0·01450 (15°), and a 26·34 per cent. solution, β=0·00519 (15°). For a 4·58 per cent. solution of *sodium sulphate,* β=0·01519 (15°), and a 16·69 per cent. solution, β=0·00775. For a 4·97 per cent. solution of *magnesium sulphate,* β=0·01501 (15°), and for a 23·76 per cent. solution, β=0·00499 (15°) ; for an 8·1 per cent. solution of *zinc sulphate,* β=0·001446 (15°), and a 48·4 per cent. solution, β=0·00510 (15°). A 22·82 per cent. solution of *potassium carbonate* has β=0·01628 (15°), and a 41·81 per cent. solution, β=0·0016 (15°) ; for a 2·1 per cent. solution of *sodium carbonate,* β=0·01639 (15°) ; and a 11·52 per cent. solution, β=0·00839 (15°).

The solubility of hydrogen in organic liquids.—Hydrogen is much more soluble in *ethyl alcohol* than it is in water. The solubility decreases the more the alcohol is diluted with water down to about 28 per cent. alcohol, when the coefficient of absorption increases ; there is therefore a minimum in the solubility curve. Thus, at 20° the absorption coefficient β is :

Per cent. alcohol	0	9·09	28·57	33·33	50·0	66·67	98·8	99·7
β . . .	0·0184	0·0133	0·0097	0·0108	0·0187	0·0237	0·0740	0·0740

W. Timofejeff (1890) found the absorption coefficient β of hydrogen in 9·88 per cent. alcohol increased from 0·0676 at 0° ; to 0·0693 at 6·2° ; to 0·0705 at 13·4° ; and to 0·0740 at 18·8°. L. Carius (1855) found rather lower numbers ; he represents the coefficient of absorption β of hydrogen in alcohol at $\theta°$ by the expression : $\beta=0{\cdot}06925-0{\cdot}0001487\theta-0{\cdot}000001\theta^2$, when $\theta°$ lies between 0° and 25°. The solubility S of hydrogen in some alcohols is—

	Methyl alcohol		Ethyl alcohol		Iso-butyl alcohol		Amyl alcohol	
	20°	25°	20°	25°	20°	25°	20°	25°
S .	0·0902	0·0945	0·0862	0·0894	0·0929	0·0976	0·0353	0·0301

The corresponding values for water are S=0·0200 (20°) and S=0·0199 (25°). The solubilities of hydrogen in a large number of organic compounds and in aqueous solutions of organic compounds have been measured.[5] In some cases it will be observed that the solubility of the gas is greater at the higher temperature.

The solubility S of hydrogen in a 2·29 per cent. *glycerol* solution at 14° was found by P. Drucker and E. Moles to be 0·01886, and in a 15·31 per cent. solution, 0·01765; while at 25°, a 4·0 per cent. solution has a solubility of 0·0170; a 50·5 per cent. solution, 0·0089; and a 95·0 per cent. solution, 0·0030. For a 2·63 per cent. solution of *propionic acid* at 20°, S=0·0186; and for a 9·91 per cent. solution, 0·0165, which rises to 0·0209 at 5°. For a solution of 89 grams of *amidopropionic acid*, $CH_3.CH(NH_2).COOH_2$, per litre, S=0·0145 (20°); for a solution with 75 grms. of *glycocol* per litre, S=0·0147 (20°); for a solution with 60·07 grams of *urea* per litre, S=0·0159 (20°); and for one with 59 grams of *acetamide* per litre, S=0·0167 (20°). The solubility of hydrogen in a 4·91 per cent. solution of *chloral hydrate* at 20° is 0·0171, and in a 63·9 per cent. solution, 0·0122; in 16·67 per cent. For *sugar* solutions at 15°, C. Müller found S=0·01479; and in 47·65 per cent. solutions, S=0·008456; with 41·4, 80·8, and 166·62 grams of *glucose* per litre, at 20°, S was respectively 0·0164, 0·0153, and 0·0141. The solubility S of hydrogen in *aniline* is 0·0303 (20°) and 0·0285 (25°); *nitrobenzene*, 0·0353 (20°) and 0·0371 (25°); *toluene*, 0·08384 (20°) and 0 08742 (25°); *xylene*, 0·07834 (20°) and 0·08185 (25°); *carbon disulphide*, 0·0336 (20°) and 0·0375 (25°); *acetone*, 0·0703 (20°) and 0·0764 (25°); *ethyl acetate*, 0·0788 (20°) and 0·0852 (25°); *amyl acetate*, 0·0743 (20°) and 0·0774 (25°); and *iso-butyl acetate*, 0·09287 (20°) and 0·09758 (25°). S. Gniewasz and A. Walfisz found the absorption coefficient of hydrogen in *petroleum* at 10° is 0·0652, and at 20°, 0·0582 (water at 20°, 0·0193); G. Fahr measured the solubility of hydrogen in the *blood* and *serum* of different animals.

As a rule, the absorption coefficient of hydrogen in organic solvents decreases with increasing concentrations of the solutions; it is also noteworthy, that the solubility of hydrogen in several organic solvents increases as the temperature rises—usually, the solubility decreases as the temperature increases. The work of A. Christoff, previously cited, shows that the solubility increases as the surface tension of the solvent decreases.

The permeability of the metals to hydrogen.—In 1863, H. St. C. Deville and L. Troost[6] showed that hydrogen gas can diffuse through red-hot platinum or iron, but not through the cold metals, and they suggested that the permeability was caused by the development of a kind of porosity of a greater degree of minuteness than the porosity of graphite and earthenware; they said that this new porosity is entirely due to the expansive agency of heat opening up intermolecular spaces in the heated metal—*la porosité résulte de la dilation que la chaleur fait éprouver aux espaces intermoléculaires.* It has been estimated that about four litres of hydrogen can pass through a square metre of palladium per minute; and about half a litre through a square metre of platinum in the same time. T. Graham and many other investigators have investigated the pressure obtained by the diffusion of hydrogen through platinum and palladium. According to A. Winkelmann, the quantity of hydrogen which diffuses through the metal is not proportional to the pressure, for at low pressures the quantity which diffuses is relatively larger than accords with this assumption. A. Winkelmann also investigated the diffusion of hydrogen through iron and platinum; and O. W. Richardson, J. Nicol, and T. Parnell also studied the diffusion of hydrogen through platinum. A. Sieverts and P. Beckmann found hydrogen begins to diffuse through copper at 640°; platinum at 500°; nickel at 450°; iron at 300°; and palladium at 240°. O. W. Richardson, J. Nicol, and T. Parnell found the speed of diffusion increased with a rise of temperature, while the temperature coefficient at the same time decreased. The speed of diffusion at a constant temperature is proportional to the square root of the pressure. The diffusion is probably connected with the absorption of the gas by the metal. The gas is absorbed on one side and given off on the other side where the partial pressure of the hydrogen is smaller. It is suggested by A. Winkelmann[7] that the hydrogen is dissociated and only hydrogen in the atomic condition can traverse the platinum. J. Schmidt raised objections to the atomic hypothesis, but neither O. W. Richardson nor A. Winkelmann accepted J. Schmidt's views. A. Lessing found the velocity of diffusion of electrolytic hydrogen increases with increasing potential. The diffusion of hydrogen through platinum has to be taken into consideration in chemical analysis when certain substances are heated over the gas flame in a platinum crucible. Reducing gases, from the coal gas, pass through the walls of the crucible and exert a reducing action on substances being calcined—*e.g.* manganese oxide.

According to G. Quincke (1877),[8] hydrogen, oxygen, and nitrogen do not diffuse through glass of 1·5 mm. thickness at ordinary temperatures, and under a pressure of 126 atmosphere, nor is there any sign of the permeability of glass up to its softening temperature. M. Berthelot maintained that hydrogen can diffuse through the walls of heated glass—ordinary and Jena. A. Sieverts and W. Krumbhaar (1910) also found that unglazed porcelain is impervious to hydrogen at 1650°, and that it can support a vacuum at 1400°. Glass surfaces absorb hydrogen. According to P. Chappius, 1 sq. mm. of glass at normal pressure, on heating from 0° to 180° gives off 0·00027 c.c. of hydrogen. Powdered quartz at 1100° can absorb 0·015 c.c. of hydrogen or helium per gram. Transparent quartz glass at ordinary temperatures and pressures is impervious to hydrogen, oxygen, etc.; but at 330°, the quartz is pervious to hydrogen for pressures varying from 560 to 960 mm. No leakage was observed with nitrogen or oxygen at pressure less than one atmosphere. Hydrogen leaked through the tube at about 430°. At a constant temperature, the leakage increased with increasing pressures as illustrated in Fig. 10. M. Bodenstein and F. Kranendisck found that 4·38×10⁻⁶ c.c. of hydrogen diffused through 1 sq. c.c. of quartz glass 1 mm. thick per hour when there was a difference of pressure of 1 atmosphere on the two sides and the temperature was 732°; at 880°, 8·65×10⁻⁶ c.c. of gas diffused under similar conditions.

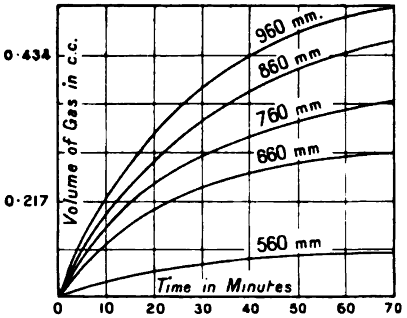


FIG. 10.—The Leakage of Hydrogen at Different Pressures from Vessels of Quartz Glass at 430°.

The solubility of hydrogen in the metals.—In 1866, the attention of T. Graham [9] seems to have been arrested by H. St. C. Deville and L. Troost's observation on the permeability of metals to gases. T. Graham could not detect any signs of the passage of oxygen, nitrogen, chlorine, steam, hydrogen chloride, carbon dioxide, carbon monoxide, methane, ethylene, hydrogen sulphide, or ammonia through a septum of platinum 1·1 mm. thick at a full red heat in an apparatus capable of detecting 0·2 c.c. per hour. He also found that when certain metals are heated in hydrogen gas, more or less of the gas is absorbed and retained as the metal cools, forming a kind of solid solution of the gas in the metal.

T. Graham heated a small piece of the metal under investigation in a porcelain tube glazed inside and out. The tube was heated to redness and exhausted. Hydrogen was then allowed to pass over the heated metal, and the metal cooled in the same gas. The tube was then evacuated, and afterwards heated, with the pump in action, until no more gas was evolved. The gas was collected over mercury and measured. The volume and weight of metal were also determined, and the results could be represented in any desired way. He expressed his results as average volumes of gas absorbed per unit volume of metal. He found:

	Vols.		Vols.
Platinum (fused) . .	4·68	Copper (wrought)	0·31
Platinum (hammered) .	3·03	Gold	0·46
Palladium (foil). . . .	495·50	Silver	0·90
Copper (sponge) . .	0·60	Iron	4·15

An osmium-iridium alloy absorbed a trace of the gas. Palladium, therefore, of all the metals, appears to possess the power of absorbing hydrogen in the highest degree. The volume of gas absorbed by a metal depends on its condition, and increases with the superficial area. The gas is retained by the metal very tenaciously, and it can be recovered from the metal only by heating to redness in vacuo. Hence, added T. Graham:

> It appears necessary to recognize in palladium a new property, a power to absorb hydrogen at a red heat, and to retain gas at a temperature under redness for an indefinite time. It may be allowable to speak of this as a power *to occlude* (to shut up) hydrogen, and the result as the **occlusion** of hydrogen by palladium.

The fixation of the gas was found to be more energetic if the metal under investigation were used as a negative electrode during electrolysis. For example, M. Thoma has shown that if palladium be employed as negative electrode during the electrolysis of acidulated water, the metal may become supersaturated with the gas and dissolve over 935 times its volume of the gas; the amount actually dissolved depends on the strength of the current. The excess is quickly evolved when the current ceases.

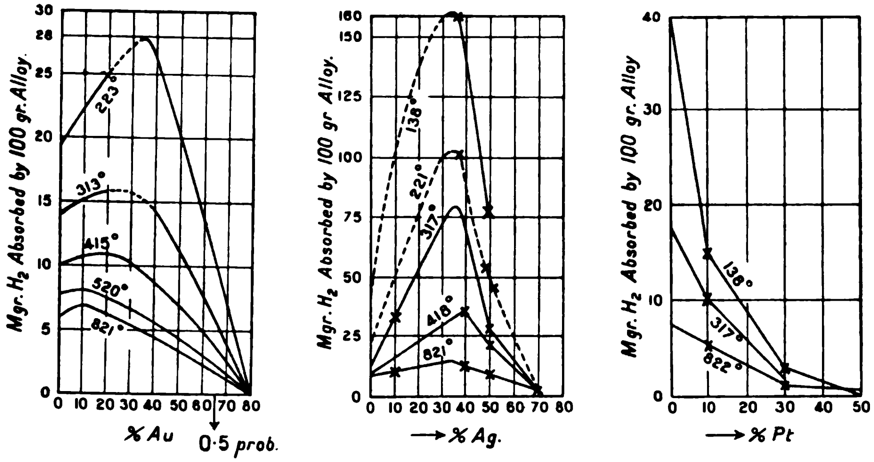
In order to prepare hydrogenized palladium, a clean piece of palladium foil about 16 sq. cm. is used as cathode in a solution of palladium nitrate—2 grams of the salt per 100 c.c. of water. The anode is also of palladium. After a current of about one ampere has passed for 20–30 minutes, the foil will be covered with a velvety-black film of palladium black. This plate is then used as cathode in the electrolysis of dilute sulphuric acid with a current of 0·8 to 1·0 amp. The plate will be saturated with hydrogen in about an hour. The foil is rapidly washed with water, and dipped in absolute alcohol and ether. It can be preserved for some weeks under air-free water.

G. Neumann and F. Streintz, like T. Graham, measured the volume of gas, reduced to standard conditions, absorbed by one volume of metal. Some of the latter's results are here included with those of the former:

	Vols. absorbed.		Vols. absorbed.
Silver (foil)	0·21	Gold (leaf)	1·4
Silver (powder)	0·9 to 0·95	Gold (precipitated)	37·0 to 46·0
Aluminium (sheet)	1·1 to 2·7	Palladium (wrought)	376·0 to 643
Cobalt (reduced)	59·0 to 153	Palladium (wire)	930·0
Copper (wire)	0·3 to 4·8	Palladium (sponge)	680·0 to 852
Copper (reduced	0·6 to 4·8	Palladium (fused)	68·0 to 200
Iron (wire)	0·46	Platinum (sponge)	1·5 to 49·0
Iron (wrought)	0·57 to 0·8	Platinum (foil)	0·8 to 1·5
Iron (reduced)	9·4 to 19·2	Lead (fused)	0·11 to 0·15
Magnesium	1·4	Zinc (electrolytic)	traces
Nickel (reduced)	17·0 to 18·0	Antimony	nil

According to G. Neumann and F. Streintz, *silver* absorbs no hydrogen—but others have reported the absorption of about one-fifth of its volume of the gas. The numbers here given are not to be taken as absolute—perhaps not even comparable. Considerable differences have been reported by other observers. Thus, according to A. Sieverts and his co-workers, hydrogen is not dissolved by *cadmium*, *thallium*, *aluminium*, *zinc*, *lead*, *bismuth*, *tin*, *antimony*, *tungsten*, *silver*, or *gold*; while *copper*, *nickel*, and *iron* do dissolve the gas. H. R. Carveth and B. E. Curry reported the occlusion of 250 vols. of hydrogen by electrically deposited *chromium*. L. Troost and P. Hautefeuille obtained evidence of the occlusion of hydrogen by *manganese*, and the presence of manganese increases the solubility of hydrogen in iron; on the other hand, E. Wedekind and T. Veit did not obtain much occlusion, but they worked with a gas containing some oxygen. C. Winkler says that *beryllium*, *manganese*, *yttrium*, and *zirconium* take up hydrogen when their oxides, intimately mixed with magnesium, are heated, but magnesium alone did not absorb the gas. The experimental conditions do not appear to be such as would furnish reliable evidence of the occlusion of gases by these elements. A. van Berghe and E. L. Lederer did not find that *molybdenum* occluded hydrogen to any marked degree; A. Sieverts and his co-workers, and G. Neumann have studied the occlusion of hydrogen by *iron*; A. Sieverts and his co-workers, W. Ipatieff, and M. Mayer and V. Altmayer have studied *nickel*; A. Sieverts, *cobalt* and *copper*. The experiments of H. E. Roscoe, and of W. Muthmann, L. Weiss, and R. Riedelbauch make it probable that hydrogen is occluded by *vanadium*; and likewise H. von Bolton,

W. Muthmann, and A. Sieverts and their co-workers suggest that hydrogen is occluded by *tantalum*. M. von Piriani says tantalum at a red heat absorbs 0·3 per cent. of gas, and more at a higher temperature. There is no evidence of the occlusion of any marked amount of hydrogen by *mercury*. T. Wilm said that *rhodium* absorbs more hydrogen than does palladium, but E. Quenessen thought this to be improbable, and A. Sieverts and E. Jurisch found rhodium absorbs very little hydrogen. F. Rother, and R. Finkener and F. Fisher show that while ordinary *iridium* does not occlude much hydrogen, under the stimulus of a prolonged cathodic bombardment it can take up 800 vols. of hydrogen. According to A. Ledeber, this, however, is doubtful evidence of occlusion. A. Gutbier and co-workers found pure iridium occludes 140 vols. of hydrogen at 20°. C. Winkler considers it unlikely that *titanium* occludes hydrogen. L. Cailletet and E. Collardeau say that *ruthenium* can take up gases during electrolysis, and T. Graham says that an *osmium-iridium* alloy absorbs no hydrogen when heated in the gas. It may therefore be said that the two elements—ruthenium and *rhodium*—as well as of *scandium*, *gallium*, and *indium*, have not been investigated. A. Sieverts and E. Bergner obtained a small occlusion of hydrogen with an impure form of *uranium*. The work of C. Winkler, C. Matignon, W. Muthmann, and H. H. Zhukoff show unmistakable evidence of the occlusion of hydrogen by *cerium* and *lanthanum*, for those metals form phases of variable composition in which the hydrogen may reach high concentrations. C. Winkler and C. Matignon found evidence of the absorption of hydrogen by *thorium*, and C. Matignon by *samarium*, *neodymium*, and *praseodymium*. Nothing definite is known of the behaviour of *europium*, *gadolinium*, *terbium*, *holmium*, *erbium*, *thulium*, and *ytterbium*.



FIGS. 11 to 13.—Absorption of Hydrogen by Palladium Alloys.

T. Graham and A. J. Berry have measured the solubility of hydrogen in *palladium-gold* alloys. A. J. Berry found that the decrease in the amount of occluded hydrogen is a simple function of the proportions of palladium in the alloy, but the occluding power of the alloy vanishes when the proportion of palladium falls below 25 per cent., roughly 0·5 gram-molecules of gold. A. Sieverts, E. Jurisch, and A. Metz extended these observations at different temperatures between 138° and 820°; they also employed *palladium-silver* and *palladium-platinum* alloys. The results with the alloys are indicated in Figs. 11–13. All proportions of platinum diminish the solubility of hydrogen; hydrogen is virtually insoluble in silver, but the addition of silver to palladium raises the solubility until a maximum is reached with 40 per cent. of silver—at 130° this alloy dissolves four times as much hydrogen as pure palladium—the solubility diminishes with increasing proportions of silver, and becomes zero with alloys containing over 70 per cent. of silver. The curves for different temperatures are illustrated in Fig. 14.

Different results are obtained with different samples of metal; this is mainly due to differences in the purity of the metal, and to the method employed in its preparation—*e.g.* cobalt in the form of ingots absorbs virtually no hydrogen, while the metal reduced from the oxide at a low temperature absorbs relatively large volumes of the gas, and if reduced at a high temperature much less gas is absorbed. In a general way, the amount of gas absorbed depends upon the *surface area* which the metal presents to the gas. Thus the colloidal palladium prepared with sodium protalbate by C. Paal and C. Amberger absorbs 300 to 400 vols. of hydrogen, and the solution prepared by C. Paal and J. Gerum absorbed 1000 to 3000 vols. The solubility of hydrogen in the metals increases proportionally with the *temperature* up to the melting point when there is an abrupt increase which again increases proportionally with the temperature. With palladium, however, the solubility does not depend on the temperature, and unlike the other metals there is an abrupt decrease in solubility (nearly one-half) as the metal melts. The dissolved gas is mainly rejected as the metal cools, and that which is retained can be recovered on heating in vacuo. If the metal is heated in an atmosphere of the gas, more and more hydrogen is retained by the cooling metal the higher the temperature to which it has been heated. The amount of hydrogen retained by iron, containing 0·04 per cent. of carbon, heated to different temperatures, is indicated in Fig. 14. The amount of gas retained by a metal also increases with the *pressure*. The relation between the amount of hydrogen absorbed by the molten metal and the pressure does not usually follow Henry's law. Thus 100 grms. of molten copper (1123°) dissolve

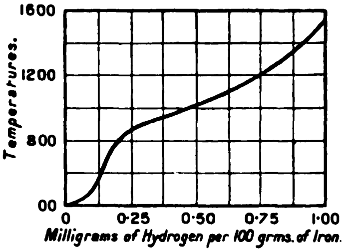


FIG. 14.—The Effect of Temperature on the Absorption of Hydrogen by Iron.

Pressure (p)	1046	883	606	281 mm.
Absorbed hydrogen (m)	0·745	0·680	0·549	0·380 mgrm.
$p^{\frac{1}{2}}/m$	43·5	43·7	45·1	44·2

showing that the quantity of hydrogen absorbed is not proportional to the pressure as it would be if it followed Henry's law—it is proportional to the square root of the pressure. Palladium increases in volume during the absorption, but its general appearance and properties—thermal and electrical conductivity, tenacity, etc.—are not much altered, although a considerable amount of heat is evolved during the absorption—4370 calories per gram of gas.

Potassium and *sodium* were found by L. Troost and P. Hautefeuille to absorb hydrogen; H. Moissan found 126 vols. of the gas were absorbed between 200° and 400°; and 237 vols. by sodium between 300° and 421°. C. Matignon found *lithium* and *thallium* absorbed no hydrogen. K. A. Hofmann, O. Ehrhart, and O. Schneider also found that *osmium tetroxide* absorbs hydrogen. F. Soddy patented the use of *calcium* as an absorbent for gases in the production of high vacua. D. P. Smith found that the elements which occlude hydrogen occupy a definite position in the periodic table—Cap. VI—and that *the capacity of a metal to occlude hydrogen is confined to those with a strong magnetic susceptibility*, for the elements which have a specific magnetic susceptibility exceeding $0·9\times10^{-6}$ at ordinary temperatures, occlude relatively large proportions of hydrogen, while those with a smaller magnetic susceptibility do not occlude hydrogen—copper, rhodium, and thorium are possible exceptions.

It was once thought that the palladium formed a chemical compound—Pd_2H—with the hydrogen, but this has not been accepted as a full explanation

T. Graham[10] thought that the gas hydrogen, during absorption, condensed to a solid metal which alloyed with the palladium. He gave the name **hydrogenium** to this hypothetical metal in order to emphasize its supposed metallic nature. It was argued that the metallic character of the occluded hydrogen is shown by the fact that if a plate of palladium be charged electrolytically with hydrogen, and subsequently immersed in a solution of copper sulphate, the metal is soon covered with a film of metallic copper: $CuSO_4+2H_{palladium}=H_2SO_4+Cu$. A similar phenomenon occurs when the plate is immersed in a solution of salts of gold, platinum, silver, or mercury, but not in solutions of salts of lead, iron, zinc, or magnesium. Solid hydrogen, however, was found by J. Dewar to have rather the properties of a non-metal than of a metal—its specific gravity, for instance, is 0·076, which is but one-eighth that (0·6 to 0·7) calculated for the absorbed hydrogen in palladium. The relation between the absorbed hydrogen and the metal is not perfectly clear.

Not only hydrogen, but several other gases are also absorbed by metals during their preparation or purification in furnaces, etc. For instance, W. Heald found that hydrogen is absorbed by many metals during their sublimation in that gas. Hence, when metals are heated to bright redness in glazed porcelain tubes exhausted by means of an air-pump, gases of various kinds are given off—*e.g.* aluminium gives off hydrogen; magnesium, hydrogen and carbon monoxide; zinc and electrolytic copper give off hydrogen, carbon dioxide and monoxide; tin and platinum give methane and nitrogen in addition to the gases just mentioned. L. Kahlenberg and H. Schlundt[11] found that when metallic sodium and mercury react with one another much heat is evolved, and 3·24 c.c. of hydrogen is evolved per gram of sodium. Allowance must always be made for the presence of occluded gases in metals, etc., which have not been heated to redness in vacuo; otherwise wrong inferences may be drawn. Indeed, at one time, H. Davy worked with the hypothesis that the elements are compounds of hydrogen with an unknown base in different proportions, and at first he seemed to succeed in getting relatively large quantities of hydrogen from sulphur, selenium, and carbon, but he got no unknown base. He soon recognized that the hydrogen he obtained was mechanically absorbed by these elements and was not a product of the decomposition of the elements, sulphur, selenium, and carbon. Alleged transmutations of one gas into another have been traced to similar phenomena in vacuum tubes. Many rocks and minerals also give off gases when heated under similar conditions, showing that they, too, have occluded gases. The meteoric iron of Lenarto containing about 91 per cent. of iron was reported by T. Graham (1867) to have yielded 2·86 times its volume of occluded gas. Since, under ordinary atmospheric pressures, iron absorbs only half its volume of gas, it was inferred that the meteorite must have come from an atmosphere containing hydrogen under a far greater pressure than our atmosphere, a deduction confirmed by spectroscopic observations on the dense hydrogen atmospheres of the sun and fixed stars.

The absorption of hydrogen or other gases in vacuum tubes has been explained as a result of the absorption of the gas by the disintegrated particles of the cathode by L. Vegard,[12] S. Brodetsky and B. Hodgson, and F. Soddy and T. D. Mackenzie; of the occlusion of the gas in the cathode by R. Riecke; of the chemical action of the gas and the cathode by K. Mey; of the chemical or mechanical action of the gas on the anode by C. A. Skinner, B. Hodgson, and V. L. Chrisler; to the chemical action of the gas on the glass by R. S. Willows, who found that the absorption was greatest with soda glass, less with lead glass, and least with Jena glass; of the occlusion of gas in the glass by A. A. C. Swinton; and by S. E. Hill, of the chemical action produced by the formation of active nitrogen.

The permeability of indiarubber to gases.—According to T. Graham, indiarubber absorbs about 0·0113 times its volume of hydrogen. In 1786, J. Priestley[13] noticed that indiarubber was permeable to gases; and J. K. Mitchell, in 1831, found that carbon dioxide diffused through a rubber membrane faster than hydrogen, and hydrogen, in turn, passed through more quickly than oxygen.

T. Graham measured the rates of diffusion of gases through rubber, and found that the rate at which the gases pass through rubber is not dependent on the densities of the gases. Equal volumes of the following gases penetrate rubber in the relative periods of time here indicated (nitrogen unity):

Carbon dioxide.	Hydrogen.	Oxygen.	Methane.	Carbon monoxide.	Nitrogen.
13·585	5·500	2·556	2·148	1·113	1·000

so that 2·556 volumes of oxygen penetrate the rubber in the same time as one volume of nitrogen. J. Dewar found with a membrane 0·01 mm. thick, and at atm. pressure, at 15°, the number of c.c. of gas which diffused per day per sq. cm.:

Air	N_2	CO	He	A	O_2	H_2	CO_2
2·0	1·38	1·88	3·5	2·56	4·0	11·2	28·0

No relation can be detected between the chemical composition or physical properties of a gas and its diffusibility through rubber. The speed increases proportionally with a rise of temperature. By plotting the logarithm of the rate against temperature, straight lines are obtained; these lines show a distinct break at 0°, suggesting that water is in some way involved; with carbon dioxide there is also a more pronounced break at $-37°$. H. Kayser found that the quantity of hydrogen which passes in unit time through a sq. cm. of surface and 1 cm. thick, when there is a difference of pressure of one atmosphere on the two faces of the rubber, can be represented by $(0·0001580\theta-0·000537\theta^2)$ c.c. per minute for temperatures θ between 9° and 33°. The effect of passing air through a vessel with rubber walls, a vacuum on the outside of the rubber, can be obtained by multiplying these numbers by the partial pressure of the gases. With air, P. Margis (1882) found that the mixture which diffused through the rubber walls contained 40 per cent. of oxygen; when this product was again passed through the apparatus a mixture containing 60 per cent. of oxygen was obtained; a third passage gave a mixture with 80 per cent. of oxygen, and after a fourth passage, the mixture contained 95 per cent. of oxygen. The phenomenon appears to depend on an absorption or occlusion of the gas by the rubber, and the subsequent evolution of the gas on the side under reduced pressure. G. Hüfner says that he found grey vulcanized rubber absorbed no measurable amount of hydrogen between $-2°$ and 13° at 760 mm. G. Austerwell and J. B. L. Juhle studied the diffusion of hydrogen through the walls of gas balloons.

According to J. Hunter,[14] cocoanut *charcoal* absorbs 4·4 times its volume of hydrogen reduced to 0° and 760 mm. The amount absorbed is proportional to the pressure (temperature constant), and inversely proportional to the temperature (pressure constant); and, according to H. Kayser, if p denotes the pressure, and v the volume of hydrogen absorbed per c.c. of charcoal, $v=6·036-1·55 \log p$ at 0°; J. Dewar found that charcoal absorbed 4 c.c. of hydrogen, and at $-185°$, 135 c.c. (reduced to n.p.t.); and J. L. Baerwald (1906) found that the volume of hydrogen absorbed at different temperatures by one volume of charcoal when the volume of gas is reduced to 0° and 760 mm.

	10°	0°	−10°	−50°	−100°	−150°	−185°
Hydrogen absorbed	3	4	4	9	24	76	135 vols.

Neither platinum nor palladium shows this remarkable increase in absorptive power at low temperatures. J. Dewar used the energetic absorption of hydrogen by wood charcoal to separate this gas from neon, helium, etc., which are absorbed to a far smaller degree, and this is in accord with the rule that the lower the boiling point, or the more volatile or less condensable the gas, the less is it absorbed by wood charcoal. J. W. McBain investigated the absorption of hydrogen by charcoal and found at the temperature of liquid air and 19 mm. pressure, the solubility is 4·1 c.c. of gas per gram. He also assumes that the absorbed gas is in the atomic condition. J. W. McBain further showed that the process of occlusion is of a dual character. If the surface of charcoal is first supersaturated by a short exposure to hydrogen at a high pressure, and a portion of the hydrogen be then removed, there is first a rise of pressure owing to the escape of the gas condensed or adsorbed on the surface, the pressure then slowly falls owing to the slow diffusion of the gas into the interior where it is absorbed or occluded to form a solid solution. He proposes to include both processes—rapid surface *adsorption*, and slow internal *absorption*—by the general term *sorption*.

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§ 7. The Physical Properties of Hydrogen

Hydrogen was once used as the standard for the atomic weights because it is the lightest element known. It is so much lighter than air that it escapes very quickly from a jar with its mouth upwards, and slowly from a vessel with its mouth downwards. For the **weight of a litre** of hydrogen at 0° and 760 mm. the data by H. Cavendish correspond with 0·092 grm.; A. L. Lavoisier, 0·0769 grm.; T. Thomson, 0·0693 grm.; J. B. Biot and F. J. Arago, 0·0732 grm.; P. L. Dulong and J. J. Berzelius, 0·0688 grm.; and J. B. A. Dumas and J. B. J. D. Boussingault, 0·0695 grm. These determinations are merely of historical interest. Later and more accurate determinations by H. V. Regnault gave 0·0896 at Paris, and when this value was corrected for the difference in volume between an exhausted and full globe, J. M. Crafts found that H. V. Regnault's value should be 0·08988 at Paris. J. P. Cooke's value at 45° and sea level is 0·089864; A. Leduc's, 0·08982; Lord Rayleigh's, 0·089979; E. W. Morley's, 0·089873; and J. Thomsen's, 0·089947. The numbers [1] thus range from 0·0896 to 0·090032 for the weight of a litre of hydrogen at 0° and 760 mm. pressure, at latitude 45° and sea level—the best representative value is taken to be 0·08985 grm. For the **density** of hydrogen (air unity), H. V. Regnault gave 0·0692 grm. (air unity), and with J. M. Craft's correction, 0·06949. J. P. Cooke gave 0·06958; A. Leduc, 0 06947; Lord Rayleigh, 0·06960. The data for the density of hydrogen, air unity, thus vary from 0·06927 to 0·06960, and the best representative value is taken to be 0·0694 (air unity). Hydrogen is 14·37, say 14½, times lighter than air; 11,160 times lighter than water; and 151,700 times lighter than mercury. According to J. Dewar, the density of hydrogen at its boiling point, —252·5°, is 0·55, air unity; and according to V. Meyer, the density does not alter at high temperatures. Liquid hydrogen has a **specific gravity** about $\frac{1}{14}$th that of water—and the variation of the specific gravity with the absolute temperature T, according to J. Dewar, is such that the specific gravity at T is $0·04136–0·000247T$; it is 0·0700 at —252·5°; 0·0754 at —258·3°; and 0·0763 at —259·9°. According to H. K. Onnes and C. A. Crommelin, solid hydrogen had a specific gravity of 0·0763 at —259·9°, and 0·08077 at —262°. The contraction on freezing is about 4·8 per cent. of the liquid volume. The **atomic volume** of liquid hydrogen is therefore 14·3; and according to J. Dewar, the molecular volume of hydrogen at absolute zero is 24·18 (extrapolation).

The **weight of a hydrogen atom** was estimated by R. D. Kleeman [2] to be $1·56\times10^{-24}$ grm., and J. Perrin estimated the mass of the hydrogen atom to be $1·4\times10^{-24}$ grm. The mean **diameter of the molecule** of hydrogen is $2·68\times10^{-8}$ cm.; the **volume of the molecule,** 10^{-25} c.c.; the mean **free path** of the molecule is $18·3\times10^{-6}$ to $17·8\times10^{-6}$ cm.; the **number of molecules per c.c.** is $2·75\times10^{19}$; the **collision frequency** is $92·8\times10^{8}$, or $1·64\times10^{29}$ per c.c. per second; and the **molecular velocity** 169,400 cm. per second. The value of J. D. van der Waals' a=0·00042, and of his b=0·00088, and J. J. van Laar has discussed the variability of these magnitudes.

Published data [3] for the **viscosity** of hydrogen gas at 60°, vary from $82·2\times10^{-6}$ to $85·74\times10^{-6}$ C. G. S. units—the mean may be taken as the best representative value. According to P. Breitenbach, at 15° the viscosity is $88·9\times10^{-6}$; at 99·2°, $182·4\times10^{-6}$; and at 302°, $139·2\times10^{-6}$; K. L. Yen gives η=0·000088216 with an accuracy of 0·15 per cent. at 23° and 760 mm. The viscosity at a temperature 23° is 0·000088216 ± 0·15 per cent. According to W. Kopsch, the viscosity decreases from $83·7\times10^{-6}$ at —0·1° to $80·2\times10^{-6}$ at —17·8°; to $71·0\times10^{-6}$ at —60·2°; to $37·42\times10^{-6}$ at —194·9°. According to J. E. Verschaffelt, the viscosity of the saturated vapour of hydrogen at 20·4° K. and 769 mm. pressure is 0·000010; and of the liquid, 0·000130. The coefficient C in W. Sutherland's equation for the relation of viscosity with temperature $\eta=\eta_0\{(273+T)/(T+C)\}(T/273)^{\frac{1}{2}}$, has the value 127; Lord Rayleigh gave 128·2; H. Markowsky, 138; and F. Kleint, 136. A gas experiences frictional effects not only when two of its layers flow past one another with different speeds—internal *friction* or viscosity—but also when it streams along the surface of a fixed body or of a body which moves with it—external friction. The gas does not adhere firmly to the solid, but slips along it. If γ be the coefficient of slip, η the viscosity, and ϵ the external friction, $\gamma=\eta/\epsilon$. For hydrogen, A. Kundt and E. Warburg, and O. E. Meyer, give $\gamma=0·0000186$. Liquid hydrogen has a **surface tension** $\frac{1}{35}$th that of water, or 0·2 of that of liquid air. According to P. L. Dulong,[4] the **velocity of sound** in hydrogen gas is 1269·5 metres per second at 0°, and according to I. B. Zoch, 1286·362 metres per second at 0°.

The value of the product *pv* for hydrogen has beenstudied by S. von Wroblewsky[5] up to 70 atm.; by E. H. Amagat up to 3000 atm.; and by W. J. de Haas up to 30,000 atm. pressure. The results show that the volume of the gas at high pressures is greater than is indicated by Boyle's law. Arbitrarily assuming that the product *pv* is unity at 0° and one atm. pressure, then,

Pressure .	1	500	1000	1500	2000	2500	2800 atm.
Volume .	1·00000	0·002713	0·001725	0·001380	0·001194	0·001078	0·001024
pv . .	1·0000	1·3565	1·7250	2·0700	2·3890	2·6950	2·8686

According to H. K. Onnes and H. H. F. Hyndmann the compressibility of hydrogen at 20° is given by equation $pv=1·07258+0·000667/v+0·00000099/v^2$. A. Jaquerod and O. Scheuer give the compressibility $-(d(pv)/dp)/pv$ between 400° and 800° as −0·00052; A. Leduc gives −0·00064; D. Berthelot, −0·00060; P. Chappius, −0·00058; and Lord Rayleigh, −0·00053. S. von Wroblewsky and W. J. de Haas found the **compressibility** of hydrogen does not follow Boyle's law at high temperatures. It falls from 0·000408 at 1000 atm. to 0·000158 at 30,000 atm. pressure. According to P. A. Guye, the value of $d(pv)/pv.dv.$ is +0·00052 from 0 up to 1 atm. pressure, and 0·00069 from 40 to 70 cm. pressure—temperature 0°. According to L. Cailletet, the compressibility at 15° falls regularly between 60 and 505 atm.; while E. H. Amagat noted that it follows Boyle's law up to 250°, at 3 to 6 mm. pressure; J. A. Siljeström found its elasticity higher than is required by Boyle's law, only at pressures below one atm.; but at very low pressures, F. Fucks, E. Budde, and C. Puschl obtained negligibly small deviations. These results were confirmed by Lord Rayleigh, who found that the product *pv* at low pressures, 3 to 6 mm., is in conformity with Boyle's law for hydrogen.

The effect of variations of temperature and pressure on the **coefficient of thermal expansion** of hydrogen is, for small pressures,

Pressure . .	0·0077	0·025	0·47	0 93	11·2	76·4	100 mm.
Temperature .	16°–132°	15°–132°	12°–185°	—	—	—	0°–100°
$a\times10^2$ . .	0·3328	0·3623	0·3656	0·37002	0·36548	0·36504	0·36626

According to P. von Jolly,[6] the coefficient of thermal expansion (pressure constant) is $a=0·0036562+0·0000010001\theta$; and according to M. W. Travers, G. Senter, and A. Jaquerod, the pressure coefficient (temperature constant) is $\beta=0·00366255$, or very nearly 1/273·03 per degree. A. Leduc gives $a=0·003662$, and $\beta=0·003664$ from 0° to 100°. A. W. Witkowsky has calculated the coefficient of thermal expansion (pressure constant) from −212° up to 100°. Hydrogen has a **thermal conductivity** about seven times larger than air.[7] The great heat conductivity of hydrogen was noticed by J. Priestley as early as 1781; and F. C. Achard in 1783. According to N N. Beketoff, the conductivity expressed in terms of the number of calories transmitted per second through a layer 1 cm. thick per sq. cm. of surface when the difference of temperature at the two sides is 1°, is 0·000327 (0°), 0·0003693 (100°), and at θ°, the conductivity is $0·000327\ (1+0·00175\theta)$; S. Weber gives 0·0004165. L. Graetz's values for the heat conductivity of hydrogen at 0° and at 100° are respectively 0·0003190 and 0·0003693. The increase of the conductivity with temperature θ° is represented by $0·0003190\ (1+0·006\theta)$. According to J. Janssen, the ratio of the cooling velocity of hydrogen to that of air is 1·000 : 7·459

—the calculated value is 1 : 7 : 1. According to P. A. Eckerlein, the thermal conductivity falls from 0·0003186 at 0°, to 0·0002393 at —59°, and to 0·0001175 at —150°.

The **specific heat** of hydrogen[8] at constant volume, C_v, is 2·4 when referred to an equal weight of water, and 0·99 referred to an equal volume of air. The specific heat at constant pressure, C_p, is 0·2438 between —28° and 9° ; and the molecular heat C_p, at 16° is 3·403 ; at —76°, 3·157 ; and at —181°, 2·644 ; from 20° to 50°, 3·4212 ; and from 20° to 100°, 3·4226. The molecular heat, C_p, rises from 3·402 at atmospheric pressure to 3·788 at 30 atm. pressure. A. Eucken gives C_v=3·20 for hydrogen at a concentration of 2·67 gram-molecules per litre at 35° K., and C_v=3·14 at 45° K. ; for hydrogen at a concentration 22·3 gram-molecules per litre C_v=3·32 at 35° K., and 3·28 at 45° K. G. Vieille estimates the **molecular heat** at constant volume and ordinary temperatures as 4·8 ; at 3100°, 6·30 ; at 3600°, 7·30 ; and at 4400°, 8·10. According to W. H. Keesom and H. K. Onnes (1918), the atomic heat of liquid hydrogen at 14·82° K. is 1·75 and 2·26 at 20·11° K. ; the atomic heat of the solid at 12·55° K. is 0·64. A. Eucken gives for the molecular heat of liquid hydrogen C_p=3·95 at 17·4° K., and 4·70 at 21·3° K. For temperatures between 11° and 95°, and pressures p up to 34 atm., S. Lussana gives for the molecular heat C_p=3·4025+0·013300(p—1). W. Nernst and H. von Wartenburg give C_v=4·68+0·00026T, where T denotes the absolute temperature. M. Pier's value for C_p between 0° and 2350° is C_p=4·700+0·0004θ ; and G. N. Lewis and M. Randall's value, C_p=6·50+0·0009T, for hydrogen molecules. According to A. Eucken, the specific heat of diatomic hydrogen below 60° K. is the same as for monatomic gases, viz. 2·98. According to R. Clausius, **the ratio of the two specific heats** is 1·3852 ; O. Lummer and E. Pringsheim give 1·4084 ; K. Scheel and W. Heuse, 1·407 ; J. Jamin and F. Richard, 1·41 ; M. C. Shields gives 1·4018 at 18° ; and W. C. Röntgen, 1·3852. According to A. Eucken, the ratio of the two specific heats at —180° is 1·604 ; according to K. Scheel and W. Heuse, 1·595 ; and according to M. C. Shields, 1·592 at —191°. This makes it appear as if the hydrogen molecule entirely loses its two degrees of rotational freedom at low temperatures. According to J. Dewar, the atomic heat of liquid hydrogen is 6·4, and this is higher than that of any other known liquid. The atomic heat is therefore in conformity with Dulong and Petit's rule. N. N. Beketoff gives the atomic heat of hydrogen absorbed in palladium as 5·88. G. N. Lewis and G. E. Gibson estimate the **entropy** of hydrogen gas at 25° to be 29·4 per gram-molecule, when the increase of entropy from absolute zero to the melting point T is $\phi=\int C_p d \log T$=0·5, from the solid to the liquid at the melting point 32/15=2·13 ; from the melting point to the boiling point 1·22 ; from the liquid to the gas at the boiling point, 218/20·5=10·73 ; and of the gas from its boiling point to 298° K., 14·80.

In 1877, L. P. Cailletet noticed the formation of a mist when hydrogen at a pressure of about 280 atm. is suddenly released ; in 1884, S. von Wroblewsky obtained signs of liquefaction when hydrogen at a pressure of 190 atm. and cooled by boiling nitrogen is suddenly relieved. In 1884–5, K. Olszewsky reported that he obtained colourless drops of liquid hydrogen by a similar process. J. Dewar (1895) first obtained sufficient liquid hydrogen to show a definite meniscus by applying the regenerative process to the gas cooled to —205°. Just below the **critical temperature,** —241°, a pressure of about 15 atm. will liquefy the gas ; above the critical temperature no pressure, however great, will liquefy the gas. The **critical pressure** is 20 atm., and the **critical volume** 0·00264. Liquid hydrogen is clear and colourless, thus resembling water ; it has a sharp meniscus, and a high refractive index and dispersion. Its **boiling point** is —252·77°, or 20·5° K. ; P. G. Cath and H. K. Onnes[9] give 20·39° K., and they found for the **vapour pressure** of liquid hydrogen, at T° K., between 24·59° K. and 32·93° K., $T \log p=-56·605+3·8015T-0·10458T^2+0·003321T^3-0·00005102T^4$ atm.; while, according to M. W. Travers, G. Senter, and A. Jaquerod, the vapour pressure is, on the absolute scale of temperatures,

Temp. (abs.) .	20·41°	19·93°	19·41°	18·82°	18·15°	17·36°	19·37°	14·93°
Vapour pres. .	800	700	600	500	400	300	200	100 mm.

Hydrogen solidifies to a transparent mass like ice with a foamy surface, when the liquid is evaporated rapidly in a partial vacuum. The unique temperature, called the **triple point,** where the liquid, solid, and vapour are all in equilibrium, is near —259° and 55 mm. pressure. The white solid is crystalline and, according to J. Dewar, its **melting point** is —259·2°. The data concerning the change of state of hydrogen can be symbolized :

$$\text{Hydrogen}_{\text{solid}} \overset{-259\cdot2^\circ}{\rightleftharpoons} \text{Hydrogen}_{\text{liquid}} \overset{-252\cdot77^\circ}{\rightleftharpoons} \text{Hydrogen}_{\text{gas}}$$

W. Wahl found the velocity of crystallization of hydrogen to be very great at about 20° K. He obtained isotropic **crystals** belonging to the cubic system—either trisoctahedrons or hexoctahedrons. Needle-like branches grow at right angles to a fully developed crystal face. The **latent heat of vaporization** of liquid hydrogen is nearly 218 cals. at its boiling point. A. Eucken gives 229 cals.; W. H. Keesom, 222 cals.; and W. H. Keesom and H. K. Onnes, 212 cals. J. Dewar's value for the **latent heat of fusion** of the solid is 15 to 16 cals.[9] per gram-atom.

M. Croullebois[10] gives 1·000137 as the mean **index of refraction** of hydrogen for white light. J. Koch gives for light of wave-lengths $\lambda=230\cdot2\mu\mu$, 1·0001594 ; $\lambda=354\cdot4\mu\mu$, 1·0001449 ; $\lambda=435\cdot8\mu\mu$, 1·0001488 ; $\lambda=546\cdot1\mu\mu$, 1·0001397 ; $\lambda=670\cdot8\mu\mu$, 1·0001385 ; and for the ultra-red rays $\lambda=6709\cdot4\mu\mu$, 1·0001361 ; and $\lambda=8678\cdot4\mu\mu$, 1·00013611 at 0° and 760 mm. Analogous observations have been made by E. Ketteler, L. Lorenz, E. Mascart, E. Perreau, K. Scheel, and by C. and M. Cuthbertson. J. W. Brühl, H. Landolt, and F. Eisenlohr have calculated the **atomic refraction** by Gladstone and Dale's formula, and J. H. Gladstone gives for the *A* line 1·29 ; J. W. Brühl and J. Traube, and H. Landolt, by Lorenz and Lorentz's formula, give 1·02 for the *A*-line. The dispersive power of hydrogen from M. Croullebois' datum is 0·1814 (air unity) ; while W. Ramsay and M. W. Travers give 0·4733. K. Hermann gives for the relative dispersion $V^{-1}=(F-C)/(\mu D^{-1})$, when $V=65\cdot9$. L. Natanson, R. Ladenburg, and S. Loria have also studied the dispersion of hydrogen. J. W. Brühl gives for the atomic dispersion of hydrogen $R_\gamma-R_a=0\cdot036$. C. and M. Cuthbertson find that b of Cauchy's dispersion formula, $\mu-1=a(1+b/\lambda^2)$, rises gradually between the red and violet. Better results are obtained with $\mu-1=C/(n_0^2-n^2)$, where the constants $C=1\cdot692\times10^{27}$, and n_0 is 12409×10^{27}—and for oxygen it is $3\cdot397\times10^{27}$, and for nitrogen $5\cdot0345\times10^{27}$. Hence, these three elements agree with P. Drude's rule $C/v=\text{constant}$, when v denotes the positive valency of the atom.

The **magneto-optic rotation** of a body refers to the angle through which a ray of polarized light is rotated when the light is passed through the body in a direction parallel to the lines of magnetic force. This phenomenon with glass was discovered by M. Faraday[11] in 1845 ; it was afterwards noticed that the amount of rotation depends on the nature of the substance, on its physical condition, on the strength of the magnetic field, and on the wave-length of the polarized light. A. Kundt and W. C. Röntgen noticed the phenomenon with gases in 1879. The rotation per cm. per unit magnetic field is called **E. Verdet's constant,** for E. Verdet showed, in 1853, that with the same medium and magnet, the rotation is directly proportional to the intensity of the magnetic field. The product of E. Verdet's constant with the molecular volume—or M/D—is called the **molecular rotation.** The molecular rotations of many substances have been found to be additive, for they are the sum of constants for the constituents of the molecules. For a pressure 85 kgrms. per sq. cm., and 9·5°, and light of wave-length λ, E. Verdet's constant[12] is $0\cdot00007585\lambda^{-1}+0\cdot00002295\lambda^{-3}$ for values of λ between $0\cdot423\mu$ and $0\cdot684\mu$.

If a continuous discharge be passed through a Geissler's tube containing hydrogen at a pressure of 0·05 to 3·00 mm., there is a white glow in the capillary, and strata, alternately pale pink and pale blue, appear about the electrodes. The white glow, in the spectroscope, appears as a multitude of lines of varying intensity, and hence is called the *white spectrum* of hydrogen. If a condenser of large capacity is introduced into the circuit, the oscillatory discharge changes the colour of the glow from white to deep red. Most of the spectral lines are obliterated and the so-called *four-line spectrum* or the *red spectrum* of hydrogen is obtained which is comparable with the blue spectrum of argon. The four-line spectrum of hydrogen[13] is conveniently observed in a Geissler's tube, with the gas at about a millimetre pressure, and through which a discharge from an induction coil is passing; the four lines, shown in Fig. 15, correspond with H_α in the red with a wave-length 6564·97; H_β in the greenish-blue 4862·93; H_γ in the indigo-blue 4341·90; and H_δ in the violet 4103·10; these lines correspond respectively with Fraunhofer's dark lines, *C*, *F*. *G*, and *h*. According to L. Janicki (1906), the red line is really a double one. If the oscillatory discharge is suitably damped, the obliterated lines preceding the four-lines spectrum gradually reappear. F. Emich considers it possible to detect up to 7×10^{-14} milligram of hydrogen by means of its spectrum in a vacuum tube. H. W. Vogel and A. Paalzoff have photographed a great many other lines chiefly in the violet and ultra-violet spectrum of hydrogen, and compared them with analogous lines in the spectra of the sun and stars. A. Wüllner and J. Plücker and W. Hittorf showed that hydrogen furnishes a second and yet a third spectrum, which A. Schuster and A. V. Angström ascribed to the presence of acetylene or sulphur. G. Salet also failed to verify the observation with pure hydrogen. Several observers, however, have verified the existence of the white spectrum in which the usual four hydrogen lines are present though not specially prominent. According to J. Trowbridge and T. W. Richards, hydrogen containing a trace of water vapour readily gives the red four-line spectrum with a continuous discharge, while the perfectly dry gas gives the white spectrum, and a very great strength of current is then required to produce the red four-line spectrum.

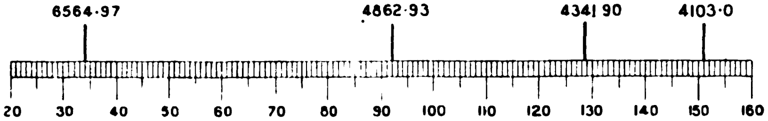

Fig. 15.—The Four-line Spectrum of Hydrogen in a Geissler's Tube.

B. Hasselberg postulates that the difference in the hydrogen spectra are due to dissociation. He says:

> As the explanation of the displacement of a spectrum by a new one with rise of temperature, and the first spectrum (of hydrogen) must be ascribed to a more complicated arrangement of molecules or to a compound of the body with itself. Since, according to the investigations of Wiedemann, in the case of hydrogen a continual rise in temperature produces first a gradual diminution of the spectrum above described, and then upon reaching a certain limit its almost sudden disappearance, these considerations lead us to the view proposed as a second alternative by Angström, according to which the spectrum belongs to a compound of hydrogen with itself. The heat-equivalent found by Wiedemann for the quantity of energy necessary to transform this spectrum into that consisting of the three characteristic bright lines, would therefore be nothing else than the thermal equivalent of the corresponding work of dissociation. This hypothesis furnishes an easy explanation of the fact that in the spectra of the sun and most stars only the characteristic lines of this gas appear as bright lines or absorption lines, as the case may be detected. The reason is to be found in the enormous temperatures existing in these bodies.

J. N. Lockyer also believes dissociation occurs in flame and spark; and A. Dufour pointed out that the gas in a Geissler's tube is under conditions specially favourable for dissociation, for the pressure is low and the temperature high.

E. Frankland and J. N. Lockyer found that with a feeble current, or by changing the pressure and temperature, the spectrum of hydrogen can be reduced to a single *F*-line. With increasing pressures the spectrum of hydrogen approaches a continuous one.

TABLE II.—BALMER'S SERIES OF LINES IN THE ARC SPECTRUM OF HYDROGEN.

H line.	n	Wave-length, λ.		Difference.
		Calculated.	Observed.	
H_α or C	3	6564·96	6564·97	+0·01
H_β or F	4	4862·93	4862·93	—
H_γ or G	5	4341·90	4342·00	−0 1
H_δ or *h*	6	4103·10	4103·11	+0·01
H_ϵ or H	7	3971·4	3971·4	—
H_ζ or *a*	8	3890·3	3890·3	—
H_η or β	9	3836·7	3836·8	+0·1
H_θ or γ	10	3899·2	3799·2	—
H_ι or δ	11	3771·9	3771·9	—
H_κ or ϵ	12	3751·4	3751·3	−0·1
H_λ or ζ	13	3735·6	3735·3	−0·3
H_μ or η	14	3723·2	3722·8	−0·4
H_ν or θ	15	3713·2	3712·9	−0·3

In 1885, J. J. Balmer discovered a remarkable relation between the vibration-periods or the wave-lengths of the spectral lines of hydrogen; if the different lines in the spark spectrum of hydrogen be numbered consecutively, starting with the H_a-line as number 3, the next 4, 5, 6 . . ., the wave-length of the nth line is given by

$$\lambda=3647{\cdot}2\frac{n^2}{n^2-4}; \text{ or } \lambda=3647{\cdot}2\frac{n^2}{n^2-2^2}$$

J. S. Ames' measurements are compared in Table II with values calculated by means of J. J. Balmer's formula. The agreement between the calculated and observed wave-lengths is very good, and hence the preceding formula may be taken to represent closely the various kinds of elastic vibration which prevail among the vibrating particles which produce **Balmer's series** of lines in the spark spectrum of hydrogen. According to R. W. Wood, the different lines of the principal Balmer's series and their accompanying channelled spectra are probably produced by different entities—either by atoms which have lost 1, 2, 3, 4, . . . electrons, or by aggregates or complexes of 1, 2, 3, 4, . . . atoms. In either case, it seems probable that the members would break up in continuously increasing numbers. W. E. Curtis' measurements led him to make a slight modification in Balmer's formula. W. Ritz and F. Paschen[14] found that there is another series of lines in the ultra-red spectrum of hydrogen—the so-called **Paschen's series**, represented by $\lambda=an^3/(n^2-3^2)$, where a is a constant; and the so-called **Lynman's series** represented by $\lambda=an^2/(n^2-1^2)$, in the ultra-violet.

F. Croze,[15] and F. Paschen and E. Back have measured the *Zeeman effect* for the primary lines of the hydrogen spectrum, *viz.* H_a, H_β, H_γ, and H_δ. J. Stark and co-workers have shown that certain hydrogen lines of the primary and secondary series are resolved into linearly polarized components under the influence of a strong electrical field of 1300 volts per cm. The longitudinal components are not polarized so that the effect of the electrical field—*Stark effect*—is in marked contrast with the Zeeman effect, for in the latter case the components are circularly polarized. With still stronger electrical fields, 104,000 volts per cm., J. Stark found a separation into further components. T. Takamine, N. Kokubu, and U. Yoshida have also investigated the Stark effect on the hydrogen lines with a field strength of 15,000 volts per cm., and found that besides the primary lines, eleven lines in the region below $\lambda=4000$ were affected. C. Fabry and H. Buisson have made estimates of the mass of the particles which emit the first and second hydrogen spectra, and found that is the same as that of an hydrogen atom. B. Reismann found hydrogen shows both its spectra at the anode and cathode of a Geissler's tube excited by a direct current discharge. H. L. P. Jolly has measured the distribution of energy in the spectrum of hydrogen.

J. Tyndall could find no absorption of invisible heat radiations by hydrogen at atm. pressure. Neither J. Janssen (1885)[16] nor V. Schumann could find an **absorption spectrum** for hydrogen gas; W. Barmeister found hydrogen gas has no infra-red absorption bands. J. Dewar (1894) did not find any in the liquefied gas. Hydrogen thus appears to be the most transparent of all known bodies; even the Schumann rays powerfully absorbed by other gases are freely transmitted by hydrogen. In 1907, A. Pflüger, and R. Ladenburg and S. Loria showed that an absorption spectrum can be obtained while the gas is in a state of luminescence during its excitation by the discharge. Several others have since studied the absorption spectrum of hydrogen.

A. L. Lavoisier and P. S. de Laplace[17] noticed that the hydrogen which is liberated by the action of sulphuric acid on iron is positively electrified; and in the case of zinc, W. Hankel showed that when the gas is positively electrified, the sulphuric or hydrochloric acid and the metal are negatively electrified. J. S. Townsend showed that the electrification is not due to the spray mechanically carried by the gas but is produced during the bubbling of the gas through the acid. J. Enright showed that this is but a special case of electrification by chemical action. J. Franck,[18] R. Pohl, and W. B. Haines have shown that free electrons exist in hydrogen gas at atmospheric pressures. Hydrogen gas, according to E. Villari, resists the passage of an electric spark less than nitrogen, oxygen, or carbon dioxide. The **discharge tension** in gases is influenced by numerous factors—temperature, pressure, form of electrodes, the character of the spark, etc.—with spherical electrodes at 0·08 cm. apart, the discharge potential is 2·4 kilovolts for hydrogen, 3·9 for air, 3·7 for carbon monoxide, 4·9 for nitrogen, and 3·4 for oxygen; with the electrodes 0·5 cm. apart, the numbers are respectively 9·7, 17·5, 15·8, 18·0, and 15·6 kilovolts. The difference between the potential of a plane and of a point placed at right angles to the plane, needed for the passage of electricity, is called the *minimum potential*. The observed minimum potentials depend on the sharpness of the point. W. C. Röntgen[19] found 1296 and 1174 volts respectively for hydrogen at 205 and 110 mm. pressure; and F. Tamm found that the decrease with high pressures is small, but more rapid with low pressures. J. Precht obtained for a + point 2135 volts and for a − point 1550 volts in hydrogen at 760 mm. E. Warburg, H. Sieveking, and F. Tamm measured the relation between the current and potential. A. L. Hughes and A. A. Dixon found the **ionizing potential** is dependent on the least energy necessary to ionize the molecules of a gas by the impact of electrons, and amounts to 10·2 volts for hydrogen; J. Franck and G. Hertz found 11 volts, F. S. Goucher, 10·25 volts; and the value calculated by K. T. Compton's formula $V=0{\cdot}194(K-1)^{-\frac{1}{2}}$ is 11·8 volts, where V denotes the ionizing potential, and K the specific inductive capacity. F. M. Bishop obtained 11 volts, and found the result independent of the pressure. W. J. Paloff obtained a similar result. F. M. Bishop also found a second type of ionization at 15·8 volts. Neither value is in accord with Bohr's theory, which requires for the ionization potential 10·2 volts for the first line of longest wave-length, and 13·6 volts for the shortest wave-lengths.

The **ionization** of hydrogen gas by Röntgen rays has been studied by R. K. McClung, A. S. Eve, J. A. Crowther, G. Shearer, H. Donaldson, N. Campbell and C. G. Barkla, and A. J. Philpot; by radium radiations by A. S. Eve, L. Wertenstein, W. Seitz and N. Campbell; by α-rays by C. G. Darwin, W. Duane and G. L. Wendt, T. S. Taylor, E. Rutherford and J. M. Nuttall, E. Marsden, and R. D. Kleeman; by β-rays, by H. W. Schmidt; by γ-rays, by T. H. Laby and G. W. C. Kaye and R. D. Kleeman; by radium bromide by H. Baker; by radiations from polonium by T. S. Taylor; by radiations from actinium by R. D. Kleeman; by light from a Geissler's tube by H. G. Cannegieter; by canal rays by R. Seeliger; by collision by E. S. Bishop and W. J. Pawloff; and by spraying by L. Block. The ionization of the hydrogen flame has been studied by M. de Broglie. The action of hydrogen on the electric discharge between various metals has been studied by A. Thiel and E. Breuning, J. N. Pring, O. W. Richardson, H. A. Wilson, A. Becker, and C. Sheard. The electric discharge in hydrogen or in hydrogen mixed with other gases has been studied by E. M. Wellisch, K. E. F. Schmidt, J. Trowbridge, K. Fredenhagen, A. P. Chattock, and A. M. Tyndall. The mean values of J. Zeleny's, J. Franck's, R. Pohl's, and A. P. Chattock's determinations of the velocities of the positive and negative hydrogen ions when the electric discharge in a field of 1 volt per cm. are respectively 6·06 and 7·69 cm. per second. J. Townsend gives for the diffusion coefficient of the positive and negative ions respectively 0·123 and 0·190 per sq. cm. per second. J. Townsend, and R. K. McClung give respectively $dn/dt=3020n^2$, and $dn/dt=-2940n^2$, where n denotes the concentration of the ions, and dn/dt the velocity of combination of the ions to form ordinary molecules. H. A. Erickson and P. Phillips have studied the effect of temperature on this reaction. F. W. Aston estimates that the minimum energy required for the ionization of the hydrogen atom in a gas is $1·7\times10^{-11}$ erg. W. B. Haines has investigated the mobilities of the positive and negative hydrogen ions. Unlike all other elements yet investigated, J. J. Thomson was never able to impart more than one charge of electricity to the hydrogen atom.

According to the ionization hypothesis, the acids are more or less ionized in aqueous solution, and they all furnish in common hydrogen ions which act as carriers of positive electricity. The characteristic properties of acids are assumed to be the characteristic properties of $H^{\cdot}$-ions; during electrolysis the positively charged hydrogen cations are discharged at the cathode, and the negatively charged anions are discharged at the anode. The electric charge carried by a gaseous ion is the same as that carried by a $H^{\cdot}$-ion during electrolysis; the charge per ion in the former case is approximately 4×10^{-10} units, although in the latter case the observed numbers vary between 1×10^{-10} and 6×10^{-10} units. Again, the value of e/m, where e denotes the charge and m the mass of the ion, is the same for all gaseous ions, and approximate to 10^7, while the value of the ratio e/m for the hydrogen ion in solution is 10^4. Consequently, the relation between the masses m of the gaseous ion and of the hydrogen ion in solution is as 1 : 1700. The gaseous ion with its negative charge was first called a corpuscle by J. J. Thomson, but the term electron is now in general use. The positively charged hydrogen ion in solution is assumed to be a hydrogen atom which has lost one of its negatively charged electrons; during the scission of the molecule in the process of ionization the electron lost by the hydrogen atom in forming the $H^{\cdot}$-ion remains attached to the other atom or radicle and so imparts a negative charge to the anion.

Solutions containing equivalent quantities of the different acids do not necessarily contain the same quantities of $H^{\cdot}$-ions, for a portion of the acid may not have suffered ionization. There is a state of equilibrium, $HA\rightleftharpoons H^{\cdot}+A'$, in which anion, cation, and un-ionized molecules are present. One or more of these three entities may be more or less hydrated in the solution. The **degree of ionization** is dependent on the concentration of the solution and on the temperature. The equivalent conductivity at infinite dilution λ_∞, when ionization is complete, is the sum of the conductivities of the $H^{\cdot}$-ion, namely, $v^{\cdot}$, and of the anion, v', so that $\lambda_\infty=v^{\cdot}+v'$, or $v^{\cdot}=\lambda_\infty-v'$. The value of the molecular conductivity μ changes with the temperature. According to F. Kohlrausch,[20] the conductivity of the hydrogen ion at $\theta°$ is $v^{\cdot}=318·1+0·0154(\theta-18)-0·000033(\theta-18)^{20}$ reciprocal ohms. W. Ostwald and R. Luther say that F. Kohlrausch's value $v^{\cdot}=352$ (25°) is too high and give $v^{\cdot}=347$ (25°); A. A. Noyes and G. V. Sammet say that F. Kohlrausch's value is too low, and give $v^{\cdot}=364·9$ (25°). V. Rothmund and K. Drucker's value is $v^{\cdot}=338$.

The **hydrogen electrode** is used in measuring the concentration of $H^{\cdot}$-ions in a solution; it is based on the definite difference of potential which exists between a platinum or palladium electrode, saturated with hydrogen gas at a given pressure, and immersed in a solution of definite acidity or alkalinity. The particular forms of the cells are indicated in laboratory manuals. The e.m.f., E, of the cell H_{2Pt} | Solution I | Electrolyte | Solution II | H_{2Pt} is given by

$$E=\frac{RT}{\epsilon}\log_e\frac{[H^{\cdot}]_1}{[H^{\cdot}]_2};\ \text{or}\ E=0{\cdot}000198T\log_{10}\frac{[H^{\cdot}]_1}{[H^{\cdot}]_2}\ \text{volts}$$

where ϵ represents the farad, 96,540 coulombs, and R the gas constant, 9·316 joules. If solution I be 0·01N-HCl, and solution II, 0·001N-HCl, and the temperature be 18°, E=0·058 volt, nearly. The hydrogen electrode with a normal solution of $H^{\cdot}$-ions may be used as a standard, and the hydrogen concentration of a given solution is determined by measuring the e.m.f. of the combination. Suppose it is 0·5 volt at 18°. Consequently, $0{\cdot}5=0{\cdot}058(\log_{10} 1-\log [H^{\cdot}]_x)$ or the required concentration of the $H^{\cdot}$-ions is $2{\cdot}4\times10^{-9}$. The total *temperature coefficient* of the hydrogen electrode is small, and is made up of a number of factors—concentration of dissolved gases, pressure of water vapour or of other gases, etc. *Pressure* raises the positive potential of the hydrogen. If the pressure of the hydrogen is p atm., the correction to be added at 18° is $E-E_p=-\frac{1}{2}$ of 0·058 log p. If the pressure be 740 mm., the correction is $\frac{1}{2}$ of 0·058 log (740/760)=0·00033 volt. The fluctuations of the barometer can usually be neglected.

The hydrogen ions often have a catalytic action accelerating the speed of some reactions, and retarding the speed of others. The catalytic action of the $H^{\cdot}$-ions on the speed of the inversion of cane sugar, the hydrolysis of methyl acetate, etc., has been used to estimate their concentration. The discharge of hydrogen ions furnishes hydrogen molecules $2H^{\cdot}=H_2$. W. Ostwald estimates the **heat of ionization** to be $H_2=2H^{\cdot}-1{\cdot}1$ Cal.; and K. Fajans, the **heat of hydration of gaseous $H^{\cdot}$-ions** to be 362 kgrm. cal. per gram-ion. The **free energy of formation of a hydrogen ion** is found by measuring the difference of potential E between hydrogen gas at a pressure p atm. and a solution of $H^{\cdot}$-ions of concentration C gram-ions per litre at the absolute temperature T, since $E=E_0+RT(\log C-\frac{1}{2}\log p)$, where R, the gas constant, is $0{\cdot}861\times10^{-4}$; and E_0 is the potential when C and p are unity. Measurements by N. T. M. Wilsmore and others give $E_0=-0{\cdot}283$ volt (25°) with the normal calomel electrode zero. The value of E_0 thus measures the tendency of hydrogen to form ions, or half the intensity of the electro-affinity. W. Nernst took the potential of the hydrogen electrode—platinum or platinized palladium saturated with hydrogen—as zero because of its position in a series of the potentials of the different elements. W. Ostwald objected to this because of the large variation which occurs with changes of pressure—one millivolt per 0·0345 atm. The relatively small electro-affinity of the hydrogen ion is correlated with its great tendency to form complex ions. Thus, with ammonia it forms $NH_4^{\cdot}$ ions, and similarly with the various amines and oxonium compounds; likewise also with the anions of the acid salts HSO_2', HSO_3', HCO_3', HC_2O_4', etc.

G. W. Osann[21] obtained a gas which he called *aktiven Wasserstoff oder Ozonwasserstoff* by the electrolysis of a mixture of distilled Nordhausen sulphuric acid and water. He claimed that the gas is a far more active reducing agent than ordinary hydrogen; but neither J. Löwenthal nor G. Magnus could confirm G. W. Osann's conclusions, and they attributed his results to the contamination of his hydrogen with some sulphur dioxide. W. Duane and G. L. Wendt exposed hydrogen, of as high a degree of purity as they could prepare, to the intense bombardment of α-radiations, and found the gas became more chemically active at ordinary temperatures, for it then combined directly with sulphur to form hydrogen sulphide; with phosphorus to form phosphine; with arsenic to form arsine; and with nitrogen to form ammonia. It reacts with mercury forming yellow crystals—possibly *mercury hydride*—which resist attack by water and weak alkali lye, but dissolve in hydrochloric and nitric acids; when gently warmed, the yellow crystals form globules of mercury. The activated hydrogen reduces potassium permanganate solutions forming manganese dioxide; it does not bleach methyl violet or indigo carmine. W. Duane and

G. L. Wendt suggest that the activated gas is related to normal hydrogen as ozone is related to oxygen—a kind of *ozonohydrogen*, H_3. They do not believe that it is monatomic hydrogen because its formation is attended by a contraction in volume. The activation of the hydrogen is not due to the formation of ions because it is not destroyed by the passage of the gas through glass wool and an intense electrostatic field; but it is removed by passing the gas through a tube immersed in liquid air. The **activated hydrogen** is not stable for its life is measured in minutes. J. J. Thomson found that in a discharge tube containing hydrogen, there are present charged atoms, charged molecules, and sometimes a constituent with three times the mass of ordinary hydrogen atoms. The potential used was of the order 20,000 volts.

A. J. Dempster found that with a potential of 800 volts hydrogen is ionized by detaching a single elementary charge from the molecule, but the gas is not dissociated; the positive molecules so formed, however, can dissociate the gas forming the complex H_3. This constituent is not stable, and is not present when there is no dissociation of the hydrogen molecule.

Liquid hydrogen is electrically non-conducting. The **dielectric constant,** K, of hydrogen[22] was found by A. Occhialini to be given by $(K-1)/(K+2)D=90154\times10^{-9}$ between 94 and 196 atm. pressure; and by extrapolation $K=1·0002705$ at ordinary pressures. Other determinations of the dielectric constant of hydrogen gas at atmospheric pressures and 0°, give 1·000264 (vacuum unity), and at 20°, 1·000273—since the dielectric constant of air at 0° is 1·000590, the dielectric constant of hydrogen at 0° is 0·999674 (air unity). At 20° and 20 atm. pressure, the dielectric constant of hydrogen is 1·00500; under 60 atm. pressure 1·01460; and under 100 atm. pressure, 1·02378. At −191°, and 760 mm., H. Riegger found 1·000928. Hydrogen is diamagnetic. The **magnetic susceptibility** of hydrogen at 1 to 40 atm. pressure and 16° is below $0·008\times10^{-16}$ volume units.[23] According to S. Henrichsen, the **atomic magnetism** of hydrogen in organic compounds is 9.

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§ 8. The Chemical Properties of Hydrogen

Although **the combustibility of hydrogen** is one of its most characteristic properties, perfectly dry hydrogen ignites with difficulty, if at all, when mixed with perfectly dry oxygen. According to H. B. Baker (1902),[1] the dried mixture may be heated to the melting point of silver—960·5°—without appreciable combination. Note, however, that moisture is a product of the reaction. Many other combustible substances, if perfectly dried, do not burn when moisture is rigorously excluded. The moisture is here said to act as a **catalytic agent**—κατὰ, down; λύω, I loosen. Finely divided platinum and many other metals will cause a mixture of hydrogen and oxygen, at ordinary temperatures, to explode; and if a jet of hydrogen, in air, impinges on finely divided platinum, the metal becomes hotter and hotter, and finally ignites the gas.

"Toy" automatic cigar lighters are made so that by turning the tap of a little hydrogen generator—not unlike the Kipp's apparatus in principle—a jet of hydrogen can be directed on a piece of spongy platinum when a "light" is desired. The platinum becomes hotter and hotter, and finally ignites the jet of hydrogen. The flame is extinguished by turning the stopcock, and the apparatus is ready for another ignition when the jet of hydrogen is again turned on to the platinum. This is the principle of the self-lighting lamp designed by J. W. Döbereiner in 1822. Impurities in the hydrogen gas, however, appear to "poison" the platinum, for the apparatus soon ceases to be effective.

Hydrogen and oxygen, so far as we can tell, may remain an indefinite time in contact with one another at atmospheric temperatures without showing any sign of chemical action. Some say that the gases do react, but very, very slowly. By measuring the diminution in the speed of the reaction from, say, 600° to 500° to 400° to 300°, and assuming that the rate of diminution of the speed of the reaction follows the same law—reduction of the speed by one half per 10° reduction of temperature—it has been estimated that no appreciable amount of hydrogen and oxygen will have combined if a mixture of these gases be allowed to stand at ordinary temperatures 1,000000,000000 years. The student has the option of accepting or rejecting statements like these. They can neither be proved nor disproved. The risks which attend this mode of reasoning about natural processes have already been indicated. As P. Duhem has said (1910): " It comes to the same thing experimentally whether we say that the velocity of a reaction is absolutely null, or that it is so small that there is no way of detecting it."

Shortly after H. Cavendish's work on hydrogen gas, there were suggestions made for using hydrogen lamps for heating purposes; thus, J. Priestley stated that oxygen could be used for producing a very high temperature if fed into the hydrogen flame by means of a suitable bellows; and F. L. Ehrmann, in his *Versuch einer Schmelzkunst mit Hülfe der Feuerluft* (Strassburg, 1785), described the effect of a hydrogen flame, strengthened by admixture with oxygen, upon many substances. About 1801, R. Hare [2] devised an oxyhydrogen blowpipe, which was fully described in his *Memoir of the supply and application of the blowpipe* (Philadelphia, 1802), published by order of the Chemical Society of Philadelphia. The *oxyhydrogen flame* is one of the hottest gas flames known; by its means Robert Hare melted barytes, alumina, and silica and obtained products resembling white enamel. Magnesia and platinum were melted; and, added R. Hare, " had I sufficient confidence in my own judgment, I should declare that silver, gold, and platinum were thrown into a state of ebullition by exposure on carbon to the gaseous flame." When a stick of quicklime is placed at the tip of the flame from a mixture of hydrogen and oxygen burning from a special jet to avoid risk of explosion, the lime does not melt, but it becomes white hot and glows with an intense white light known as *Drummond's light* [3] or the *lime-light* or the *calcium light*. T. Drummond said that the lime-light is of such dazzling whiteness that it is plainly visible sixty-eight miles away. If zirconia be used in place of lime, the *zircon light* is obtained. According to T. Drummond, the light given by zirconia is less powerful than that of lime; and that by magnesia is only half as intense. C. H. Pfaff says that if the light of a wax candle be unity, the light emitted by a cylinder of lime one-fifth the diameter of the flame of a candle is 153 when heated by the oxyhydrogen flame; 76 by the ether-oxygen flame; 69 by the alcohol-oxygen flame; and 19 by the oxygen-coal gas flame. A. Pleischl and M. A. Gaudin studied the flame from oxygen and turpentine, and oxygen and oil gas. The oxyhydrogen flame is used for the autogenous welding of metals, for soldering platinum, for making vessels of fused quartz, etc.

Hydrogen unites chemically, directly or indirectly, with most of the non-metallic and with many of the metallic elements—more particularly the alkali and alkaline earth metals. The binary compounds of the metals with hydrogen are usually called **hydrides**. A. L. Lavoisier, in his *Traité élémentaire de chimie* (Paris, 1. 116, 1789), foresaw the probability of the formation of hydrides, for he said:

> As combustible substances have in general a great affinity for oxygen, they ought likewise to attract, or tend to combine with each other; *quæ sunt eadem uni tertio, sunt eadem inter se*; and the axiom is found to be true. Almost all metals, for instance, are capable of uniting with each other, and of forming what, in common language, are called alloys. Sulphur, phosphorus, and carbon readily unite with metals. Hydrogen is likewise capable of combining with many combustible substances. It is worthy of being examined whether hydrogen in its concrete state, uncombined with caloric, be susceptible of combination with sulphur, phosphorus, and the metals. There is nothing that we know of which, *a priori*, should render these suppositions impossible; for combustible bodies being in general susceptible of combination with each other, there is no evident reason for hydrogen being an exception to the rule. However, no direct experiment yet establishes either the possibility or impossibility of the union. Iron and zinc are the most likely of all metals for entering into combination with hydrogen; but, as these have the property of decomposing water, and as it is very difficult to get them entirely free from moisture in chemical experiments, it is hardly possible to determine whether the small portions of hydrogen gas obtained in certain experiments with these metals were previously combined

with the metal in the state of solid, or if they were produced by the decomposition of a minute quantity of water. The more care we take to prevent the presence of water in these experiments, the less is the quantity of hydrogen produced; and when very accurate precautions are taken, even that quantity becomes insensible.

The hydrides of the non-metals are usually, not always, more stable than the hydrides of the metals. Water can be regarded as an oxygen hydride, as well as a hydrogen oxide. Hydrogen gas reacts directly with fluorine, and this at temperatures as low as —210°, when the fluorine is liquid, or even at still lower temperatures where the fluorine is solid, and the hydrogen liquid.[4] The product of the reaction is hydrogen fluoride, HF; chlorine and bromine unite with hydrogen in light but not in darkness, forming in the one case hydrogen chloride, HCl, and in the other, hydrogen bromide, HBr. Iodine commences to unite with hydrogen at about 200° forming hydrogen iodide, HI. Aqueous solutions of the hydrides of fluorine, chlorine, bromine, and iodine are well-known acids—respectively called hydrofluoric, hydrochloric, hydrobromic, and hydriodic acid. Sulphur or selenium reacts with hydrogen at about 250°, and tellurium at 400°, forming respectively hydrogen sulphide, H_2S, hydrogen selenide, H_2Se, and hydrogen telluride, H_2Te. Hydrogen does not unite with nitrogen by direct heating, but it does so when stimulated by electric sparks or the silent electrical discharge—ammonia gas, NH_3, is the product of the action. Ammonia, NH_3, is a nitrogen trihydride; it is a well-known base. Similar compounds of phosphorus—phosphine, PH_3—arsenic—arsine, AsH_3—and antimony—stibine, SbH_3—also have basic properties; they are obtained indirectly, since direct union, if it occurs at all, is so insignificant when these elements are heated together that it is not at all certain if combination has occurred at all. Carbon and hydrogen do not react at ordinary temperatures. When an electric arc is formed between carbon electrodes in an atmosphere of hydrogen, the two elements unite forming acetylene, C_2H_2, and traces of other hydrocarbons—*e.g.* methane, CH_4. Carbon begins to react with hydrogen, forming methane CH_4, at about 1200°. Carbon forms an extensive series of hydrides usually called hydrocarbons—*e.g.* methane, CH_4; ethylene, C_2H_4; acetylene, C_2H_2; napthalene, $C_{10}H_8$; anthracene, $C_{14}H_{10}$; etc. The direct formation of the silicon or boron hydrides by heating the two elements together has not been satisfactorily demonstrated. Lithium metal burns in hydrogen gas forming lithium hydride, LiH. The alkali and alkaline earth metals unite directly with hydrogen when heated over 300° to form hydrides—*e.g.* potassium and sodium hydrides—KH and NaH respectively; calcium hydride, CaH_2, is the active agent in hydrolith. The hydrides of neodymium, praseodymium, cerium, yttrium, samarium, thorium, lanthanum, iron, cuprous and cupric copper, and silver have also been reported —the last three are said to have been formed by the reducing action of hypophosphorous acid on solutions of the salts of the respective elements. The alleged compounds are probably of the nature of the so-called palladium-hydrogen alloy—with occluded hydrogen.

The different products of the action of hydrogen on the metals may be arranged in three classes: (1) Compounds of the non-metals and metalloids—*e.g.* stibine, SbH_3—in which hydrogen seems to play the *rôle* of a positive univalent element, while the other element behaves as a negative or non-metallic element. As a rule, these compounds are gaseous at ordinary temperatures and pressures, or are very volatile. (2) Compounds of the alkali and alkaline earth metals. They are transparent and crystalline; volatile without decomposition in an atmosphere of hydrogen at comparatively low temperatures. They are probably hydrides proper, being related to the chlorides and nitrides in that the hydrogen plays the *rôle* of a non-metallic univalent element. (3) Unlike the two preceding types, these products are metallic, and form solid phases whose composition varies with external conditions. The typical example is the palladium-hydrogen alloy.

D. P. Smith[5] has shown that if A. Werner's periodic arrangement of the elements be employed, the metals which form the compounds of the first class are confined at the extreme right; and in Table III they are marked off with heavy lines. The compounds of the second class are confined to a group on the extreme left. The central part of the table is occupied by (i) metals whose relation is unknown; (ii) metals which occlude appreciable amounts of hydrogen represented by symbols in clarendon type; and (iii) metals which do not occlude anything but a relatively small amount of hydrogen—represented by symbols in brackets. The dot attached to the symbol means that the available evidence is conflicting or doubtful. The occluding elements thus appear to form a central group with subgroups on the left and right.

TABLE III.—A. WERNER'S PERIODIC TABLE MODIFIED TO SHOW THE RELATION OF THE ELEMENTS TO HYDROGEN.

H																		He
Li												(Be).	B	C	N	O	F	Ne
Na												(Mg).	(Al)	Si	P	S	Cl	A
K	**Ca**		**Sc**	**Ti**	**V**	**Cr.**	**Mn.**	**Fe**	**Co**	**Ni**	**Cu**	(Zn)	Ga	Ge	As	Se	Br	Kr
Rb	**Sr**		(Y).	(Zr).	**Nb**	.(Mo)	—	Ru	(Rh)	**Pd**	(Ag)	(Cd)	In	Sn	Sb	Te	I	X.
Cs	**Ba**	**Rare earth metals**	—	—	**Ta**	(W)	—	(Os)	(Ir).	**Pt**	(Au)	(Hg)	(Tl)	.(Pb)	(Bi)	—	—	—
—	**Ra**	**Th U**	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

The action of hydrogen on oxides and salt solutions.—Hydrogen gas reduces a great many metal oxides forming the metal and water: $MO+H_2=H_2O+M$. The oxides of silver and palladium are reduced by hydrogen gas in the cold. F. Wöhler[6] found black palladious oxide to be reduced by hydrogen with incandescence. The oxides of copper, lead, cadmium, tin, iron, cobalt, nickel, antimony, etc., must be heated before reduction occurs. If the mixture of hydrogen and metal oxide were confined in a closed vessel, the reaction would come to a standstill, but when the oxide is heated in a stream of hydrogen gas, the water vapour is whisked away from the seat of the reaction before it has time to set up the back reaction. The reduction of cupric oxide, CuO, to the extent of 1·7 per cent. can be detected after 15 minutes' exposure to a stream of hydrogen between 87° and 90°; 7 per cent., at 100°; and the reduction is complete in 15 minutes at 150°. The results differ with the physical condition of the oxide. Thus, according to F. Glaser, yellow mercuric oxide shows signs of reduction at 75°, and the red oxide at 140°. The reduction of ferric oxide was similarly detected after 15 minutes' exposure at 220°; magnetic oxide at 290°, and ferrous oxide at 305°. The reduction of manganese dioxide could be detected at about 145°, pyrolusite at about 190°; manganoso-manganic oxide, Mn_3O_4, at about 255°; and with manganous oxide no action could be detected at 600°–1300°. The temperatures at which a reduction can be detected with lead dioxide is 140°; lead monoxide, 190°–195°; cobalt sesquioxide, 110°; cobalt monoxide, 165°; nickel sesquioxide, 70°; and nickel monoxide, 225°. In view of the relatively easy reduction of, say, lead dioxide, PbO_2, at 140°, and the more difficult reduction of the monoxide, PbO, at 190°, it is highly probable that the higher oxide is first reduced to the lower oxide, and a higher temperature is then needed for the subsequent reduction of the monoxide to metal. This, for example, is the case with

$$MnO_2 \xrightarrow[145^\circ]{} Mn_3O_4 \xrightarrow[255^\circ]{} MnO \xrightarrow[1300^\circ]{} Mn\text{ ; and } Fe_2O_3 \xrightarrow[220^\circ]{} Fe_3O_4 \xrightarrow[290^\circ]{} FeO \xrightarrow[305^\circ]{} Fe$$

The oxide to be reduced may be placed in a porcelain boat which is heated in a tube through which a current of hydrogen is passing; or it may be heated in a crucible fitted with a perforated lid and tube through which a slow current of hydrogen passes. This form of crucible—called a *Rose's crucible*—is used in analytical work. For example, in certain analytical processes, cobalt is precipitated as hydroxide, and after drying, is ignited in a Rose's crucible with a stream of hydrogen, and finally weighed as metal.

According to M. Berthelot, the displacement of the oxygen from oxides, sulphur from sulphides, etc., is readily effected when the reaction generates heat, but not if the reaction absorbs heat. The greater the amount of heat developed, the more readily will the reaction occur. Contrast the heat developed during the formation of the three oxides: silver oxide, 7 Cals.; lead oxide, 51 Cals.; and zinc oxide, 85·4 Cals. The heat developed during the formation of steam is nearly 58 Cals. Hence, with silver oxide, there will be an evolution of 51 Cals. during the reduction to silver; similarly, with lead oxide there will be an evolution of 7 Cals.; but with zinc oxide, on the contrary, there is no energy to spare—rather is there a deficiency of 58—85·4 = —27·4 Cals. This is supposed to explain how silver oxide can be reduced at ordinary temperatures by hydrogen, while zinc oxide requires a high temperature:

	Silver oxide, Ag_2O.	Copper oxide, CuO.	Lead oxide, PbO.	Iron oxide, FeO.	Zinc oxide, ZnO.
Heat of reduction .	+51	+21	+7	+8·4	−27·4
Reduction begins at .	0°	90°	190°	305°	—

The rule is not rigidly exact; for one thing it takes no account of the variation in the thermal value of the reaction with temperature. According to F. Glaser, cadmium oxide shows signs of reduction at 282°, and zinc oxide at 454°.

Many metal chlorides and other salts, etc., are also reduced by hydrogen. Thus, iron, silver, and palladium chlorides are readily reduced by hydrogen gas forming hydrogen chloride and the metal; antimony sulphide is reduced to antimony; etc. According to C. Brunner, when hydrogen is passed through solutions of salts of platinum, or palladium, the metal is slowly precipitated; with silver salts, the reaction is far from complete since but a small fraction of the total silver is precipitated; iridium salts are scarcely affected; and gold and mercury salts are not reduced. B. Renault (1873) and H. Pellet (1873) claimed that silver salts are not reduced by thoroughly purified hydrogen and that the alleged reduction is a secondary effect due to the presence of arsine, silane, or other impurities; but J. W. Russell, N. N. Beketoff, and A. R. Leeds showed that reduction does take place with the pure gas. If the temperature or the pressure be augmented, the reaction may be completed. Thus, at the temperature of the water-bath, platinum, palladium, rhodium, and iridium are completely precipitated; and at 200 atm. pressure, silver is completely precipitated. E. Schobig says the reduction also occurs in darkness. Similar remarks apply to solutions of salts of nickel, cobalt, lead, bismuth, etc. The deposition of nickel is complete at 200° and 180 atm. pressure. E. Reichardt investigated the colorations produced by hydrogen on paper treated with silver nitrate; J. B. Senderens, the influence of hydrogen on hot solutions of silver nitrate; J. W. Russell, the precipitation of platinum, palladium, and gold from solutions of their salts, the reduction of cupric nitrate to nitrite, and the formation of a basic salt with mercurous nitrate; and F. C. Phillips, the influence of hydrogen on solutions of platinum, and palladium chlorides. N. N. Beketoff, J. Löwenthal, and W. Ipatjeff have studied the precipitation of silver, mercury, copper, zinc, cadmium, lead, etc. $\frac{1}{10}N$-solutions of silver and mercury salts give the metals at room temperatures and 200 atm. pressure; copper sulphate gives no metal at 600 atm.; $\frac{1}{10}N$-copper nitrate gives copper at 200° and 600 atm. Nickel salts behave similarly. Cobalt, lead, iron, and bismuth salts give the metals only at high temperatures and pressures.

Hydrogen gas is not oxidized by (*i.e.* it does not reduce) solutions of ferric chloride, potassium ferricyanide, nitric acid (specific gravity 1·42), chromic acid, or aqua regia. R. Bunsen, however, stated that in darkness ferric chloride is reduced by hydrogen to ferrous chloride. J. Milbauer studied the oxidation of hydrogen by sulphuric acid, $H_2SO_4+H_2=2H_2O+SO_2$, under the action of different catalytic agents at different temperatures. With pure hydrogen, there is no appreciable effect at ordinary temperatures, but the action is quite marked at 140°. Potassium permanganate is reported [7] to be gradually reduced in acid, neutral, or alkaline solutions at ordinary temperatures. A. C. Vournasos found that the nascent hydrogen liberated by heating dry sodium formate reacts with several elements which do not combine directly with free hydrogen. For example, phosphine is obtained when phosphorus vapour is passed over sodium formate melted at 200°; with a mixture of phosphorus and four times its weight of sodium formate, at 400°; and with a mixture of sodium formate and neutral sodium phosphite, or anhydrous disodium phosphate. Arsine is likewise obtained from sodium arsenite; stibine from sodium antimonide; hydrogen sulphide from sulphur, from sodium sulphide, or from mercury, lead, or tin sulphide; nitrides give ammonia; cyanides give hydrogen cyanide; alkali carbides give acetylene; and silicon chloride or sulphide give silicon hydride.

Hydrogen is a far more vigorous reducing agent if it acts in the presence of finely-divided metals—nickel, platinum, etc.—than when alone. Colloidal platinum or palladium is more effective than even the finely-divided platinum or palladium black. A solution of ferric chloride in the presence of platinum is reduced by hydrogen gas. There is a continuous catalytic action of the platinum on the gas and the layer of solution adhering to the metal. F. Lehmann found that osmium dioxide acts as a catalytic agent on the reduction of oleic acid and liquid oils by hydrogen. The finely-divided metals alone reduce neutral solutions of potassium permanganate, and accordingly decolorize dilute solutions, and the solution at the same time becomes alkaline, owing probably to the formation of potassium hydroxide and a brown manganic oxide—$Mn(OH)_4$, or possibly $MnO(OH)_2$—in symbols: $2KMnO_4+3H_2+2H_2O\rightarrow2KOH+2Mn(OH)_4$. Finely-divided gold, platinum, silver, arsenic, antimony, tungsten, and all the common metals reduce dilute neutral solutions of permanganate. Mercury also reduces permanganate, and D. Borar (1911) represents the reaction by the equation: $2KMnO_4+3Hg+H_2O\rightarrow2KOH+2MnO_2+3HgO$. Whatever be the mechanism of the reaction, the observed fact is that hydrogen can do its work much more quickly in the presence of platinum black; or, if the alternative statement be preferred, that the finely-divided metal can do its work more quickly in the presence of hydrogen. The point is illustrated by A. Smith's lecture experiment:

> Three test tubes are filled with dilute acidified potassium permanganate solution. Zinc dust added to the one generates hydrogen and causes decolorization; a little platinum black is added to the second, and hydrogen gas is led through this and the third solution. The contact action of the platinum enables the hydrogen quickly to reduce the permanganate, while the third portion remains unaltered.

F. Kuhlmann showed that the presence of certain metals can also induce a reaction between nitric oxide and hydrogen with the formation of ammonia; [8] and P. Sabatier and J. B. Senderens have studied the reaction between hydrogen and many organic compounds—thus, carbon monoxide is transformed into methane; ethylene or acetylene is also hydrogenized to methane; aldehyde or ketone to alcohol; benzene to hydrobenzene; etc.

In 1839, T. de Saussure [9] observed that various organic substances (peas, corn, humus) in the act of decomposition may excite the combination of hydrogen and oxygen, and that mixtures of these gases "behave with fermenting substances the same as with platinum." Several micro-organisms are also reported by A. J. Nabokich and F. A. Lebedeff, N. Bronislaff, J. Nikitinsky, and B. Niklewsky to possess the property of oxidizing hydrogen.

The nascent state—status nascens.—Hydrogen is not particularly active, chemically, at ordinary temperatures, but when the gas is exposed to an elevated temperature, or to an electrical discharge, the bonds which hold the atoms together appear to be relaxed, and hydrogen is then a potent agent, for its reactivity is great. The hydrogen which is generated by many exothermal reactions, at the moment of its birth, *in statu nascendi*, appears to be in a specially active state, for it can inaugurate many reactions which gaseous hydrogen cannot invoke. For instance, hydrogen gas can be passed into an acidified solution of ferric chloride or into water in which silver chloride is suspended without producing any appreciable change, but if metallic zinc be placed in the acidified solution, the brisk evolution of hydrogen is soon attended by the reduction of the ferric to ferrous chloride in the one case, and of the silver chloride to metallic silver in the other. Hydrogenized palladium or platinum[10] can also do chemical work which ordinary hydrogen cannot do, for instance, it can reduce a solution of ferric to ferrous chloride as illustrated by the symbols: $FeCl_3+H_{palladium}=FeCl_2+HCl$; it can reduce solutions of chlorates to chlorides; nitrates to nitrites and ammonia; mercuric to mercurous chloride; ferricyanides to ferrocyanides; sulphurous acid to sulphur and hydrogen sulphide; indigo-blue to indigo-white; nitrobenzene, $C_6H_5NO_2$, to aniline, $C_6H_5NH_2$, and it can unite with chlorine, iodine, and oxygen in the dark at ordinary temperatures. Charcoal saturated with hydrogen can also reduce chlorates to chlorides, ferricyanides to ferrocyanides, but not nitrates to nitrites. The main sources of nascent hydrogen are the amalgams of sodium, magnesium, and aluminium; the copper-zinc couple with water; or the metals zinc, tin, and iron with dilute acids, or, maybe, with alkaline solutions. Hydrogen iodide in a sealed tube at 150°–275° gives nascent hydrogen which is particularly active on account of the elevated temperature.[11] According to M. Berthelot, it reduces organic compounds to the hydrocarbon stage in which the molecule contains the maximum amount of hydrogen consistent with the quadrivalency of carbon, *e.g.* ethyl iodide and ethyl alcohol form ethane; glycerol forms propane; etc.

It has been suggested, without proof, that the hydrogen in palladium is in the atomic condition, for atoms are supposed to be more chemically active than molecules because some preliminary work has to be done in order to split the molecules into atoms before the reaction can occur, whereas atoms are ready to react immediately. This hypothesis was suggested by A. Laurent in 1846. He ascribed the greater activity of the elements in their nascent condition to their atomic condition. He reasoned that in the molecules (HH) and (BrBr) the affinity of bromine for bromine and of hydrogen for hydrogen is sufficient to prevent the one combining with the other, whereas if atomic hydrogen be in contact with atomic bromine combination sets in without the need for a preliminary rupture of the molecules of the two elements. Consequently it was inferred that the atoms of hydrogen in their nascent state do the work of reduction before they have spent part of their energy in grouping themselves into molecules. P. A. Favre and J. T. Silbermann (1846) adduced physical evidence in favour of A. Laurent's theory of the nascent state, and showed that carbon burning in an atmosphere of nitrous oxide, N_2O, develops considerably more heat than when it burns in oxygen because the energy required to decompose the molecules of ordinary oxygen is greater than the energy required to decompose the molecules of nitrous oxide. G. Bodländer also explains the greater activity of the hydrogen occluded in metals as due to its being there present in the atomic condition.

D. Tommasi (1898)[12] has emphasized the fact that this explanation does not make clear why nascent hydrogen from zinc and sulphuric acid is able to reduce chlorates or bromates to chlorides or bromides respectively, while hydrogen from sodium amalgam will not do so; nor does it explain why zinc and hydrochloric acid will reduce salts of vanadium pentoxide, V_2O_5, to the dioxide, V_2O_2, while magnesium and hydrochloric acid furnishes the trioxide, V_2O_3, under similar conditions. Nitrobenzene, $C_6H_5NO_2$, can be reduced to the base aniline, $C_6H_5NH_2$, in acidic but not in alkaline solutions—say by sodium amalgam and water. The *base* hydroxylamine is formed by the reduction of nitric acid in *acidic* solutions, and hyponitrous *acid* by reduction in *alkaline* solutions. It might be expected that if the work of reduction is really performed by nascent hydrogen, this agent should possess the same properties from whatever source it is derived; whereas the fact is that **the reducing power of nascent hydrogen varies according to the nature of the chemical reaction which gives it birth.** Hence, the greater activity of nascent hydrogen is probably caused by some influence other than the supposed atomic condition of the element *in statu nascendi*.

M. Berthelot considers that the disengagement of hydrogen in these reactions is but the result of a secondary reaction, and that the main reaction is the formation of a complex with the substance to be reduced. He calls these complexes *les systèmes reducteurs*. In reducing potassium chlorate by zinc and sulphuric acid, the system $Zn : H_2SO_4 : KClO_3$ with some water may be first formed, and this passes into the system $ZnSO_4 : H_2 : KClO_3$ or $ZnSO_4 : KCl : H_2O$, or into a system consisting of all these products. There are many reactions which are attributed to *l'hydrogène naissant*—*e.g.* reductions with sulphurous acid, ferrous hydrates, ammonium hydrosulphide, etc.—in which hydrogen is never evolved, and in which the reduction may be performed in *les systèmes reducteurs*. In the case of zinc and ferric chloride it might be then argued that the effects attributed to *l'hydrogène naissant* are really produced by the direct action of the metal; in symbols: $Zn+2FeCl_3=ZnCl_2+2FeCl_2$; and not through the consecutive reactions; $Zn+2H_2O=Zn(OH)_2+2H$; and $H+FeCl_3=HCl+FeCl_2$.

The energy which is set free during a reaction under ordinary conditions appears as heat, and this may make the gas at the seat of the reaction more reactive; or, before the energy has degraded to heat, it may be available for doing chemical work so that the difference between the so-called nascent and ordinary hydrogen lies in the greater availability of the energy of the former. D. Tommasi argues that the reducing properties of nascent hydrogen depend on the nature of the reaction from which it is derived, and that the greater affinity of hydrogen *in statu nascendi* arises from the momentary association of hydrogen with n calories of energy liberated by the reaction. Accordingly the term "nascent hydrogen" is synonymous with $H+n$ cals. The difference in the reducing properties of hydrogen produced by different reactions is determined by the amount of heat liberated in the reaction. For example:

$H_2SO_4Aq.+Cd=21{\cdot}5$ Cals.
$2HClAq.+Zn=34{\cdot}2$,,
$2HBrAq.+Zn=34{\cdot}2$,,
$H_2SO_4Aq.+Zn=37{\cdot}7$ Cals.
$H_2SO_4Aq.+Mg=112{\cdot}0$,,
$2Na$ (amalgam)$+Aq.=180{\cdot}0$,,

The greater the thermal value of the reaction, the greater is the activity of the nascent hydrogen. In some cases, the reduction is not due to $H+n$ cals., but to the metal $M+n$ cals.; for example, in the reduction of potassium chlorate by zinc and dilute sulphuric acid, the zinc unites with the oxygen of the chlorate, forming zinc oxide: $KClO_3+3Zn=KCl+3ZnO$. If a chlorate, dissolved in a dilute solution of sulphuric acid, be electrolyzed with platinum electrodes, perchloric acid is formed at the anode, and with a zinc anode, potassium chloride, but no perchlorate appears at the electrode.

When hydrogen is developed on the surface of a metal immersed in a suitable solvent, W. Ostwald[13] has pointed out that the gas in the smallest—probably submicroscopic—bubbles must be under a great pressure owing to the surface tension of the water. He calculates this pressure to be near 15,000 atm. for gas bubbles of approximately molecular dimensions, 10^{-7} cm. diameter. It has been suggested that the gas under this enormous pressure is more chemically active than when it is under ordinary atmospheric pressures.

The decomposition voltage of sulphuric acid with a platinized platinum electrode has a definite and specific value which is different from the value obtained when electrodes with other metals—*e.g.* smooth platinum, zinc, lead, etc.—are used and the difference between the voltage required to liberate hydrogen at the surface of a metal and at the surface of a platinized platinum electrode under similar conditions has been styled the overvoltage. The point where the evolution of gas begins may be taken as the point where bubbles of hydrogen begin to form, or the point where a break appears in the voltage curve. M. le Blanc (1890) takes the **overvoltage** as the excess back electromotive force generated at the given electrode over that at a platinum electrode when the charging circuit is rapidly closed and as rapidly broken making a new circuit through a commutator. The overvoltage depends on the nature of the metal, current density, temperature, etc. W. A. Caspari[14] found that with platinized platinum the overvoltage amounts to 0·005 volt; with smooth platinum, 0·08 volt; meaning that the formation of gas bubbles could be first observed on the electrode in *N*-sulphuric acid, at these voltages. With iron, sodium hydroxide was used. The overvoltages with some other metals are:

Au.	Fe.	Ag.	Ni.	Cu.	Pd.	Cd.	Sn.	Pb.	Zn.	Hg.
0·02	0·08	0·15	0·21	0·23	0·46	0·48	0·53	0·64	0·70	0·78 volt.

A. Coehn and K. Dannelberg, E. Müller, and A. Thiel and E. Breuning, obtained the same results with rather smaller voltages, but the order was the same as W. A. Caspari's. These numbers may be taken to represent the potential at which the hydrogen is liberated at the different electrodes. There is a similar overvoltage at the oxygen anode—with platinized platinum, 0·39 volt; polished platinum, 0·62; palladium, 0·39; and gold, 0·59 volt. G. Carrara found the overvoltages quite different in alcoholic and aqueous solutions. If there were no overvoltage, water could be decomposed by a current of 1·22 to 1·23 volts, but the voltage actually required is 1·23 plus the overvoltages at the two electrodes.

When hydrogen separates on a metal electrode, its chemical energy is augmented by the overvoltage beyond what it would possess if it were in the gaseous state under ordinary atmospheric pressure. The hydrogen from, say, a mercury or lead cathode is evolved at a higher potential and therefore possesses greater energy than from a platinum cathode. Lead or mercury thus possesses, in a high degree, the property of rendering difficult the escape of hydrogen from the cathode, so that many electrolytic reductions are possible with these metals—*e.g.* of caffein or uric acid—which are not produced by cathodes of other metals. While the reducing power and hydrogen overvoltage generally run parallel, E. Müller, J. Tafel and K. Neumann, C. F. Böhringer, and A. Chilesotti have shown that it does not necessarily follow that all reductions take place more readily at the cathode with the higher overvoltage. For instance, nitrites are more readily reduced than nitrates at cathodes of zinc, iron, lead, platinum, or gold, while nitrates are more readily reduced at cathodes of spongy copper or silver, and at a mercury cathode in hot solutions. Caffein is more readily reduced at a mercury than at a lead cathode, and the converse obtains in the reduction of succinimide. Obviously, therefore, factors other than hydrogen alone are involved, and these may mask the relation between the hydrogen overvoltage and high reducing power. For example, one substance may be more readily absorbed by one cathode than another, so that the effective concentrations at the cathode are different; the electrode may act as a catalytic agent on the reaction, or apparently inert substances in the solution may modify the overvoltage.

J. Tafel has shown that traces of certain metals exercise what may be called a poisonous influence on other metals in reducing the overvoltage or *super*-voltage of the hydrogen and so decreasing the effectiveness of the lead and mercury cathodes; thus, 0·004 mgrm. of platinum per 10 sq. cm. of lead cathode surface will prevent many electrolytic reductions possible in its absence. Silver, tin, copper, mercury, zinc, and iron are also enemies of electro-reduction. J. Tafel and B. Emmert found that the toxic effect cannot be attributed to the formation of a skin of the metal on the surface of the cathode.

Various hypotheses have been devised to explain what is taking place when an overvoltage occurs. F. Haber suggested that the formation of films of gas on the electrodes increases the resistance; H. G. Möller considered the overvoltage to represent the energy required to give a film of gas thick enough to generate bubbles; F. Föster suggested an oxide is formed at the anode, and a hydride or solid solution of a hydride at the cathode; while W. Nernst and J. Tafel believe that the effect is due to the slowness with which the electrode gets into equilibrium with the surrounding conditions, for metals with a slight tendency to occlude gases require energy to force the gas into the electrode and thus produce high voltages. J. Tafel, E. Müller, G. N. Lewis and R. E. Jackson and others have suggested that the discharge of the $H^{\cdot}$-ions at the cathode, $2H^{\cdot}=H_2$. takes place in two stages, $H^{\cdot}=H$ and $2H=H_2$, so that monatomic hydrogen acts as an intermediate compound, and while the reaction $H^{\cdot}=H$ takes place quickly, the reaction $2H=H_2$ which causes the polarization of the electrode is slow. The potential of the hydrogen electrode thus depends upon the concentration of monatomic hydrogen. C. W. Bennett and J. G. Thompson, and W. D. Bancroft also favour an hypothesis based on these reactions. D. Reichinstein[15] attributes the poisoning of the electrodes by the presence of certain impurities to the lowering of the overvoltage by increasing the rate of conversion of the monatomic to ordinary hydrogen. Similarly also, the effect of certain impurities—iron, cobalt, nickel, etc.—on the yield of caustic soda by the amalgam process, observed by J. W. Walker and C. S. Paterson, is attributed to the decrease in the overvoltage by the impurities acting catalytically in increasing the speed of the conversion of monatomic into ordinary hydrogen. Similar explanations have been applied to O. Aschan's observation that impurities in the sodium amalgam diminished the yield in the hydrogenation of benzoic acid; to E. Bamberger's observation of the great differences in the reducing power of different samples of zinc dust; and to G. Fernekes' observation that alcohol and many other organic substances augmented the speed of the reaction between sodium amalgam and water. The so-called nascent hydrogen is thus assumed to consist of electrically neutral monatomic hydrogen, and the difference in the nascent hydrogen derived from different sources is due to the difference in the effective concentration of the monatomic hydrogen, which in turn is determined by the rate of conversion of the monatomic into ordinary hydrogen.

Hydrogen is not a poisonous gas.[16] When small animals are placed in hydrogen, they are "drowned," suffocated for want of oxygen. The injurious action of hydrogen is therefore negative; the gas acts merely by preventing access of oxygen to the lungs. According to C. W. Scheele, F. Fontana, and H. Davy, the pure gas excites disagreeable sensations and loss of muscular power, but when mixed with air, it may be breathed a longer time. The violent symptoms described by G. Cardone as attending the respiration by hydrogen must have arisen from impurities in the gas. When hydrogen is inhaled, the voice becomes shrill—approaching falsetto. The pitch of organ pipes and other wind instruments is raised if a blast of hydrogen be used in place of air. According to F. Hatton, hydrogen has scarcely any appreciable influence on bacteria, but M. Berghaus says their power of multiplying becomes smaller in an atmosphere of hydrogen gas.

The detection and determination of hydrogen.—The determination of hydrogen in the presence of methane and other hydrocarbons is based on the contraction which occurs after complete combustion with oxygen by explosion in a eudiometer; by fractional combustion with air in contact with palladium-asbestos—methane does not oxidize at 100°, hydrogen does; by absorption by spongy palladium; by the reduction of or absorption in palladium chloride—dry or in solution—after the removal of olefine gases and carbon monoxide because these gases also reduce palladious chloride. A nearly neutral one per cent. solution of palladious chloride completely absorbs small quantities of hydrogen in a few hours; the absorption is retarded by using strongly acid solutions. According to F. C. Phillips,[17] a one per cent. solution of palladious chloride is reduced in the cold by hydrogen gas. $\frac{1}{2000}$th part of hydrogen can be detected in a gas by this reaction.

The presence of hydrogen gas can be established by spectrum analysis. In the absence of other hydrogen compounds, the gas can be passed over red-hot copper oxide whereby water is formed. A. Gautier found that one part of hydrogen in 5000 of air is completely oxidized when passed over a layer of cupric oxide about 70 cm. long at the rate of 2 or 3 litres per hour; with a tube 30 cm. long, about 70 per cent. of the hydrogen is oxidized. This reaction enables the amount of hydrogen in dry air to be determined. C. Paal and C. Amberger used a colloidal palladium solution for the absorption of hydrogen; C. Paal and W. Hartmann used a colloidal solution of palladium containing sodium picrate. A. Lidoff described a method for the volumetric determination of hydrogen by combustion with magnesium powder; T. Zerewitinoff used magnesium-methyl iodide. A. Jacquelin proposed to absorb hydrogen from a mixture of methane, CH_4, and ethylene, C_2H_4, by sodium or potassium at about 300°. C. Zengelis found that palladium or platinum absorbs hydrogen and the product colours blue a solution made by dissolving a gram of molybdenum trioxide in dilute sodium hydroxide, acidifying the solution with hydrochloric acid, and diluting the mixture to 200 c.c.

The atomic weight and valency of hydrogen.—Hydrogen was for a long time the standard unit for the atomic weights; but now oxygen =16 is the generally accepted standard. Reports of the atomic weight of hydrogen, determined through the ratio O : H lie between 16 : 0·99937 and 16 : 1·0087; and the best representative value for the atomic weight of hydrogen is taken to be **1·008.** The molecular weight of the gas is then 2·016—the molecule being therefore diatomic, H_2. According to W. Vaubel,[18] the molecular weight of hydrogen in the liquid state is nearly 5·2. The valency of hydrogen is the unit for evaluating the valencies of the other elements. R. de Forcrand [19] has favoured the assumption that hydrogen is best regarded as a bivalent element; this would entail doubling the valency of all the other elements. The doubled scheme is said to offer some advantages in dealing with the constitution of the subhalides and suboxides. There is a difficulty already discussed, in assigning a place for hydrogen in the periodic table.

The quantities of some of the metals which are equivalent to a definite quantity of oxygen have been already determined, and the results agree with the quantities of the different metals found to be chemically equivalent to one gram of hydrogen. One gram of a given metal dissolving in a suitable acid will always displace the same amount of hydrogen whatever be the reacting liquid used—*e.g.* aluminium in sodium hydroxide, in sulphuric acid, or in hydrochloric acid; but the amounts furnished by different metals are different. **The weight of a metal required to displace one gram of hydrogen is called the hydrogen equivalent of the metal.** J. D. van der Plaats [20] determined the equivalent of zinc by measuring the volume of hydrogen evolved by the dissolution of a given weight of the metal in sulphuric acid, and found that 13·8758 grms. of zinc gave 2·3767 litres of hydrogen, so that if a litre of hydrogen weighs 0·89872 grm. under standard conditions, one gram of hydrogen is equivalent to 64·89 grms. of zinc. J. W. Mallet [21] also determined the hydrogen equivalent of aluminium by dissolving it in a solution of sodium hydroxide; and E. Kohn-Abrest, by dissolving it in hydrochloric acid. J. Torrey likewise determined the hydrogen equivalent of iron. As a mean of twenty-one determinations, J. Thomsen found the ratio H : Al=0·111902 ± 0·000015; and he also found the ratio O : Al =0·88787 ± 0·000018, from which it follows that O : H=7·9345 ± 0·0022.

The dissociation of the hydrogen molecule.—According to I. Langmuir (1912),[22] the electrical energy required to maintain a tungsten wire at a given temperature in hydrogen increases at an abnormal rate with temperature, so that while the theoretical value calculated from the heat losses by hot wires agrees with observations up to 1900° K., after that, there is a rapid increase until, at 3500° K., it is four times the calculated value. No secondary electrical effects could be detected. At small pressures, the heat losses are greater than at atmospheric pressures, presumably because of dissociation. This phenomenon is not observed with the other gases tried. When a tungsten wire is heated to 1300°–2500° in hydrogen under a pressure of 0·001 to 0·02 mm., the gas slowly disappears. Hydrogen is not absorbed by the wire to any great extent, but is deposited on the glass bulb, if the latter be cooled by liquid air. When the liquid air is removed and the wire cooled, the hydrogen is liberated. Langmuir explains the phenomenon on the assumption that hydrogen is dissociated into atoms by the hot wire, and that some atoms diffuse into the tube and are condensed in the same condition on the glass walls. The hypothesis that the **hydrogen is in the atomic condition** is used to explain the greater chemical activity of the gas, for, if phosphorus is present in the bulb, the two combine, forming phosphine (phosphorus hydride), a reaction which has not been observed with ordinary hydrogen under ordinary conditions; the hydrogen also reacts with oxygen at room temperatures; tungstic oxide, WO_3, and platinic oxide, PtO_2, are chemically reduced by the dissociated gas; copper oxide is reduced almost immediately to metallic copper; ferric oxide is reduced to a lower oxide; zinc oxide is not reduced excepting over long periods of time when the colour of the dry zinc oxide gradually turns grey, although silica, close beside it, remains quite white. T. Ismardi (1915) has shown that the degree of dissociation α of hydrogen into atoms is 0·557 at 3200° K. and 25 mm. pressure; and 0·5 at the same temperature and 50 mm. pressure. Similarly, at 3100°, the degree of dissociation is 0·255 at 100 mm. pressure, and 0·230 at 200 mm. pressure. The degree of dissociation α was calculated from the expression: $\log(\alpha^2-1)^{-1}=-Q/RT-\log T+\log p-2{\cdot}95$, where Q represents the heat of dissociation which is 64,000 cals., or $2H=H_2+64{,}000$ cals.; R is the gas constant; and p the pressure. Assuming the heat of the reaction at 2500° K. to be 64,000 cals., the free energy of the reaction $2H=H_2$ at $T°$ K. is given by G. N. Lewis and M. Randall as $F=61{,}000-3{\cdot}5T\log T+0{\cdot}00045T^2+20{\cdot}2T$. E. Briner estimates the heat of formation $2H=H_2$ at 2427° as 130 Cals., and the equilibrium constant as 0·10.

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§ 9. The Diffusion of Gases

Owing to the fact that air is fourteen times as heavy as an equal volume of hydrogen under the same physical conditions, if a jar of hydrogen be placed mouth upwards under a jar of air, mouth downwards, most of the hydrogen will flow upwards into the upper cylinder, and air will flow downwards into the lower cylinder. The action is analogous with what would occur if the lower cylinder contained a light oil and the upper cylinder water. The oil and water would change places. The two liquids can be left an indefinite time without mixing, for the two liquids—oil and water—are immiscible. Several of the earlier chemists used to argue that gases like those under consideration would behave like the liquids, but J. Priestley[1] noticed that this is not the case; and in 1805, J. Dalton's experiments demonstrated that two gases—hydrogen and air—when brought into contact, do not arrange themselves according to their specific gravities, but spontaneously diffuse, mutually and equally through each other, and spread throughout the two vessels so that a homogeneous mixture of air and hydrogen is obtained. This phenomenon is so marked, that it was once considered that the molecules of a gas mutually repelled one another owing to the presence of a "self-repulsive force." Gases are miscible in all proportions; had the two liquids been mutually soluble in one another in all proportions—say alcohol and water instead of oil and water—they also would diffuse one into the other so as to form a homogeneous solution of alcohol and water.

The process of diffusion in the case of liquids appears to be very much slower than with gases. The molecules of gases seem to lead a more or less independent existence. This is illustrated by the rapidity with which the molecules of, say, ammonia can travel from one end of a room to the other and affect the sense of smell. In liquids, however, the molecules are much less mobile. This can easily be proved by dropping a small grain of aniline dye into a tumbler of clear still water. The water will be uniformly coloured in a few weeks. The molecules of solid substances have practically lost their mobility—but not all. Carbon laid in contact with pure, hot, solid iron will diffuse into a mass of the metal; gold or platinum in contact with lead will diffuse into the lead.[2] J. Violle found that carbon will diffuse into the solid body of hot porcelain; and metallic silver will diffuse into hot glass, staining it yellow. According to C. E. van Orstrand and F. P. Dewey (1915), the coefficient of diffusion, of gold into solid lead at 197° is 0·0076; at 150°, 0·0043; and at 100°, 0·0002. The penetration of gold into lead at 197° can be detected at a depth of 2·5 cm. after 54 days; the penetration of the lead into gold at a depth of 0·2 mm.—but the methods of detecting lead in gold are not so sensitive as for gold in lead.

The transfer of gases in bulk from one vessel to another is an effect of gravitation, whereas diffusion is not an effect of gravitation. C. L. Berthollet (1809)[3] confirmed J. Dalton's observation that hydrogen is rather more penetrative and diffusive than any other gas tried. In 1829, T. Graham experimented on the interdiffusion or miscibility of gases with one another, and the subject was pursued further by J. Loschmidt (1870) and A. von Obermayer (1880). J. Loschmidt placed two tubes containing different gases one over the other, and, after opening a channel between them, determined the amounts of the different gases which had changed places after the lapse of a definite interval of time. The results were expressed in terms of what is called the **coefficient of diffusion,** k, which represents the quantity of gas travelling per second through a surface of one sq. cm., and along a distance one centimetre in length. Then, at 0°, the coefficient of diffusion, k_0, of hydrogen into air is $k_0=0{\cdot}64$; into steam, 0·69; into oxygen, 0·67; and into

	C_2H_6	C_2H_4	SO_2	N_2O	CO_2	CH_4
k_0 .	0·46	0·48	0·48	0·43	0·63	0·65

and likewise for carbon dioxide into

	N_2O	C_2H_4	CO	O_2	Air	H_2	CH_4
k_0 .	0·092	0·101	0·140	0·141	0·142	0·553	0·159

It is doubtful if the assumption that the coefficient of diffusion k is altogether independent of the relative proportions of the two gases, is quite valid.[4] It is assumed that the gases exert no chemical or physical attractive forces on one another. J. Loschmidt found that *the quotient obtained by dividing the coefficient of interdiffusion by the square root of the product of the molecular weights of the two interdiffusing gases is approximately constant*—1·8. This is illustrated in Table IV.

TABLE IV.—THE INTERDIFFUSION OF GASES.

Interdiffusion of gases of molecular weights M_1 and M_2.	Diffusion coefficient k.	$\frac{k}{\sqrt{M_1M_2}}$
Carbon dioxide into air	0·0512	1·825
Carbon dioxide into hydrogen	0·2001	1·877
Carbon dioxide into oxygen	0·0507	1·904
Carbon dioxide into carbon monoxide	0·0506	1·776
Carbon dioxide into methane	0·0571	1·514
Carbon dioxide into nitrous oxide	0·0354	1·557
Oxygen into hydrogen	0·2598	2·079
Sulphur dioxide into hydrogen	0·1728	1·955
Carbon monoxide into oxygen	0·0649	1·942
Carbon monoxide into hydrogen	0·2312	1·730

J. Loschmidt also found that the coefficient of diffusion k at a pressure p, and at absolute temperature T, is related with the diffusion coefficient k_0 at 273° K., and standard pressure, such that

$$k=k_0\left(\frac{T}{273}\right)^n\frac{760}{p};\quad\text{or }k=k_0(1+a\theta)^n\frac{760}{p}$$

where a denotes the coefficient of thermal expansion of the gas, and θ the temperature. J. Stefan and J. Loschmidt found that the index n is 2, but A. von

Obermayer found $n=2$ (nearly) applies only for binary mixtures of carbon dioxide with nitrous oxide, air, and oxygen; for other mixtures $n=1·5$ (nearly).

Long before J. Loschmidt, Thomas Graham[5] showed that the speed at which the molecules of a gas can diffuse or travel through thin porous membranes or septa—porous earthenware, plaster of Paris, etc.—into air or a vacuum is related to the specific gravity of the gas. For example, hydrogen diffuses nearly four times as fast as oxygen; the relative densities of oxygen and hydrogen are nearly as 1 : 16; and the relative rates of diffusion of the two gases are nearly as $\sqrt{16} : 1$; *i.e.* as 4 : 1. Hence follows **Graham's law of diffusion: the relative speeds of diffusion of gases are inversely proportional to the square roots of their relative densities.** Graham measured the speed of diffusion of gases through thin porous plates and found the numbers indicated in the last column of the subjoined table.

TABLE V.—SPEEDS OF DIFFUSION OF SOME GASES AND GRAHAM'S LAW.

Gas.	Relative density H = 1.	Speed of diffusion calculated from $\frac{1}{\sqrt{\text{Relative density}}}$	Observed speed of diffusion (Hydrogen = 1).
Hydrogen, H_2	1	1	1
Methane, CH_4	8	0·354	0·351
Ethylene, C_2H_4	14	0·267	0·266
Carbon monoxide, CO	14	0·267	0·278
Nitrogen, N_2	14	0·267	0·265
Oxygen, O_2	16	0·250	0·248
Hydrogen sulphide, H_2S	17	0·243	0·248
Nitrous oxide, N_2O	22	0·213	0·214
Carbon dioxide, CO_2	22	0·213	0·212
Sulphur dioxide, SO_2	32	0·177	0·177

The third column represents the theoretical numbers calculated on the assumption that the speeds of diffusion are inversely as the relative densities. Graham's numbers have been recalculated to H=1 instead of air=1, and whole number approximations for the relative densities have been introduced. The observed numbers for the speed of diffusion agree very closely with those obtained by calculation. There is an interesting application of the law:

To find the relative density of a gas by comparing its speed of diffusion with that of another gas of known density.—Let D_1 and D_2 represent the relative densities of two gases one of which, D_1, is known, the other, D_2, being unknown. Suppose that the relative speeds of diffusion of the two gases V_1 and V_2 are known. Then, it follows from Graham's law, $V_1\sqrt{D_1}=V_2\sqrt{D_2}$; or $V_1^2D_1=V_2^2D_2$. Given any three of these numbers, the fourth can be calculated by arithmetic.

EXAMPLES.—(1) The speeds of diffusion of carbon dioxide and of ozone were found by Soret (1868) to be as 0·29 (V_1) is to 0·271 (V_2). The relative density of carbon dioxide is 22 (D_1) when H=1. What is the relative density of ozone (D_2)? From the preceding relation, it follows that $\sqrt{D_2}=0·29\times\sqrt{22}\div0·271=0·29\times4·69\div0·271$; or $D_2=(5·02)^2=25$ nearly.

(2) A. Ladenberg (1898) found that ozonized air required 367·4 seconds to diffuse under conditions where pure oxygen required 430 seconds: what is the specific gravity of the ozonized air, assuming that the specific gravity of oxygen is unity? Ansr. 1·3698.

The slow mutual diffusion of gases makes them dissolve each other irresistibly so that there is no limit to the extensive expansion of the smallest bubble of gas which may be formed or liberated in air. It is this ceaseless interchange of gases which plays a part in preventing cities being speedily enveloped and stifled by their own noxious exhalations from the natural functions of their teeming population, and from the deadly vapours of their fires and furnaces. The ready diffusion of gas through the walls of buildings plays a part in ventilation. Most building materials are porous, and permit the passage of gases through them in both directions. The diffusion does not take place so readily when the walls are saturated with moisture —*e.g.* in new buildings, etc. The diffusion is illustrated by the following demonstration:

One leg of a U-tube is enlarged, as shown in Fig. 16, and the widened end fitted with a plug of plaster of Paris. The mercury of the other leg of the U-tube is connected with a battery and electric bell, and a wire fused in the other leg of the tube, so that when the liquid rises electric contact is made, and the bell will ring. If a beaker of hydrogen be placed over the plaster of Paris plug, hydrogen will rapidly diffuse into the enlargement, and create a pressure which depresses the mercury in the one leg, and raises it in the other so as to ring the bell. A device based on this principle has been suggested as an alarm indicator for the escape of coal gas in rooms, or fire-damp in coal mines. These gases, like hydrogen, diffuse through the walls of porous pots faster than the air can escape and produce an internal pressure. Conversely, if the enlarged bulb be bent downwards and a jar of carbon dioxide be lifted upwards so that the porous septum is bathed in this gas, air escapes from the interior faster than the heavier carbon dioxide can enter. This reduces the pressure in the interior, and causes a movement of the mercury in the opposite direction. Instead of using a plaster of Paris septum, porous pots fitted on to glass tubes can be employed, and the conditions can be so arranged that the pressure of the gas sprays a jet of liquid like a miniature fountain.

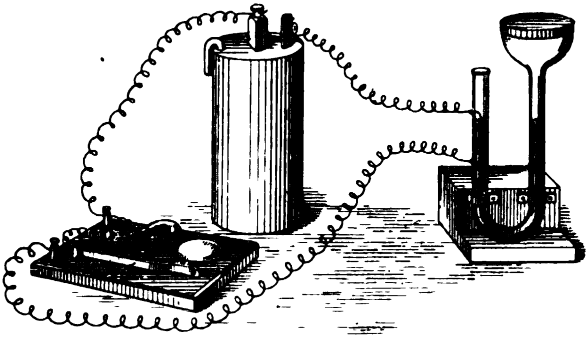

Fig. 16.—Diffusion Experiments.

In diffusing through porous walls, or through unglazed earthenware vessels, the gases actually travel through the pores of the material. The diffusion of gases through metals and indiarubber appears to follow a different procedure, for the gas probably dissolves in these substances, diffuses while in solution through the solid, and is liberated on the opposite side. The diffusion of gases through rubber is well illustrated by filling toy balloons of thin rubber with hydrogen gas; the balloons soon collapse. If the balloons be inflated with air, and then immersed in hydrogen gas, they swell out and burst. For similar reasons, a soap bubble blown with air and then made to float on carbon dioxide gas, will gradually sink in the gas owing to the diffusion of the heavy gas through the walls of the bubble.

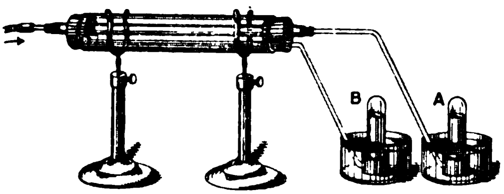

Fig. 17.—H. St. C. Deville's Experiment on Atmolysis.

The separation of a mixture of gases by diffusion.[6]—If a slow current of electrolytic gas, that is, the mixture of hydrogen and oxygen obtained by the electrolysis of water, be allowed to pass through the stem of a churchwarden clay pipe, or porous earthenware tube, and the gas issuing from the pipe be collected in a gas trough, it will no longer explode when brought in contact with a flame. On the contrary, it will rekindle a glowing chip of wood, showing that oxygen is present. In passing through the tube, hydrogen escapes by diffusion through its porous walls much more rapidly than the heavier oxygen. If the porous tube be surrounded by a glass tube, and fitted with a gas delivery tube, as shown in Fig. 17, the gas which collects in the receiver *A* will contain an excess of oxygen, and that in receiver *B* an excess of hydrogen. This phenomenon—the separation of one gas from another by diffusion—has been called, by T. Graham, **atmolysis**—ἀτμός, vapour; λύω, I loosen. If a current of steam be passed through a porous tube at a high temperature, and if the porous tube be surrounded by another tube of glazed impervious porcelain, the water vapour will be dissociated by the heat into hydrogen and oxygen; since the hydrogen diffuses much faster than the oxygen, hydrogen will pass from the inner tube into the annular space between the two tubes. The hydrogen may be collected in a suitable gas trough. Similarly, the residual oxygen can be collected from the gaseous steam passing along the inner tube. Of course, the hydrogen is contaminated with more or less oxygen, and the oxygen with more or less hydrogen. In 1906, A. Jouve and G. Gautier [7] proposed to separate carbon monoxide and hydrogen industrially by filtration through a porous partition.

Are the molecules of a gas all alike?—Experiments on atmolysis enable a conditional answer to be returned. If a gas like hydrogen or oxygen be filtered through a septum of porous earthenware, no difference can be detected in the properties of the gas on each side of the partition. If some of the molecules of, say, hydrogen have a greater density than the others, it should be possible to separate two kinds of hydrogen of different density. This cannot be done, and hence, it is inferred that within the limits of experimental observation, the molecules of hydrogen are all alike, for if there be a difference, it is too small to be detected. Similar remarks apply to oxygen and many other gases. W. Ramsay and J. N. Collie (1897) [8] showed that helium is probably a single substance because repeated diffusion did not alter its density; Lord Rayleigh and W. Ramsay (1895) showed that atmospheric nitrogen is probably a physical mixture of nitrogen with a heavier gas, because repeated diffusion altered its density; and F. W. Aston (1913) separated neon into two gases with densities 19·9 and 22·1, and hence inferred that neon is probably a mixture of two gases of different densities.

The effusion of gases.—T. Graham (1832) [9] found that the law of diffusion holds good for the passage of a gas through a very fine aperture in a metal plate. T. Graham called the phenomenon the effusion of gases to distinguish it from diffusion. The theory was indicated by D. Bernoulli [10] in 1738. The speed of effusion varies inversely as the square root of the density. If a gas of density D_1 flows out of the tube in the time t_1, then, according to the law of effusion: $D_1 : D_2 = t_1^2 : t_2^2$. In words, **the times required for the efflux of equal volumes of different gases, under like conditions of pressure, etc., are directly proportional to the square roots of the densities of the gases.** Thus T. Graham found (air unity):

TABLE VI.

Gas.	Square root of density.	Time of efflux.	
		Glass tube.	Perforated brass plate.
Hydrogen	0·263	0·277	0·276
Methane	0·745	0·756	0·753
Carbon monoxide	0·984	0·987	—
Ethylene	0·985	—	0·987
Nitrogen	0·986	0·984	0·986
Oxygen	1·051	1·053	1·053
Nitrous oxide	1·237	1·199	—
Carbon dioxide	—	1·218	1·203

The method for determining the specific gravity of coal gas based on this principle is considered one of the best. Thus, the time of effusion observed for gas was 2′25·1″ or 145·1 seconds, and for air, 3′40·8″ or 220·8 seconds. Hence, the specific gravity of the gas is $(145\cdot1/220\cdot8)^2=0\cdot432$. R. Bunsen (1857)[11] utilized this fact to determine the specific gravity of a gas when but a small quantity is available. In N. H. Schilling's effusion apparatus (1879) the gas is introduced into a glass tube, luted to a brass cover, *viâ* the cocks *b*, *c*, Fig. 18. This tube is placed in a cylinder filled with water and the temperature is indicated by the thermometer *T*. The perforated platinum plate is fixed at *b*. The time taken for the tube to sink from the level *P* to the level *O* on the cylinder is noted. The experiment is repeated with another gas of known density. A. Ladenberg (1898)[12] used this apparatus to determine the specific gravity of ozone. A. Debierne (1910) used Bunsen's effusion method for determining the density of the emanation from radium; and F. Emich (1903) modified the apparatus so that it could be used at high temperatures between 1400° and 2000°.

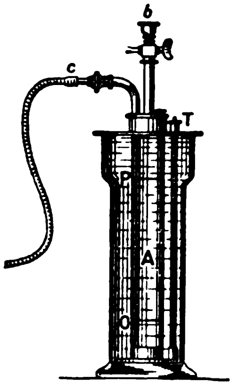

FIG. 18. — Schilling's Effusion Apparatus.

EXAMPLES.—(1) N. H. Schilling (1879) found that a given volume of air effused in 285 seconds while the same volume of coal gas effused in 209 seconds, hence the relative density of coal gas with respect to air unity is $(209)^2/(285)^2=0\cdot538$.

(2) A. Ladenberg (1898) found that a mixture containing 86·16 per cent. of ozone required 267·5 seconds under conditions where pure oxygen required 430 seconds. Hence, determine the specific gravity of ozone. From a previous example, it follows that the specific gravity of the ozonized oxygen is 1·3698, oxygen=1. The specific gravity of ozone is 1·456, if oxygen be unity; and 46·6, if oxygen O_2 be 32. Note that this does not establish the molecular weight by Avogadro's hypothesis, because, in determining the proportion of ozone in the mixture, by estimating the amount of iodine liberated by a given volume of the gas, it was assumed that the reaction proceeds as indicated in a preceding equation, which in turn assumes that the formula of ozone is O_3.

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CHAPTER VIII

OXYGEN

§ 1. History of the Discovery of Oxygen

A substance is discovered only when it has been shown to differ from all other known substances.—G. W. VON LEIBNIZ.

THE history of the discovery of oxygen is intimately connected with Lavoisier's discovery of the cause of combustion. C. W. Scheele's laboratory note-books, preserved in the Royal Academy of Science at Stockholm, are said to prove that he discovered oxygen some time before 1773. C. W. Scheele exposed alkaline liver of sulphur, moist iron filings, phosphorus, etc., to the action of air confined in a jar over water; and he also burnt phosphorus, hydrogen, and a candle in air confined under similar circumstances. By measuring the volume of water which entered the vessel at the end of the process, C. W. Scheele found what fraction of the original volume had disappeared. He concluded:

> Thus much I see from the experiments mentioned, that the air consists of two fluids differing from each other, the one of which does not manifest in the least the property of attracting phlogiston, while the other, which composes between a third and a fourth part of the whole mass of air, is peculiarly disposed to such attraction.

C. W. Scheele failed to find the *lost air* in the liver of sulphur, etc. He then attempted to explain the facts by assuming that heat is a compound of fire-air (oxygen) and phlogiston, and concluded that by a double affinity, the fire-air combined with the phlogiston of the liver of sulphur, and escaped through the pores of the glass by which it had been confined. Where weight disappears, analysis is impossible, and C. W. Scheele left the composition of air to be explained by those who believed that elastic fluids cannot penetrate glass. In some further experiments, he sought an air which would behave towards liver of sulphur, phosphorus, etc., like that part of common air which had the peculiar property of attracting phlogiston from inflammable bodies. He first obtained what he called *Feuerluft*—**fire-air**—by heating a mixture of nitre and sulphuric acid, and found that a candle burned in the gas briskly and brightly. He obtained fire-air in several other ways—namely, by heating red oxide of mercury; black oxide of manganese; black oxide of manganese and sulphuric acid; nitre; etc.—and noticed that it was absorbed by those substances which caused a portion of common air to disappear. He said:

> These experiments show, therefore, that this fire-air is just that air by means of which fire burns in common air; only it is there mixed with a kind of air which seems to possess no attraction at all for the inflammable substance, and this it is which places some hindrance in the way of the otherwise rapid and violent inflammation.

C. W. Scheele's mind was probably a little misled by the phlogiston hypothesis, for he did not see that during combustion the burning body absorbs something from the air. The **vitiated air**—*verdorbene Luft*—which remained did not support combustion. C. W. Scheele also found the specific gravity of the vitiated air to be rather less, and that of fire-air rather greater, than that of common air.

C. W. Scheele did not publish an account of his work until 1777;[1] meanwhile, Joseph Priestley independently prepared the same gas which he called *dephlogisticated* *air.* He encountered the gas while examining the effect of heat upon a great variety of substances confined in a cylinder inverted over mercury, and he decomposed them by focussing the sun's rays upon them by means of "a burning lens of 12 inches diameter, and 20 inches focal distance." Joseph Priestley[2] announced his discovery of oxygen in these words:

> On the 1st of August, 1774, I endeavoured to extract air from *mercurius calcinatus per se*—that is, mercuric oxide, or red oxide of mercury—and I presently found that by means of this lens, air was expelled from it very readily. Having got about three or four times as much as the bulk of my materials, I admitted water to it and found that it was not imbibed by it. But what surprised me more than I can well express, was that a candle burned in this air with a remarkably brilliant flame.

and furthermore he said[3] that he ascertained the nature of this air very gradually during the following March, 1775. He then tried the effect of adding one measure of nitric oxide to two measures of the new air, and found that the new air behaved like common air. He added:

> I did not take notice of what I might have observed if I had not been so fully possessed by the notion of there being no air better than common air, that the redness was really deeper, and the diminution something greater than common air would have admitted. I now concluded that all the constituent parts of air were equally and in their proper proportion imbibed in the preparation of this substance, and also in the process of making red lead.

Until the first of March, J. Priestley said that he had no suspicion of the new air being fit for respiration; he then tried the mouse experiment of John Mayow, and found the new air was longer respirable than common air. His ideas, however were not so clear as those of J. Mayow, for instead of regarding air, with J. Mayow, as a constituent part of nitric acid, J. Priestley thought air to be a compound of nitric acid and earth; and added that in December, 1777,

> No doubt remained in my mind that atmospheric air, or the thing that we breathe, consists of the nitric acid and earth, with so much phlogiston as is necessary to its elasticity, and likewise so much more as is necessary to bring it from a state of perfect purity to the mean condition in which we find it.

It is therefore fairly evident that neither of the so-called discoverers of oxygen—Priestley and Scheele—had clear or accurate views of the nature of this gas, because they interpreted their results in the light of hypotheses which we now know to be wrong. This, however, does not detract from the merit of the discovery *per se.* Between August, 1774, and March, 1775, when J. Priestley had no doubt that the new air had all the properties of common air, A. L. Lavoisier, having heard an account of the new gas from J. Priestley himself, ascertained its relation to various bases and to the atmosphere; and thus, said W. V. Harcourt,[4] a property of this gas which under Priestley's observations led to nothing, in the hands of A. L. Lavoisier gave rise to one of the most important investigations in the annals of chemistry.

It must be added that J. Priestley's observation[5] in 1772 that a candle burnt with an enlarged flame in the gas obtained by heating nitre was perhaps as much a discovery of oxygen as the experiment of August 1, 1774. J. Priestley then said:

> All the kinds of factitious air on which I have yet made the experiment are highly noxious, except that which is extracted from saltpetre or alum: but in this, even a candle burned just as in common air. In one quantity which I got from saltpetre, a candle not only burned, but the flame was increased, and something was heard hissing similar to the decrepitation of nitre in an open fire; this experiment was made when the air was fresh made, and while it contained some particles of nitre which it would probably have deposited afterwards.

Joseph Priestley seems to have thought that the gas was fixed air, and he did not recognize his mistake until three years later.

For a century before this time, philosophers had suspected some kind of relationship between nitre and air, although there was no agreement as to the form of that relationship. Some, like N. Henshaw (1661),[6] maintained that the effects were due to the distribution of actual particles of nitre in the air, for " the air is everywhere full of a volatile kind of nitre." R. Boyle also, in 1664, made a similar suggestion; T. Hobbes considered that nitre consisted of "many orbs of salt filled with air"; while R. Hooke (1664) believed that the portion of air which rendered air a solvent of combustible bodies, is " like, if not the very same, with that which is fixed in saltpetre " ; and J. Mayow followed this up by demonstrating that the gas in the atmosphere which, in combining with bodies, produces the phenomenon of combustion, is identical with one of the components of nitre because (i) that salt is produced in the atmosphere; and (ii) the effects produced by both in enabling substances to burn are the same—for instance, he showed that the acid component of nitre, of nitric acid, and of the product obtained by heating antimony in the focus of a burning glass, all furnish the same substance.

There has been some discussion as to whether the alchemists were acquainted with oxygen, for there are indications in old books that this gas was known in the early centuries. Zosimus, in the fourth century, said :

> Take the soul of copper which is borne upon the water of mercury, and disengage an aeriform body.

According to F. Hoefer,[7] the *water of mercury* must here have referred to liquid mercury, and the *soul of copper* to red mercuric oxide which floats on mercury which has been heated in air. If so, the aeriform body given off when the soul of copper is heated must have been oxygen. This is an ingenious and probable interpretation of the passage, although it is easy to read into old writings a meaning which the original was not intended to express. Again, in 1742, J. H. Cohausen [8] referred to the *white dove* mentioned in the writings of Philalethes. It was said that atmospheric air is not respirable if the white dove be removed. In 1660, Robert Boyle [9] related, in a gossiping style, that Cornelius Drebell invented a kind of submarine, and that he had a chemical liquid which he accounted the chief secret of his navigation; for when the air was fouled by respiration, he could, by unstopping a vessel full of the liquid, speedily restore such vital parts as would make the air fit for use again.

Although clothed in mystical language, as was customary with the writers on alchemy of this period, it does seem as if the preparation of oxygen and its property of supporting life may have been suspected by some of the alchemists; but, their statements are so often mixed with what we know to be false, and their means of handling gases were so crude, that it requires some licence to be able to say that they discovered this gas. It has also been claimed that oxygen was discovered by E. Swedenborg,[10] half a century before Priestley, but the claims are based upon obscure and unintelligible passages which carry their own refutation.

However, P. Eck de Sultzbach [11] in 1489, did know that red oxide of mercury gave off a *spirit* when heated; about 1557, J. Cardan,[12] and about 1674, Ole Borch —the familiar term for Olaus Borrichius—obtained a *flatus* by the action of heat on saltpetre. This must have been either oxygen or nitrous oxide gas, because J. Cardan said that the gas nourished flame, and rekindled a glowing splint. A few years later, R. Boyle [13] said :

> On September 4, 1678, I exposed one ounce of minium in an open glass to the sunbeams concentrated by a burning glass, and found that it had lost three-fourths of a grain of its weight, though much of the minium had not been touched by the solar rays. . . . On May 30, the same experiment was repeated in a light glass phial sealed hermetically, but such plenty of air was produced that the glass phial broke into a hundred pieces.

Stephen Hales prepared the gas in a similar manner about 1727, and collected it over water; and in 1774, P. Bayen obtained the same gas by heating precipitated mercuric oxide in a retort. In the light of subsequent events, it appears as if these observers had really isolated oxygen gas, but one and all failed to establish its identity as a distinct individual. In some cases, the observations do not seem to have been clearly understood, probably because of the dominating influence of the idea that air was the only ponderable gaseous element. Had any one of these observers not only isolated the spirit or flatus, but also shown that it had specific properties, *sui generis*, which distinguished it from other known substances, he would have been credited with the discovery of oxygen.

The Chinese appear to have known something about oxygen in the eighth century, long before Joseph Priestley's and C. W. Scheele's experiments. Whatever be the facts of the case, the work of the Chinese played no part in the European discovery of this gas. In a paper *On the chemical knowledge of the Chinese in the eighth century*,[14] J. Klaproth, quoting from the Chinese, said :

> There are many substances which rob the atmosphere of part of its *yin*, the chief of these are the metals, sulphur and carbon. . . . The *yin* of the air is always pure, but by the aid of fire, *yin* can be extracted from nitre, or from a black mineral (black oxide of manganese) found in the marshes. It also enters into the composition of water, where the union is so close that decomposition is extremely difficult. . . . Gold never amalgamates with the *yin* of the air.

It will therefore be obvious that many erring steps have stumbled on the threshold of the discovery of oxygen. Although J. Priestley and C. W. Scheele are usually credited with the discovery of this gas, it is extremely difficult to decide whose name deserves the highest place in the discovery, for R. Hooke and J. Mayow inferred its existence in nitre and in air ; P. Eck de Sultzbach and R. Boyle disengaged the gas from red lead or minium ; S. Hales collected the gas in a jar over water ; and J. Cardan, C. W. Scheele, and J. Priestley observed that it supported combustion. Before answering the question : Who discovered oxygen ? it is necessary to answer : What is meant by the term discovery ?

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§ 2. The Action of Heat on Mercuric Oxide

In the thirteenth century, the Latin Geber knew that if mercury be heated in air, it forms the red oxide ; and P. Eck de Sultzbach, as previously stated, appears to have known that if the red oxide be heated, it gives off a spirit or gas. Here then is a paradoxical result : Heating mercury in oxygen furnishes mercuric oxide ; heating mercuric oxide furnishes oxygen and mercury. Several investigations [1] have been made to determine the conditions of temperature and pressure which determine the course of this reaction—evidently one of the balanced type, symbolized $2HgO \rightleftharpoons 2Hg + O_2$. Unlike the reaction between steam and iron in closed vessels, Fig. 4, Cap. III, the reaction is here complicated by the vaporization of the mercury. If p_0 denotes the partial pressure of the oxygen at any assigned temperature, and p_m that of the mercury, Guldberg and Waage's law gives the relation $p_0p_m^2$=constant. The product $p_0p_m^2$ is least when the partial pressure of the mercury vapour is twice that of the oxygen, *i.e.* when the two elements are in the same proportion as they exist in the solid phase. When the system is in equilibrium, mercury and oxygen are uniting to form mercuric oxide, and mercuric oxide is decomposing to form mercury vapour and oxygen. When the speeds of the two reactions are perfectly balanced, the system is in equilibrium, and the gases exert a definite pressure called **the equilibrium or dissociation pressure** on the walls of the vessel as measured by the manometer. This pressure thus measures the concentration of the gases, and one-third of the pressure is due to oxygen, and two-thirds to the mercury. When the temperature of mercuric oxide in vacuo is raised the speed of decomposition of the oxide is augmented more than the rate of re-combination of the two gases, and consequently, the equilibrium pressure or the concentration of the gases increases as the temperature is raised, until finally, all the mercuric oxide is decomposed, and the mixed gases then obey the ordinary gas laws. J. B. Taylor and G. A. Hulett represent the relation between the absolute temperature, T, and the dissociation pressure, P, by the expression $\log P = -5273{\cdot}5T^{-1} + 1{\cdot}75 \log T - 0{\cdot}001033T + 5{\cdot}9461$. The following values of the total pressure P at different temperatures are selected from G. B. Taylor and G. A. Hulett's determinations :

Temperature . .	360°	390°	420°	450°	480° C.
Equilibrium pressure .	90	180	387	810	1581 mm.

The curve showing the equilibrium pressure at different temperatures is indicated in Fig. 1. When the relation between the total pressure of the oxygen plus mercury and temperature can be represented by a point on this curve, the system is in equilibrium ; if by a point to the right of the curve, mercuric oxide will be decomposing and this will continue until the pressure attains its equilibrium value ; and if by a point to the left of the curve, the gases will be recombining and mercuric oxide will be formed until the pressure is reduced to its equilibrium value. Assuming the partial pressure of oxygen in air is one-fifth of 760 mm., *i.e.* 152 mm., and that mercuric oxide is heated in air, the oxide will commence to decompose when heated above 426°, and the temperature must be kept below this limit if it is desired to form mercuric oxide by heating mercury in air.

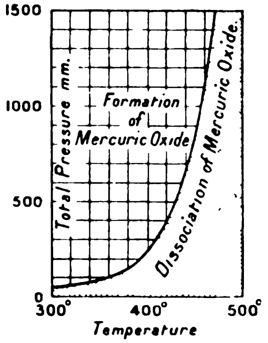

FIG. 1.—Equilibrium Pressure of Mercuric Oxide (Partial pressure of oxygen = ⅓ Total pressure).

Were it not for the cost, the preparation of oxygen by heating mercuric oxide would be very convenient. Ten grams of mercuric oxide give not quite half a litre of oxygen. The mercury is a by-product of the reaction.

Mercuric oxide decomposes more rapidly if it be previously mixed with powdered platinum or with certain metal oxides—*e.g.* ferric oxide, manganese dioxide, cadmium oxide, etc. These substances are not chemically changed during the decomposition of the mercuric oxide, and they can be used indefinitely over and over again. Hence, the oxides, which accelerate the decomposition of mercuric oxide are called catalytic agents. Stannic oxide or alumina do not exert any appreciable catalytic effect.

Many other oxides are available in place of mercuric oxide—*e.g.* gold and silver oxides decompose at temperatures even lower than mercuric oxide, while manganese peroxide (pyrolusite) decomposes at a higher temperature—over 400°. The preparation of oxygen by heating manganese dioxide was formerly one of the cheapest methods of preparing the gas on a commercial scale. The process was also used by C. W. Scheele in 1777 ; and by J. Priestley in 1779. Unlike silver, mercury, and gold oxides, the manganese oxide does not break down into the corresponding metal and oxygen, but rather into a complex oxide similar in composition to the mineral hausmannite—Mn_3O_4. The reaction is symbolized: $3MnO_2 = Mn_3O_4 + O_2$. Fairly pure manganese dioxide will furnish 88 to 89 litres of oxygen per kilogram; but pyrolusite, the native form of manganese dioxide, may give as low a yield as 34 litres of oxygen per kilogram, and the gas is contaminated with carbon dioxide and nitrogen or nitrogen oxides derived from impurities in the mineral.[2] Gold, silver, and mercuric oxides are not often used as sources of oxygen on account of the expense.

It will be observed that the alternate oxidation of mercury by roasting in air and the decomposition of the resulting oxide suggests a means of extracting oxygen from the air. Similarly, palladium sponge is directly oxidized when heated to redness in air, and the resulting oxide, Pd_2O, reforms the metal with the evolution of oxygen at a little higher temperature. When rhodium sponge is similarly treated, the oxide, RhO, is formed; and with iridium sponge, the oxide Ir_3O. These two oxides give oxygen and the metal[3] at about 1200°.

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§ 3. The Action of Heat on Potassium Chlorate

Potassium chlorate is a white crystalline solid which melts to a clear liquid when heated to about 340°. According to A. Rilliet and J. M. Crafts,[1] potassium chlorate begins to give off oxygen below its melting point and the decomposition goes on several weeks before it becomes imperceptibly small; when the limit is reached, a rise of temperature starts a fresh decomposition, tending towards a new limit. At about 10° above its melting point, the melted chlorate appears to boil, because bubbles of oxygen gas are copiously evolved. The potassium chlorate is decomposing. When the bubbling ceases, the molten mass becomes very viscid or even solidifies. The potassium chlorate has decomposed into potassium perchlorate, potassium chloride, and oxygen. If the temperature be raised still further—over 600°—the mass again melts to a clear liquid and the potassium perchlorate decomposes, giving off more oxygen. The final products of decomposition are potassium chloride and oxygen, and the reaction is accordingly symbolized: $2KClO_3 = 2KCl + 3O_2$. Hence, potassium chlorate can be used in place of mercuric oxide for the preparation of oxygen gas. Ten grams of potassium chlorate will give nearly 2¾ litres of oxygen. Purified and fused potassium chlorate gives oxygen free from chlorine and ozone, O_3. The gas is of a high degree of purity, and this process was used by E. W. Morley in his work on the atomic weight of oxygen.

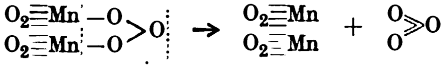
If potassium chlorate be suddenly heated to a temperature above that at which decomposition occurs, the salt may detonate in an open vessel under ordinary pressure. Some disastrous explosions have been produced by potassium chlorate. M. Berthelot's experiment (1899)[2] illustrates the explosive nature of this salt.

One end of a glass rod is drawn out into a thread, and the narrow end is dipped several times in molten potassium chlorate so that each layer of salt solidifies before the rod is dipped again. When a bead has been formed at the end of the rod, dip the rod into a test-tube heated red hot at one end so that the salt is about a centimetre from the bottom of the tube.

Take care not to touch the sides of the tube. As the chlorate melts, it slowly drops to the bottom of the test-tube; each drop of chlorate as it falls explodes with a sharp detonation.

C. L. Berthollet[3] first made oxygen by the chlorate process in 1785; and in 1832, J. W. Döbereiner noticed that the potassium chlorate decomposes completely at a much lower temperature if it be mixed with manganese dioxide; the reaction also progresses more smoothly and is more under control. Other agents can be employed—*e.g.* the oxides of copper, iron(ic), lead, cobalt, vanadium, uranium, and tungsten. With ferric oxide, the evolution of oxygen begins between 110° and 120°; with manganese dioxide, between 200° and 205°; and with platinum black, between 260° and 270°. The stimulating action of alumina and chromic oxide is less marked; and baryta, lime, magnesia, and zinc oxide have no influence. Powdered glass, sand, and china clay promote the decomposition of the chlorate to a small extent. Although oxygen can be easily obtained by heating manganese dioxide, MnO_2, to about 600° in a fireclay, porcelain, or iron retort ($3MnO_2 \rightarrow Mn_3O_4 + O_2$), and potassium chlorate, when heated *alone*, does not give off oxygen below about 240°, yet a *mixture* of the two gives off oxygen at about 205°—a temperature below the melting point of the chlorate. After the action, manganese dioxide still remains, but the potassium chlorate has decomposed into potassium chloride and oxygen. Manganese dioxide can be recovered from the residue by lixiviating the mass with water. The water dissolves the potassium chloride, and leaves the manganese dioxide as a residue. The temperature of the reaction with ferric oxide and cupric oxide is nearly the same as with manganese dioxide; with platinum black, it is 270°, and 285° with lead dioxide.[4] Cobaltic and nickelic oxides behave like manganese dioxide and accelerate the decomposition of potassium chlorate. The nitrogen is probably derived from nitrogeneous impurities in the dioxide, and is not a result of the oxidization of atmospheric nitrogen because a similar result is obtained if the dioxide be heated in a current of inert gas—say carbon dioxide.

C. F. Schönbein[5] reported that the gas obtained from lead dioxide, mercuric oxide, silver oxide, and chlorates contains traces of ozone, but A. R. Leeds showed that the ozone reactions obtained by C. F. Schönbein were produced by traces of chlorine. According to W. Spring and E. Prost, the amount of chlorine formed is insignificant if the chlorate be decomposed in a platinum vessel, but quite marked quantities are obtained when porcelain vessels are used. In the presence of carbon dioxide or phosphoric oxide, it is possible that chloric anhydride, Cl_2O_5, is disengaged from the chlorate, and that this unstable gas is instantly decomposed into chlorine and oxygen. According to O. Brunck, ozone, not chlorine, is formed in the reaction in amounts which increase with increasing proportions of manganese dioxide mixed with the chlorate. Thus, with equal parts of chlorate and the dioxide the oxygen contained 0·3 per cent. of ozone, whereas with 25 times as much of the dioxide, the oxygen contained 1·55 per cent. of ozone. If alkalies be present no ozone is formed, and with sodium carbonate, sodium peroxide is found in the residue. Nickelic and cobaltic oxides, like manganese dioxide, give oxygen contaminated with ozone; while mercuric oxide, lead dioxide, and silver oxide, give ozonized oxygen when heated with potassium chlorate. O. Brunck also claims that if these mixtures are heated in a stream of carbon dioxide no ozone is formed. It is quite certain that the gas from the mixture of potassium chlorate and manganese dioxide has usually the smell of ozone or chlorine. Traces of these two substances behave so much alike in the usual test, that one can be easily mistaken for the other. Both chlorine and ozone, for example, give a blue coloration with a solution of starch and potassium iodide. E. H. Cook[6] has reported 0·03 per cent. of chlorine in the oxygen derived from the chlorate. H. McLeod has shown that when potassium chlorate and manganese dioxide are heated, some chlorine is produced, and claims that there is no evidence of the simultaneous formation of ozone. For instance, the residue left after the reaction is over gives an alkaline solution when extracted with water. O. Brunck obtained no alkaline residue. The gas also gives a precipitate of silver chloride when it is passed through a solution of silver nitrate, suitable precautions being taken to prevent fine particles of potassium chloride being carried along with the stream of gas. O. Brunck explains the discrepancy between his own results and H. McLeod's by showing that the latter's apparatus contained traces of organic matter which would decompose the ozone, and that H. McLeod used *unnötig* high temperatures. Above 400°, O. Brunck also obtained chlorine, and he suggests that the manganese dioxide forms with the chlorate, permanganic anhydride, Mn_2O_7, and that this gives the ozone form of oxygen, O_3, in accord with the scheme : $Mn_2O_7 \rightarrow 2MnO_2 + O_3$; or graphically :



$$\begin{matrix} O_2\equiv Mn-O \\ O_2\equiv Mn-O \end{matrix}\!\!>\!O \;\rightarrow\; \begin{matrix} O_2\equiv Mn \\ O_2\equiv Mn \end{matrix} + \begin{matrix} O \\ O \end{matrix}\!\!\geqslant\! O$$

and if chromic oxide is used a chromic anhydride, Cr_2O_6, is similarly formed and decomposed. Most of the ozone is decomposed at the temperature of the reaction, $2O_3=3O_2$.

Potassium chlorate, mixed with manganese dioxide, is commonly used in the laboratory for the preparation of oxygen ; and with the idea of lessening the violence of the action still more, the addition of 10 to 30 per cent. of common salt has been recommended ;[7] but this is usually considered unnecessary. The chlorine can be removed by passing the gas through magnesia, whiting, or soda ash distributed over some inert material like glass wool or asbestos. If a highly pure gas is needed, fused potassium chlorate can be used alone. The cost of oxygen by the chlorate process is nearly double that by the pyrolusite process. By the former process, 1000 cub. ft. of oxygen are said to cost £8 to £10, and by the latter £4 to £5, against 3*s*. 6*d*. by the liquid air process.

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§ 4. The Occurrence and Preparation of Oxygen

The occurrence of oxygen.—Oxygen is widely distributed on the earth in very large quantities. It is an essential constituent of air and water. About one-fourth —23·2 per cent.—of the atmosphere by weight, and about one-fifth by volume consists of free oxygen. J. H. Jeans' estimate[1] of the number of molecules of oxygen per c.c. at a height *h* kilometres is

$h=0$	$h=20$	$h=80$	$h=160$	$h=800$
21×10^{17}	7×10^{16}	25×10^{11}	3×10^{6}	0

Water contains about 88·8 per cent. of combined oxygen. Oxygen also forms a material part of rocks since a great many minerals contain a considerable proportion of oxygen. F. W. Clarke estimates that 45 to 53 per cent.—nearly one-half—the total weight of rocks, and eight-ninths of the water which make up the half-mile crust of the earth, is combined oxygen. Oxygen therefore is by far the most abundant element, being nearly equal in amount to all the others put together. Natural waters hold a small amount of oxygen in solution.

Oxygen is an essential constituent of animal and vegetable tissue and fluids. It is absorbed from the atmosphere by animals and plants during respiration; and given off by plants when they assimilate carbon dioxide from the air in sunlight. This fact was established by J. Priestley on August 17th, 1776, by showing that plants could live in fixed air in which animals perish, and that plants can restore to fixed air the properties of common air when in sunlight, but not in darkness. The explanation of J. Priestley's observation was possible only after the function of oxygen in respiration was recognized. R. Perceval, and J. Senebier showed that the amount of oxygen given off depends on the proportion of carbon dioxide in the atmosphere, and J. Ingenhousz proved that sunlight is necessary for the reaction. The oxygen contains no ozone. Some plants—*e.g. bact''rium photometricum*, can produce oxygen without the agency of light; and chlorophyllous animals give off oxygen in sunlight.[2]

H. Draper[3] showed, in 1877, that oxygen is present in the sun; J. Trowbridge (1896), however, believed that the spectral lines thought to be oxygen were due to iron; but later, from the analogy of the solar spectrum with the spark spectrum of water vapour, J. Trowbridge (1902) assumed that the sun contains dissociated water vapour and consequently also free oxygen.

The preparation of oxygen.—There are many methods available for preparing oxygen—the particular process to be employed must be determined by cost and convenience.[4] If but a few litres of gas, not specially purified, are required, cost is not very serious, and convenience is perhaps the most important factor; if pure oxygen be required, a complicated apparatus may be needed, and neither cost nor labour must be spared. An elaborate apparatus may be needed to remove traces of impurities—say, traces of ozone and chlorine from the oxygen. Pure potassium chlorate alone will give a gas of a high degree of purity. If large quantities of gas are needed, say for industrial purposes, the cost factor is of prime importance. Generally speaking, the success of industrial operations depends upon the ability of the chemist to manufacture his products cheaply. In former times, oxygen was made commercially by heating pyrolusite, and also by the chlorate method; but the cost was too great for these processes to compete successfully with the cheaper methods by barium peroxide, or the fractional distillation of liquid air. The different methods of preparing oxygen can be conveniently classed:

1. *Processes dependent on the decomposition of oxides or oxy-compounds by heat.*—The methods of preparing oxygen by heating mercuric oxide, and by heating potassium chlorate are typical. Several dioxides also yield oxygen when heated—*e.g.* manganese dioxide, lead dioxide, barium dioxide, etc. The nitrates of potassium or sodium give oxygen contaminated with nitrogen or nitrogen oxide.[5] Oxygen was probably obtained by this method by J. Priestley in 1771—some years before the date generally accepted for his discovery of this gas. The first British patent for the manufacture of oxygen was by S. White[6] in 1849, and this was effected by heating nitre.

When the vapour of sulphuric acid is passed over fragments of brick or earthenware heated to bright redness, oxygen, sulphur dioxide, SO_2, and water are formed: $2H_2SO_4=2H_2O+2SO_2+O_2$. By washing the products in water or in a solution of sodium hydroxide, the sulphur dioxide is arrested. In this way, H. St. C. Deville and H. Debray [7] obtained 140 litres of oxygen from a kilogram of concentrated sulphuric acid—between 6 and 7 per cent. of the acid escaped decomposition. W. S. Squire (1875) patented this process of making a mixture of oxygen and sulphur dioxide for the manufacture of sulphur trioxide—the water was removed by a desiccating agent. H. St. C. Deville and H. Debray also obtained 6·8 litres of oxygen by calcining zinc sulphate *au rouge blanc.* The sulphate decomposes in an analogous manner to the acid.

When potassium or sodium permanganate is heated, it also furnishes fairly pure oxygen.[8] It is well to cover the salt with a heavy layer of glass wool to retain any dust from the decomposition of the permanganate. The product of this reaction, after scrubbing by passage through a layer of solid potassium hydroxide, and drying by passage over phosphorus pentoxide, has been used in some refined determinations of the relative density of the gas. The decomposition proceeds at a lower temperature in the presence of steam forming an alkali manganite (G. Rousseau), or a mixture of manganic oxide and alkali hydroxide (C. M. T. du Motay and C. R. M. de Marechal), and a regular stream of oxygen.[9] The hypochlorites or hypobromites furnish oxygen when they are heated. Cupric metaborate, CuB_2O_4, gives off oxygen [10] at about 1000° forming the sesquiborate: $12CuB_2O_4=6Cu_2O.2B_2O_3+3O_2+10B_2O_3$.

2. *Processes dependent on the decomposition of oxides and oxy-compounds by chemical means.*—There is probably no real distinction between many of the thermal and chemical processes. Heat may be required to start the reaction in either class; and the thermal processes all involve chemical reactions. Many dioxides yield oxygen when treated with water or dilute acid, in some cases at atmospheric temperatures. Sodium peroxide, for example, is slowly decomposed by water into sodium hydroxide and oxygen: $2Na_2O_2+2H_2O=4NaOH+O_2$. If a catalytic agent, say manganese dioxide, be present, the reaction is not inconveniently slow for small quantities of gas. The trade name for a mixture of fused sodium peroxide with a small quantity of manganese dioxide is *oxone*; *oxylith* [11] is a compressed mixture of sodium peroxide with about 62 per cent. of dry chloride of lime. It slowly decomposes in contact with water, giving off oxygen: $CaOCl_2+H_2O+Na_2O_2=Ca(OH)_2+2NaCl+O_2$. Numerous other mixtures have been patented for this purpose; as well as vessels—generators or auto-generators—for producing the gas. When sodium peroxide is gently warmed with a salt containing water of crystallization—*e.g.* Glauber's salt, or sodium carbonate—a steady stream of oxygen is given off.[12] Many other methods are available for the preparation of oxygen. Heating sulphuric acid with manganese dioxide; [13] with chromic acid or potassium dichromate; [14] with potassium permanganate; etc., and this more particularly when a powerful oxidizing agent, rather than gaseous oxygen, is required. The reaction with manganese dioxide is symbolized: $2MnO_2+2H_2SO_4=2H_2O+2MnSO_4+O_2$, and with potassium dichromate: $2K_2Cr_2O_7+8H_2SO_4=2Cr_2(SO_4)_3+2K_2SO_4+8H_2O+3O_2$. Other salts rich in oxygen may be used. Hydrogen peroxide is sometimes convenient for preparing small quantities of oxygen, although the cost is rather high. For instance, a 10 per cent. solution of hydrogen peroxide mixed with a substance which provokes its catalytic decomposition—*e.g.* chloride of lime; [15] manganese dioxide; lead dioxide; [16] potassium ferricyanide in alkaline solution [17] ($2K_3FeCy_6+2KOH+H_2O_2=2H_2O+2K_4FeCy_6+O_2$); or potassium dichromate.[18] A concentrated solution of potassium permanganate gives off oxygen at ordinary temperatures when acidified with sulphuric acid.

Heat a mixture of, say, 20 grams of potassium permanganate with 80–100 c.c. of dilute sulphuric acid (one volume of the concentrated acid, with four volumes of water) in a flask with a delivery tube and safety funnel. Oxygen begins to come off when the temperature is about 50°, and continues in a steady stream. Ten grams of the permanganate with between 40–50 c.c. of the dilute sulphuric acid give just over a litre of gas.

A. Baumann (1890) [19] charges a Kipp's apparatus with lumps of pyrolusite and a mixture of commercial hydrogen peroxide with 15 per cent. by volume of sulphuric acid. A steady and continuous stream of oxygen is said to be evolved. The hydrogen peroxide can be replaced in any of the preceding mixtures by a peroxide of the alkalies or alkaline earths. L. Wolter (1908) recommends a fused mass of equal parts of sodium peroxide, and potassium nitrate with one-eighth of its weight of magnesia. Hydrochloric acid is dropped on the coarsely pulverized mass. L. Santi recommends warming a solution of ammonium chloride with barium peroxide: $2BaO_2+4NH_4Cl \rightarrow 2BaCl_2+4NH_3+2H_2O+O_2$, for a steady stream of oxygen. G. Neumann[20] similarly charges a Kipp's apparatus with cubes made from barium dioxide, pyrolusite, and gypsum in the proportions 2 : 1 : 1, together with hydrochloric acid (specific gravity 1·12).

There are numerous other reactions in which oxygen is evolved—*e.g.* a mixture of steam and chlorine[21] passed through a red-hot tube gives a mixture of hydrogen chloride, HCl, and oxygen: $2Cl_2+2H_2O=4HCl+O_2$. According to D. Muller, a temperature of 120° suffices for the reaction. Chlorine water decomposes into oxygen and hydrogen chloride when exposed to sunlight. The finely-divided metals of the platinum family decompose chlorine water even in darkness, forming oxygen and hydrogen chloride; according to C. F. Schönbein,[22] bromine and iodine water do not decompose in this way in darkness.

According to J. L. Gay Lussac, dry chlorine will displace the oxygen from certain oxides. This is the case, for instance, with the oxides of the alkaline earths, lead, or cadmium. If silver hydroxide be placed in a jar of chlorine gas, the oxygen and chlorine will change places.[23] So also if commercial "chloride of lime" which contains much calcium hypochlorite, $CaOCl_2$, be heated to redness: $2CaOCl_2=2CaCl_2+O_2$. According to H. St. C. Deville and H. Debray, a kilogram of the chloride of lime will furnish 40 to 50 litres of oxygen contaminated with a little chlorine which can be removed by washing the gas with soda lye. E. Mitscherlich[24] has also shown that a fairly steady stream of oxygen can be obtained by heating a mixture of a concentrated solution of bleaching powder, and a small quantity of a nickel or cobalt salt, at about 85°. Other hypochlorites, as well as hypobromites, can be employed. The cobalt or nickel salt forms a higher oxide which acts catalytically. The cobalt or nickel salt can be replaced by other metal oxides—*e.g.* oxides of manganese, iron, or copper. A current of chlorine or bromine passed through a boiling solution of caustic alkali or milk of lime, containing a salt of the metal, gives a 90 per cent. yield of oxygen. A hypochlorite or hypobromite is first formed, *e.g.*: $2NaOH+Br_2=NaOBr+NaBr+H_2O$; and the hypobromite, NaOBr, then decomposes: $2NaOBr=2NaBr+O_2$. According to C. F. Schönbein, an aqueous solution of iodic acid can be boiled without decomposition, but if platinum black be present, it decomposes into iodine and oxygen.

By heating a mixture of calcium sulphate and silica, N. A. Helouis[25] obtained a mixture of sulphur dioxide and oxygen, and a residue of calcium silicate. By heating a mixture of sodium nitrate with twice its weight of zinc oxide, sodium zincate, $Zn(ONa)_2$, and a mixture of nitrogen with 71·4 per cent. of oxygen is formed: $2ZnO+4NaNO_3=2Zn(ONa)_2+2N_2+5O_2$.

4. *Processes in which oxygen is obtained from the atmosphere.*—Many ingenious processes—both chemical and physical—have been devised for the continuous manufacture of oxygen, and inventors have been particularly sanguine—at first. These processes are often of much theoretical interest; but however interesting a process may be, and however enthusiastic the inventor, an installation will have a short life commercially if it cannot bring money into the pockets of the investors.

(*a*) *Chemical processes.*—These depend on the oxidation of a substance by air so as to form a compound which gives up the oxygen and re-forms the original substance. This can be again oxidized, and so the cycle can be continued indefinitely. Thus, mercury can be oxidized by heating it in air at about 400°, and the resulting mercuric oxide broken up into oxygen and mercury at about 600°. The oxidation is too slow for the process to be industrially useful. J. T. A. Mallet (1865)[26] patented a process for extracting oxygen from air by the alternate oxidation of cuprous chloride,

$4CuCl+O_2=2Cu_2OCl_2$, by exposure to moist air; and, subsequent deoxidation of the cupric oxychloride by heating to dull redness. C. M. Tessie du Motay and C. R. Maréchal (1866)[27] heated a mixture of pyrolusite and caustic alkali at a high temperature while exposed to air, oxygen from the air takes part in a reaction forming an alkali manganate—say Na_2MnO_4; the manganate then gives up its oxygen when heated in a current of steam, and the residue again forms manganite when heated in air. This process has not proved a great success although many works were erected and numerous modifications have been patented. G. Kassner (1889)[28] heated a mixture of chalk and lead oxide in contact with air whereby calcium plumbate, Ca_2PbO_4, is formed. When this is treated with potassium or sodium carbonate, caustic alkali remains in solution and calcium carbonate and lead peroxide are precipitated: $Ca_2PbO_4+2Na_2CO_3+2H_2O=4NaOH+2CaCO_3+PbO_2$. When the precipitate is dried, and heated to about 500°, oxygen is evolved, and the residue is ready for the regeneration of calcium plumbate. The caustic lye obtained as a by-product is claimed to make the process economical; but this is doubtful since the process has had no commercial success in spite of numerous modifications.

Oxygen was formerly made on a manufacturing scale by the **barium peroxide process** of L. Q. and A. Brin (1880). This depends upon a very interesting reaction discovered by J. B. J. D. Boussingault[29] in 1851. When barium oxide—BaO is heated in air to about 500°, it is rapidly oxidized to barium dioxide: $2BaO+O_2=2BaO_2$. If the barium dioxide be heated to a still higher temperature, 800°, the oxygen is given off and barium oxide remains as a residue: $2BaO_2=2BaO+O_2$. The phenomena attending the decomposition of barium peroxide in closed vessels are quite analogous with the decomposition of mercuric oxide except that non-volatile barium oxide appears in place of volatile mercury. The curve, Fig. 2, can therefore be readily interpreted. Some other oxides behave in a similar manner. For example, as found by H. Debray and A. Joannis, and by G. H. Bailey and W. B. Hopkins, cupric oxide, CuO, at a red heat forms cuprous oxide, Cu_2O; and re-forms cupric oxide when heated in air at a lower temperature. J. B. J. D. Boussingault tried to apply the barium peroxide reaction industrially, but it was found that after the baryta had been oxidized about a dozen times, it lost its power. M. Gondolo claimed to have used the barium oxide over a hundred times without deterioration, by mixing the barium oxide with a little lime or magnesia, and potassium manganate. The cause of the trouble was recognized by MM. Brin Frères in 1879. The barium oxide can be reoxidized and used over and over again, provided the air be freed from carbon dioxide, organic matter, dust, and any substance which forms a compound with barium oxide which is not decomposed under the given conditions. The regulation of the temperature offered practical difficulties which were overcome by keeping the temperature constant in the vicinity of 700°. Barium oxide is then transformed into the dioxide if the pressure be about 2 kilograms per sq. cm.—normally the atmospheric pressure is 1·033 kilograms per sq. cm. The peroxide is decomposed into the oxide and oxygen at the same temperature under a reduced pressure—about 0·05 kilogram per sq. cm. The gas pumped off under these conditions contained about 90–96 per cent. of oxygen, and 4–10 per cent. of nitrogen.

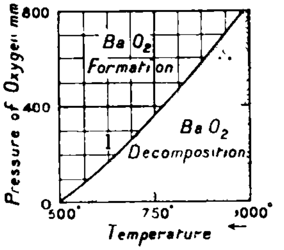

Fig. 2.—Equilibrium Pressure Curve of Barium Peroxide.

After an industrial life of nearly 20 years, Brin's process failed to compete successfully against the newer and cheaper method of preparation by the fractional distillation of liquid air. The relative costs of the two processes are said to be: 3*s*. 6*d*. per 1000 cub. ft. for the liquid air process against from 7*s*. to 12*s*. for Brin's process. The same amount of oxygen costs 16*s*. 8*d*. when manufactured by electrolysis with electrical energy at ½*d*. per unit. The oxygen obtained from liquid air is about 98 per cent. purity; that from the barium process about 94 per cent.

purity. In 1907, the British Oxygen Co. made about 30,000 cub. ft. of oxygen per day by the liquid air process, and in 1917, about 1,000,000 cub. ft. per day.

(*b*) *Mechanical and physical processes.*—Oxygen is more soluble than nitrogen in water; and J. T. A. Mallet[30] patented a process for extracting oxygen from the atmosphere by pumping off the air dissolved under pressure by water. The product was again dissolved under pressure in water; and again pumped from the liquid. By repeating the operation eight times, a gas containing 91 per cent. of oxygen was obtained. The use of liquids other than water—*e.g.* glycerol—have been patented as solvents; but these processes have not been commercially successful. Although the ratio of oxygen to nitrogen dissolved by the liquid may be greater than with water, the actual amount dissolved may be less, and, according to G. Claude,[31] *celui rend illusoire leur usage.* Similar remarks apply to the greater adsorption of oxygen from air by wood charcoal than is the case with the absorption of nitrogen.[32] Repeated absorption followed by the expulsion of the adsorbed gases by heating under a reduced pressure furnishes a product rich in oxygen. P. Margis[33] obtained a 95 per cent. oxygen by the repeated diffusion of air through indiarubber membranes—oxygen passes through the rubber much faster than nitrogen. The fractional distillation of liquid air furnishes most of the oxygen gas for commerce.

5. *Processes dependent upon the electrolysis of water.*—Nearly all the oxygen on the market is now obtained by the liquid air process. Comparatively little oxygen is obtained by the electrolytic process, since this is profitable only when the hydrogen can be readily sold at good prices.[34] As indicated in connection with the electrolytic preparation of hydrogen, one ampere of electricity decomposes 0·335 grm. of water per hour, and liberates 0·0373 grm. or 0·414 litre of hydrogen, and 0·298 grm. or 0·207 litre of oxygen. By converting the number of calories involved during the formation of water, and converting into equivalent electrical units, it follows from Kelvin's rule that 1·5 volts are needed for the decomposition of water. In practice 2·5 volts is the minimum employed; and with this voltage 12 kilowatt hours are needed to furnish a cubic metre of oxygen and two cubic metres of hydrogen; in practice 12 to 14 kilowatt hours are consumed in producing these amounts of hydrogen and oxygen. This works out at about 16*s.* 8*d.* per 1000 cub. ft., when the electrical energy costs ½*d.* per unit. A. d'Arsonval installed a plant for electrolytic preparation of oxygen about 1885. He used as electrolyte a 30 per cent. solution of sodium hydroxide with sheet-iron cylinders as electrodes. He used a current density of 2 amps. per sq. decimetre, and enclosed the anode in a woollen bag to serve as diaphragm. The hydrogen was not used. With 60 amps. about 100 or 150 litres of oxygen were obtained per diem. D. Latchinoff used an apparatus in which the gases were under pressure. Other forms are indicated in connection with the electrolytic preparation of hydrogen. There have been several explosions from the use of electrolytic oxygen, owing to the hydrogen getting mixed therewith.[35]

The oxygen obtained by any of these processes is pumped into steel cylinders under a pressure of 100-150 atmospheres, and sold as *compressed oxygen.* The gas may be obtained from the cylinders at any desired rate by regulating the valve.

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§ 5. Catalysis

Materializing abstractions is a vice of thought.—H. S. R. ELLIOTT.

The action of manganese dioxide on the decomposing potassium chlorate is very curious. It acts as a **stimulant.** We do not know precisely how the manganese dioxide does its work, although we can form a rough idea of what is taking place. Many other oxides act similarly, but not quite so vigorously—*e.g.* ferric, copper, cobalt, or nickel oxide, vanadium pentoxide, V_2O_5, tungstic oxide, WO_3, uranic oxide, U_3O_8, may be used in place of manganese oxide. It is quite a common thing to find that the speed of reactions is accelerated or retarded by the presence of a foreign substance whose composition at the end of the reaction is the same as it was at the beginning. For example, in the combustion of hydrogen, platinized asbestos or moisture may act as catalytic agents; similarly metallic oxides stimulate the decomposition of mercuric oxide, potassium chlorate, etc. Indeed, there are probably few chemical reactions, if any, which are not affected by the presence of a catalytic agent. These agents are conveniently grouped together as catalytic agents, and the general phenomenon is called *catalysis;* if the catalytic agent retards the speed of the reaction, the phenomenon is conveniently called **negative catalysis.** It must be clearly understood that **catalysis is simply a term for grouping those reactions whose speed is modified, or for those reactions which can be started by the presence of a small amount of a substance which is found to possess, at the end of the reaction, the same chemical composition as it had at the beginning.** The catalytic agent may be chemically affected by interaction with the products of the reaction, etc. W. Ostwald[1] ingeniously compares the action of a catalytic agent with the action of oil on a machine, or of a whip on a sluggish horse. W. Ostwald, and his followers, believe that the reaction *must* be actually in progress before the catalytic agent can act; although if W. Ostwald's analogy be pursued it runs against his hypothesis, for we know that friction may be so great as to stop the running of a machine, when a little lubricating oil would have prevented the stoppage. Ostwald's limitation is quite arbitrary, and, so far as we can see, does not agree with all the facts.

Some have tried to evade the difficulty either by refusing to recognize it, or by reserving the term **catalytic reactions** for those reactions whose speed is merely accelerated by the catalyst; and using the term **trigger reactions** for those reactions which do not start unless their potential energy is released by contact with another substance. Of course, the introduction of a new term does not remove the difficulty. Again, different products may be obtained by a reaction with and without a catalytic agent; and further, different catalytic agents, with the same reacting materials, may furnish different end-products. So far as the evidence goes: **Catalytic agents can not only start, accelerate, or retard the speed of chemical reactions, but they can also in some cases direct or determine the course of a reaction.**

Francis Bacon long ago cautioned us against allowing words to govern thought instead of thought governing words. The word catalysis itself explains nothing. To think otherwise would lay us open to Mephistopheles' gibe:

> A pompous word will stand you instead
> For that which will not go into the head.

This means that too much trust must not be placed in words. It is just when ideas fail that a word comes in most opportunely. There is no difficulty in covering an obscure idea by a word so that the word appears to explain the idea. In passing back from the word to the idea, it becomes easy to believe that the "subjective abstraction has an objective existence," or that because there is a word, something real must lie behind the word. These remarks about the term catalysis might be applied, *mutatis mutandis,* to many of the terms in common use in chemistry—passive resistance, chemical affinity, the ions of the ionic theory, adsorption, colloids, etc.

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§ 6. Consecutive Reactions

Theories are abstractions which, while they place in relief that which is important for *certain fixed* cases, neglect almost necessarily, or even disguise, what is important in other cases. A theory always puts in place of a fact something *different*, something more simple, which is qualified to represent it in some *certain* aspect, but for the very reason that it is different does not represent it in other aspects.—E. MACH (1892).

The representation of a chemical reaction by means of an equation emphasizes the character of the initial and of the end products of the reaction, but it conveys no idea of the mechanism of the reaction—*how* the different materials interact to give the final products. With the growth of knowledge, reactions represented by the older chemists by simple equations resolve themselves into reactions of greater and greater complexity. **The regular type of chemical equation shows but the beginning and end of the reaction.** Such equations are sometimes considered to represent "the essential and determining features" of the reaction, because they indicate what might be called the main products of the reaction, and they are accordingly used in the arithmetic of chemistry. However, chemists are continually striving to obtain a completer view of the real mechanism of a reaction. The truth, not simplicity, is the ultimate object of their quest. There can be no doubt that quite a number of intermediate stages temporarily subsist before the drama of the reaction closes with the final act—the formation of the end products. There is plenty of evidence leading us to infer the existence of a kaleidoscopic sequence of changing scenes during the progress of what are usually considered simple reactions. Some suppose that water has no more right to representation in the chemical equation than the glass of the vessel in which the reaction occurs. As we progress in our studies, we shall find that water profoundly modifies the properties of most substances with which it is in contact. This, said C. L. Berthollet (1803), is a striking illustration of the effect of words on the ideas we form, and even on the results of observation. We begin by considering a solvent as the liquid employed in making solutions, and that these in turn are mere mixtures of solvent and the dissolved substance; consequently, attention is rarely directed to the action of the solvent under other conditions because in them it retains the name of solvent. It must, however, never be forgotten that **all the substances present in a reacting system exercise an action,** and if there are circumstances in which the solvent may be neglected, there are others in which it contributes efficaciously to the result.

The fate of the molecules of manganese dioxide.—As a result of quite a number of experimental investigations on the decomposition of potassium chlorate [1] and a study of the available circumstantial evidence, we are able to get, in imagination, a peep behind the curtain which hides the course of the reaction. Firstly, it is not quite correct to say that the manganese dioxide is not changed in any way during the reaction because a microscopic examination of the manganese dioxide, before and after the reaction, shows that it has undergone a physical, if not a chemical, change—crystalline manganese dioxide has apparently become amorphous. The manganese dioxide does appear to take part in the reaction in spite of the fact that it has the same chemical composition at the end as it had at the beginning. Secondly, the manganese dioxide is *probably* oxidized by the decomposing chlorate to form one of the unstable higher oxides of manganese, but exactly what oxide we do not know. This uncertainty is expressed by writing the unknown oxide MnO_{n+2}, where the numerical value of n is not known with certainty. This stage of the reaction can then be represented by the equation:

$$\tfrac{1}{3}nKClO_3+MnO_2=\tfrac{1}{3}nKCl+MnO_{n+2} \quad . \; . \; . \; . \; . \quad (1)$$

Thirdly, the unstable oxide produced by the oxidizing action of the potassium chlorate probably breaks down almost as soon as it is formed, regenerating the manganese dioxide, and liberating free oxygen:

$$2MnO_{n+2}=2MnO_2+nO_2 \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

The manganese dioxide so formed is again oxidized, and the oxide again decomposed regenerating manganese dioxide anew. This cycle of changes continues until the potassium chlorate is all decomposed. The opening and closing scenes are represented:

$$2KClO_3[+MnO_2]=2KCl[+MnO_2]+3O_2$$

Equations (1) and (2), expressed in the most general form, indicate that we are dealing with a reaction in which

$$A \rightarrow \mathbf{M} \quad \text{and} \quad \mathbf{M} \rightarrow B$$

where A and B respectively denote the initial and final products of the reaction, and **M** the intermediate products. In the reaction just considered, **M** is represented by MnO_{n+2}. Under the prevailing conditions, A does not form B directly. **Consecutive reactions are those in which intermediate products are produced which do not necessarily appear as final products in the reaction.** Consecutive reactions occur in stages; one stage must be in progress before another can start. The speed of formation of B from A obviously depends on the speed of the intermediate reactions. If the reaction $A \rightarrow \mathbf{M}$ be very rapid, and $\mathbf{M} \rightarrow B$ be very slow, the intermediate product **M** will accumulate in the system, and could be recognized and probably isolated. Several examples are known. On the other hand, if $A \rightarrow \mathbf{M}$ be very slow, and $\mathbf{M} \rightarrow B$ be very fast, it would be hopeless to look for intermediate products, and the evidence in support of the assertion that the reaction involves a sequence of consecutive or intermediate reactions must be circumstantial, not direct proof. It will be obvious that the same reasoning must apply in a longer series of intermediate reactions, say, $A \rightarrow \mathbf{M}$; $\mathbf{M} \rightarrow \mathbf{N}$; $\mathbf{N} \rightarrow B$. Similarly, one or more of the intermediate reactions might be a concurrent reaction or an opposing reaction.

The favourable influence of some inert powders—powdered glass, sand, and china clay—shows that the effect may be in part due to an action similar to the effect of finely-divided particles in promoting the evolution of gases from liquids. There is evidence to show that all catalytic agents do not act in the same way; thus the acid oxides of vanadium, uranium, and tungsten, and chromic oxide, phosphoric acid, and phosphorus pentoxide favour the evolution of chlorine;[2] oxide of silver, and the dioxides of lead and barium favour the formation of perchlorate.

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§ 7. Concurrent or Side Reactions

> Compounds are not marked by nature with chemical formulæ but by properties, and it is by these we have to distinguish them.—J. D. HENRICHS.

Attention must be again directed to the curious way potassium chlorate decomposes when heated. When potassium chlorate, $KClO_3$, is heated, not only is potassium chloride, KCl, formed, but, as G. S. Sérullas and N. A. E. Millon have shown, just after the development of oxygen has begun, the residue contains a considerable amount of potassium perchlorate, $KClO_4$. According to J. C. G. de Marignac, when the chlorate has lost from 4 to 5 per cent. of oxygen, there is between 64 and 65 per cent. of perchlorate, and between 12 and 13 per cent. of chlorate in the residue; and when the chlorate has lost between 8 and 9 per cent. of oxygen, the residue contains between 65 and 66 per cent. of perchlorate and no chlorate. Hence, part of the salt is transformed into perchlorate and part into oxygen and chloride. Contrary to the opinion of N. A. E. Millon, J. C. G. de Marignac could find no sign of the formation of potassium chlorite, $KClO_2$, at any stage of the process.[1] It will be observed that an indefinitely long array of possible equations could be deduced for the thermal decomposition of potassium chlorate, for, as J. Bottomley (1878) has shown, if potassium perchlorate and chloride, as well as oxygen, be the end-products of the reaction, the equation can be written:

$$2mKClO_3=2nKClO_4+2(m-n)KCl+(3m-4n)O_2$$

where m and n are any integers subject to the condition that $3m$ be not less than $4n$. For instance, if m be 11, and n be successively assigned values 1, 2, 3, . . . 8, the reaction can be symbolized by one of the following eight equations:

$$22KClO_3=2KClO_4+20KCl+29O_2$$
$$22KClO_3=4KClO_4+18KCl+25O_2$$
$$\ldots \quad \ldots \quad \ldots \quad \ldots$$
$$22KClO_3=16KClO_4+6\ KCl+O_2$$

and similarly when other values are assigned to m. It must be emphasized that most chemical equations represent unproved and simplified hypotheses as to the course of reactions. A chemical equation should, if possible, summarize ascertained facts, and symbols should not be treated as if equation-building were merely an algebraic operation.

The following illustrates one of the many possible ways [2] of building equations to satisfy the rules of chemistry *only when the initial and final products are known.* In the preparation of oxygen by the action of sulphuric acid, H_2SO_4, upon potassium dichromate, suppose the by-products are chromic sulphate, $Cr_2(SO_4)_3$, potassium sulphate, K_2SO_4, and water, and that it is desired to find their relative proportions: Write $xK_2Cr_3O_7+yH_2SO_4 \rightarrow zCr_2(SO_4)_3+uK_2SO_4+vH_2O+wO_2$. It follows that $x=u$ (K); $x=z$ (Cr); $7x=v+2w$ (O); $2y=2v$ (H); $y=3z+u$ (SO_4). There are here five algebraic equations and six unknowns; hence it is possible to solve these equations only in terms of any one of the unknowns, x, y, z, u, v, w—say u. Accordingly, $x=u$; $y=4u$; $z=u$; $v=4u$; $w=\frac{3}{2}u$. Obviously each of the unknowns must be a positive whole number, and $u=2$ is the *smallest number* which will satisfy this condition. In that case, $x=2$; $y=8$; $z=2$; $u=2$; $v=8$; $w=3$; or $2K_2Cr_2O_7+8H_2SO_4 \rightarrow 2Cr_2(SO_4)_3+2K_2SO_4+8H_2O+3O_2$.

In the numerous systems of balancing equations, there is a temptation to suppose that the result of the algebraic operation represents a real process. Chemical equations cannot be demonstrated by the manipulation of chemical symbols. J. von Liebig (1846) stigmatized this operation "a senseless form of jugglery." Practice in the art of balancing equations according to algebraic rules may have limited uses, but it is utterly bad if it conveys the impression that reactions must take place as the equation demands. Facility in the art may thus display ignorance, not learning. Accordingly, equation-building is not emphasized so much as formerly in modern works on chemistry.

The fate of the molecules of potassium perchlorate.—When potassium chlorate is heated, part of the chlorate decomposes into potassium chloride and oxygen: $2KClO_3 \rightarrow 2KCl+3O_2$, and part oxidizes another part of the chlorate into potassium perchlorate, $KClO_4$; in symbols, $KClO_3+3KClO_3 \rightarrow KCl+3KClO_4$. These two reactions proceed side by side—concurrently, yet independently. Measurements of the relative proportions of potassium perchlorate and oxygen formed at different temperatures show that the potassium perchlorate reaction proceeds nearly twice as fast as the other reaction. The lower the temperature, the greater the relative speed of the perchlorate reaction. Hence, as the potassium perchlorate accumulates in the system, the molten mass becomes more and more viscid, and if the temperature be below the melting point of potassium perchlorate (610°), the mass solidifies when enough potassium perchlorate has accumulated in the system, even though the temperature be higher than the melting point of potassium chlorate (340°). When the temperature is raised high enough, the potassium perchlorate decomposes into potassium chloride and free oxygen. Here again the opening and closing scenes are represented by the equation: $KClO_4 = KCl + 2O_2$; but the whole reaction can be perhaps better represented by the scheme:

$$6KClO_3 \begin{array}{l} \nearrow \overset{\text{Between 340–610°}}{KCl+3KClO_4} \overset{\text{Above 610°}}{\longrightarrow} 4KCl+6O_2 \\ \searrow 2KCl+3O_2 \end{array}$$

or generally remembering our ignorance of the molecular weight of the molecules of solid potassium chlorate, etc.

$$(m+n)KClO_3 \begin{array}{l} \nearrow \overset{\text{Between 340–610°}}{\tfrac{1}{4}mKCl+\tfrac{3}{4}mKClO_4} \overset{\text{Over 610°}}{\longrightarrow} mKCl+\tfrac{3}{2}mO_2 \\ \searrow nKCl \quad +\tfrac{3}{2}nO_2 \end{array}$$

The final products of both reactions are potassium chloride and oxygen, and this is the sole justification for representing the reaction by the equation $2KClO_3 \rightarrow 2KCl+3O_2$. The fact that no appreciable quantity of potassium permanganate is formed when a mixture of potassium chlorate and manganese dioxide is decomposed, shows that the catalytic agent particularly favours one of the two reactions.

This view of the mechanism of the decomposition of potassium chlorate by heat shows how the relative proportions of potassium chloride and perchlorate, and oxygen depend on the temperature, and almost an infinite number of equations are possible. This must be borne in mind when reading many text-books, for the reaction is often represented by a set of complex equations—*e.g.* P. F. Frankland and J. Dingwall[3] represented the reaction by $8KClO_3=5KClO_4+3KCl+2O_2$ at a moderate heat, followed by $2KClO_3=KClO_4+KCl+O_2$ at a higher temperature; and finally, at a still higher temperature: $KClO_4=KCl+2O_2$. It can be shown that all so far proposed are special cases of the simple equations described in the text.

The cyclic reactions between the manganese dioxide and potassium chlorate proceed rapidly at a temperature much lower than that at which the perchlorate reaction has acquired an appreciable velocity. In fine, the catalytic agent accelerates at least one of the two concurrent reactions. It must not be supposed that the above outline gives a complete representation of this remarkable reaction. The products of the reaction may interact with themselves or with the catalytic reagent. In some cases part of the oxygen comes off as ozone, and the products of the reaction may contain a little chlorine. Traces of potassium permanganate have been detected among the residual products. The chlorine and potassium permanganate are probably formed by a reaction between the potassium chloride and the manganese dioxide.

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§ 8. The Physical Properties of Oxygen

Oxygen is at ordinary temperatures a colourless gas without smell. H. V. Regnault (1847)[1] found that the **weight of a litre** of oxygen at 0° and 760 mm. at Paris weighs 1·42980 grms., and this value corrected by J. M. Crafts (1888) for the difference in volume between the full and the vacuous globe gave 1·43011 grms., and corrected by J. Thomsen for 45° latitude at sea level, 1·42929. P. von Jolly's value at Paris is 1·42892 grms., when corrected by Lord Rayleigh, 1·42971. E. W. Morley found for the weight of a normal litre of oxygen $1{\cdot}42900 \pm 0{\cdot}000034$ grm. A. Leduc also found 1·42939 grms. in 1891, and 1·4293 grms. in 1896, at Paris. Lord Rayleigh (1893) gave 1·42952 grms. at n.p.t.; and J. Thomsen found 1·42904 grms. at n.p.t. when reduced to 45° latitude and sea level. E. W. Morley (1896) gave 1·42900 grms., J. Thomsen 1·42906 grms. at 45° and sea level. A. Jaquerod and A. Pintza (1904) gave 1·4292 grms.; A. Jaquerod and F. L. Perrot (1905), 1·42893 grms.; P. A. Guye's calculation of R. W. Gray's determination (1905) gave 1·42896; A. Jaquerod and M. Tourpaïan (1911), 1·4290; and A. F. O. Germann (1915), 1·42906. The best representative value for the weight of one litre of oxygen under these conditions is taken to be **1·42905** grms. A. F. de Fourcroy, L. N. Vauquelin, and B. R. Séguin found the **relative density** of oxygen to be 1·087; R. Kirwan, 1·103; H. Davy, 1·088; W. Allen and W. A. Pepys, 1·088; J. B. Biot and F. J. Arago, 1·1036; T. Thomson, 1·1056; T. de Saussure, 1·1056; P. L. Dulong and J. J. Berzelius, 1·1026; H. Buff, 1·106; J. B. A. Dumas and J. B. J. D. Boussingault, 1·1057; J. von Wrede, 1·1052. The gas in these early determinations was often saturated with moisture, and the measurements afflicted with numerous errors so that they are only of historical value. Later more accurate determinations are by H. V. Regnault, who found the **relative density** of oxygen, air unity, to be 1·10564; P. von Jolly, 1·10505; J. P. Cooke, 1·10534; A. Leduc, 1·10506 (1891) and 1·10523 (1896); J. Giesen with the microbalance, 1·1051; and Lord Rayleigh, 1·10530. The reported numbers for the relative density of oxygen are between 15·861 and 15·96 when hydrogen is unity. The best representative values are taken to be **1·10523** when air is unity, and **15·87** when hydrogen is unity. Lord Rayleigh (1908–11) found no appreciable difference in the density of oxygen prepared from different sources—the electrolysis of water heating potassium chlorate or potassium permanganate—outside the limits of experimental error. The vapour density of oxygen at −182° is normal.

According to J. Dewar, the specific gravity of liquid oxygen at 760 mm. and −182·5° is 1·1181; at −195·5°, 1·1700; and at −210·5°, 1·2386. J. Drugman and W. Ramsay[2] give 1·1321 at −183·6° and 759 mm., and 1·1310 at −183·3° at 762 mm. The **specific volume** of the liquid is then 0·8838; and the molecular volume 28·28. According to G. le Bas, the atomic volume of oxygen at the critical temperature is 26·5; the atomic volume of terminal oxygen in organic compounds is 7·2, and of ethereal oxygen, 10·8. J. Dewar estimates the molecular volume at absolute zero to be 21·21. E. C. C. Baly and F. G. Donnan give the interpolation formula $1{\cdot}248874 - 0{\cdot}00481(T-28)$ for the density of the liquid oxygen at a temperature between 69·28° K. and 88·94° K. The specific gravity of solid oxygen at −252·5° is 1·4256. J. Dewar represents these results by the expression $1{\cdot}5154 - 0{\cdot}004420T$, where T denotes the absolute temperature; otherwise expressed, liquid oxygen is about 1·13 times as heavy as an equal bulk of liquid water at 4°. J. K. H. Inglis and J. E. Coates have measured the specific gravity of mixtures of liquid oxygen and nitrogen.

The **weight of an oxygen atom** is $16 \times 1{\cdot}56 \times 10^{-24}$ grm.; the mean **diameter of the molecule** of oxygen $3{\cdot}62 \times 10^{-8}$ cm.; the mean **free path** of the molecule $6{\cdot}3 \times 10^{-6}$ cm.; the **number of molecules** per c.c. is $2{\cdot}75 \times 10^{19}$; the **collision frequency** $1{\cdot}64 \times 10^{29}$ per sec. per c.c. of gas; and the **molecular velocity** is 42,500 cm. per sec.

The value of J. D. van der Waals' $a=0·00273$, and his $b=0·00142$.[3] L. L. Grunmach calculates the molecular weight of liquid oxygen to be 41·51. The **viscosity** of oxygen at 0° is 0·001873; A. von Obermayer gives 0·000189; and K. Schmitt, 0·0001926. K. L. Yen claims $\eta=0·000204235$ at 23° and 760 mm. with an accuracy of 0·15 per cent. The viscosity increases with a rise of temperature such that at $\theta°$ A. von Obermayer found that the viscosity is $0·0001928(1+0·000283\theta)$; the observed value at 20° is 0·0002060; at 99·74°, 0·0002485; and at 185·8°, 0·0002885, or $0·0001878(1+0·003665\theta)^{0·787}$; W. Sutherland gave for the viscosity η at $\theta°$, $\eta=\eta_0\{(273+T)/(T+C)\}(T/273)^{\frac{3}{2}}$, where $C=127$; F. Kleint gives $C=136$; H. Markowsky, 138; and Lord Rayleigh, 128·2. According to O. Völker,[4] the viscosity decreases on a falling temperature, being 0·0001693 at −39·48°; 0·0001474 at −76·12°; 0·0001128 at −129·8°; and 0·0001050 at −152·5°. The **surface tension**[5] of liquid oxygen is 13·074 ± 0·066 dynes per cm., and the **specific cohesion** is 23·038. The molecular weight by R. Eötvös' formula is 41·51, so that the molecules of the liquid are rather more complex than corresponds with the formula O_2. E. C. C. Baly and F. G. Donnan, however, find the molecular surface energy $\sigma(Mv)^{\frac{2}{3}}=1·917(153·77-T)$, which gives a constant 1·917, not far from that required for a normal liquid with molecules O_2. According to P. L. Dulong,[6] the **velocity of sound** in oxygen gas at 0° is 317·17 metres per second at 0°; and S. R. Cook finds the velocity is 328·55 metres per second at 21°; 282·4 at −28·4°; 264·26 at −66·5°; 210·12 at −137·5°; and 173·92 at −183·0°.

E. H. Amagat[7] has investigated the **isothermal *pv*-curves** for Boyle's law at 0°, 15·65°, 99·50°, and 199·50° for pressures from one to 1000 atm., and for 0° and 15·6° up to 3000 atm. The values for 0° are:

Pressure	1	500	1000	1500	2000	2500	2900 atm.
Volume	1·00000	0·00231	0·00174	0·00153	0·00141	0·00133	0·00128
pv	1·0000	1·1570	1·7360	2·2890	2·8160	3·3238	3·7120

There is a minimum in the curve for $pv=0·9135$ near 150 atm. and 0°; for $pv=0·9920$ near 150 atm. and 15·65°; and the minimum was not observed at higher temperatures. According to A. Leduc, the compressibility of oxygen[8] at 11·2°, $-(d(pv)/dp)/pv$, is 0·00076. A. Jaquerod and O. Scheuer give the compressibility of oxygen between 400 and 800 mm. pressure as 0·00097; Lord Rayleigh gives 0·00094; and D. Berthelot, 0·00085. In 1886, C. Bohr measured the value of *pv* for pressures less than normal, and concluded that at a pressure of 0·70 mm., as indicated in Fig. 3, there is a break in the curve showing the relation between the pressure and the product *pv*. C. Bohr's observation was confirmed by E. C. C. Baly, W. Ramsay, A. Campetti, and A. Batelli; and it was thought to agree with the anomalous result in the radiometer repulsion of oxygen at a pressure of 0·76 mm. which was found by W. Crookes to be six to twelve times as great as that of nitrogen or of carbon monoxide or dioxide; and of H. Ebert's experiments on the dark space in vacuum tubes. It might be thought that experimental work with all this backing could be accepted with some degree of confidence. W. Sutherland[9] interprets the result as an effect of the spontaneous change of oxygen into ozone, at a certain degree of rarefaction, and with increasing rarefaction the transformation of oxygen into ozone continues so as to keep the number of molecules of ozone per unit volume constant, when all the oxygen molecules are used up, ozone alone remains, and it follows Boyle's law. No chemical test enabled R. Threlfall and F. Martin to detect ozone in suitably expanded oxygen. Neither Lord Rayleigh nor M. Thiesen could establish Bohr's

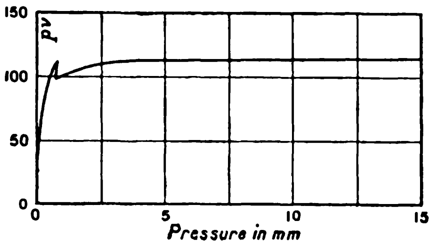

FIG. 3.—C. Bohr's Critical Value in the *pv*-curve of Oxygen at 0·7 mm. pressure.

anomaly. Lord Rayleigh found that there is no deviation from Boyle's law exceeding one part in 4000 for pressures between 0·01 and 150 mm. of mercury. M. Thiesen attributes Bohr's anomalous result to some unrecognized experimental error. Liquid oxygen is very compressible in comparison with many other liquids—*vide* water; A. Eucken found for the compressibility, β, between 10 and 20 atm., $\beta=1\cdot95\times10^{-3}$ kgrm. per sq. cm.; and calculated from the relation $C_p-C_v=Tv\alpha^2/\beta$, at 20·4° K., $\beta=2\cdot06\times10^{-3}$ kgrm. per sq. cm.

The **coefficient of thermal expansion** of oxygen gas is given by P. von Jolly[10] as $\alpha_p=0\cdot00367430$; H. K. Onnes' value for the liquid oxygen is $\alpha=00157$ at −252·6°, or 20·4° K. The **thermal conductivity** of oxygen[11] at 0° is 0·00005694, and between 7° and 8°, 0·0000563; S. Weber gives $5\cdot768\times10^{-5}$. The **specific heat** at constant pressure,[12] C_p, is 0·2175; or from 20° to 440° $C_p=0\cdot224$; and from 20° to 630°, 0·230. The specific heat at constant volume is 0·1544; or, the molecular heat at constant volume, at the absolute temperature T, is represented by W. Nernst and H. von Wartenberg by $4\cdot68+0\cdot00026T$ cals. per gram-molecule. For constant pressures the molecular specific heat may be taken as $C_p=6\cdot50+0\cdot0010T$, P. A. Müller, and O. Lummer and E. Pringsheim's measurement of the ratio of the two specific heats of oxygen is 1·398 from 5° to 14°; and 1·402 from 16° to 20°. G. N. Lewis and M. Randall give for the best representative value of the molecular heat of oxygen gas, $C_p=6\cdot50+0\cdot0010T$, which gives at 0 , 6·77; H. V. Regnault found 6·85; and M. Pier 6·89. The equation also gives 8·77 at 2000°, while M. Pier found 6·70. The higher values of L. Holborn and L. Austin, and of A. Eucken were obtained indirectly with oxygen admixed with nitrogen. The **entropy** of oxgyen gas at 25°, calculated by G. N. Lewis and G. E. Gibson, is 48·23 per gram-molecule, when the increase of entropy from absolute zero to the first transition point T is $\phi=\int C_p d\log T=2\cdot20$; $17\cdot5/23\cdot5=0\cdot74$ is the entropy of the transformation to the second form; the increase of entropy when the temperature of the solid rises from the first to the second transition temperature is 2·58; and $167\cdot4/42\cdot5=3\cdot94$ is the entropy of the second transition temperature; and the increase of entropy in rising from the second transition temperature to the melting point is 2·62; the increase of entropy in passing from the solid to the liquid state is $105\cdot5/54\cdot1=1\cdot95$; in passing from the melting to the boiling point, 6·52; in passing from the liquid to the gaseous state, $1599/90\cdot3=17\cdot72$; and in passing from the boiling point to 298° K., 7·96.

For a long time oxygen proved incoersible to all attempts to liquefy it by compression and cooling. J. Natterer, for instance, obtained no liquid at a pressure of 1354 atm. On the 16th December, 1877, L. Cailletet, and a little later R. Pictet,[13] obtained the liquid; and soon afterwards, S. von Wroblewsky, K. Olszewsky, J. Dewar, and many others prepared the liquid in quantity and investigated its properties. The **critical temperature** of oxygen is between −113° and −119°—say −118°; the **critical pressure** lies between 44·1 and 50·0 atm.—say 50 atm.; and the **critical volume** is 0·00426. If therefore the temperature is near but below or at −119°, a pressure of 50 atm. will liquefy the gas; and if the temperature exceeds −119° no pressure, however great, can liquefy the gas. Liquid oxygen has a pale blue colour. L. Grunmach found the **boiling point** of oxygen to be −182·65° at 762·22 mm. pressure; its vapour pressure[14] at −182·4° is 800 mm.; at −193°, 200 mm.; and at −211·2°, 7·5 mm. K. Scheel gives for the boiling point of oxygen at a pressure p mm. of mercury, $-183\cdot0^\circ+0\cdot01258(p-760)-0\cdot000007(p-760)^2$. The vapour pressure of liquid oxygen at T° absolute is given by $\log p=-399/T+1\cdot75\log T-0\cdot0051T+6\cdot9484$. According to W. P. Juliusberger, the **vapour pressure** between −212° and −119° is given by $\log_{10} p=3\cdot54595-313\cdot7T^{-1}+1\cdot40655\log_{10} T$ mm. The **latent heat of vaporization** of liquid oxygen is 58·0 cals. per gram, or 1856 cals. per gram-molecule. The last-named constant does not vary linearly with temperature, since at −183° the latent heat of vaporization is 52·09 cals.; at −201·5°, 59·10 cals. H. Alt's value at 760 mm. is 50·97 cals. per gram; A. Eucken's value is 1599 cals. per gram-molecule. J. Dewar (1896) cooled liquid oxygen by a spray of liquid nitrogen and obtained a hard pale blue solid with a **melting point** −227° at 0·9 mm. pressure. According to A. Eucken, the melting point is 54·1° K., or −218·9°; and the **latent heat of fusion** of oxygen is 105·5 cals. per gram-molecule.

There are signs of two transition points respectively at −249·5° and −230·5°, in the heating curve of solid oxygen. These are supposed to correspond with at least three **allotropic forms** of the solid element. A. Eucken (1916) estimates that the heat of the γ to β transformation is 17·5 cals. and of the β to α 167·4 cals. With the previous notation, therefore,

$$\alpha\text{-Oxygen}_{\text{solid}} \overset{-249{\cdot}5^\circ}{\rightleftharpoons} \beta\text{-Oxygen}_{\text{solid}} \overset{-230{\cdot}5^\circ}{\rightleftharpoons} \gamma\text{-Oxygen}_{\text{solid}} \overset{-218{\cdot}9^\circ}{\rightleftharpoons} \text{Oxygen}_{\text{liquid}} \overset{-182{\cdot}5^\circ}{\rightleftharpoons} \text{Oxygen}_{\text{gas}}$$

It is very unusual to find the heat of fusion less than the heat of transition such as is the case with solid oxygen. A. Eucken found the molecular heats of the different forms of solid oxygen to be: α-oxygen or oxygen III to be $C_p=2{\cdot}5$, $C_v=2{\cdot}48$ at 17·0° K., and $C_p=4{\cdot}42$, $C_v=4{\cdot}28$ at 21·8° K.; β-oxygen, or oxygen II, $C_p=5{\cdot}92$, $C_v=5{\cdot}62$ at 26·95° K., and $C_p \doteq 10{\cdot}52$ and $C_v=9{\cdot}12$ at 39·5° K.; γ-oxygen, or oxygen I, $C_p=11{\cdot}0$ at 44·7° K., and 10·76 at 51·3° K. The value of C_v is here calculated from the value of C_p from W. Nernst and F. A. Lindemann's relation $C_p-C_v=ATC_p^2$, where A is a constant $3{\cdot}2\times10^{-4}$. A. Eucken further gave for liquid oxygen, $C_p=12{\cdot}81$ at 57·4° K.. and 12·62, at 73° K., Debye's function=113.

W. Wahl [15] found that oxygen becomes viscid when cooled near to the point of solidification, and **crystals** grow in the viscid mass very slowly. If the cooling be rapid, a vitreous glass is formed. The crystals which grow in the cooling mass are dark between crossed nicols, but their crystalline form has not been established. If the oxygen be cooled by boiling hydrogen, a fine-grained mass of double refracting crystals belonging to the hexagonal system is formed. The transition point of α- to β- oxygen is not far below the melting point. Most of the physical constants of solid oxygen, determined at the boiling point of hydrogen, refer to the second crystalline form. J. Dewar found that when the charcoal vacuum was turned off, the vapour pressure remained near 0·46 mm. for some time and then rose rapidly to 1·11 to 1·12 mm. and then remained constant during melting. W. Wahl suggests that 0·46 mm. is the vapour pressure of the α- and β-crystals at the triple-point; and 1·12 mm. the vapour pressure of the α-crystals, liquid and vapour. The existence of two crystalline modifications of oxygen is interesting in view of the polymorphism of sulphur, and the analogies between the compounds of sulphur and oxygen. Ozone also is polymerized oxygen. The phenomena observed by I. Langmuir [16] to be associated with the formation of atomic hydrogen are largely duplicated when oxygen is substituted for hydrogen. The resulting **atomic oxygen** reacts with tungsten even at liquid air temperatures.

The mean **index of refraction** of oxygen gas is less than that of any other gas; for white light $\mu=1{\cdot}000270$; for the C-ray, 1·000255; for the G-ray, 1·000294; for the E-ray, 1·000315: and for the green mercury line, $\mu=1{\cdot}0002727$. E. Mascart (1877),[17] L. Lorenz (1880), H. C. Rentschler (1908), and C. and M. Cuthbertson (1909) have determined the **dispersion** of oxygen. The latter find for wave-lengths, from 4861 to 6563, Cauchy's formula $\mu=1+0{\cdot}00026509\lambda^{-1}+(1+7{\cdot}33\lambda^{-2}\ 10^{-11})$ holds good; but the general results with Cauchy's formula are not very good. Better results are obtained with a formula of the type used by W. Sellmayer, with the dispersion formula $\mu-1=c/(n_0{}^2-n^2)$, where n_0 is the frequency of the free vibration which has received a theoretical interpretation from the electron theory of P. Drude. The constants are $\mu-1=3{\cdot}397\times10^{27}/(12804\times10^{27}-n)$. The index of refraction of liquid oxygen for the D-ray is, according to G. D. Liveing and J. Dewar, 1·2236. According to J. Dewar, the atomic refraction of the liquid for the D-line is 3·182, and this is not far from J. H. Gladstone's value 3·0316 for gaseous oxygen. J. H. Gladstone gives for the atomic refraction of singly linked oxygen in combination 2·8; and of doubly linked oxygen 3·4; and J. W. Brühl 1·506 for hydroxylic oxygen; 1·655 for ethereal oxygen; and 2·328 for carbonylic oxygen. J. F. Homfray calculates the atomic refraction of quadrivalent oxygen to be 2·73. J. W. Brühl also gives for the atomic dispersion $R_\gamma - R_\alpha = 0{\cdot}019$ for hydroxylic oxygen; 0·012 for ethereal oxygen; and 0·086 for carbonylic oxygen. According to L. H. Siertsema, **E. Verdat's constant** for oxygen at a pressure of 10 k.grams. per sq. cm. and 7°, is $0{\cdot}0002722\lambda^{-1} + 0{\cdot}00001915\lambda^{-3}$ for wave-lengths between $0{\cdot}423\mu$ and $0{\cdot}684\mu$. For pressures between 38 and 100 atm., the constant changes proportionally with the density of the gas.

In 1864, J. Plücker and W. Hittorf[18] established the fact that one and the same element can under different conditions produce more than one spectrum. Several different spectra of oxygen have been recorded. A. Schuster distinguishes four main **spark spectra of oxygen**: (i) The *elementary line spectrum* which appears at the highest temperature to which oxygen can be subjected such as occurs when the Leyden jar and air-break are introduced into the electric circuit. This spectrum consists of a number of lines particularly in the more refrangible part of the spectrum. (ii) The *compound line spectrum* appears at a lower temperature than the elementary line spectrum, and predominates when the Leyden jar and air-break are removed and the exhaustion of the tube is not very high; if the exhaustion is high a special spectrum from the negative glow is superposed on the four-line spectrum. There are: one red line, two green lines, and one blue line as illustrated in Fig. 4. According to A. Schuster, these four lines have the wave-lengths 6156·86 (red); 5435·55 (green); 5329 41 (green); and 4367·62 (blue). With an increase of pressure, the more refrangible lines widen first while the blue line remains sharp.

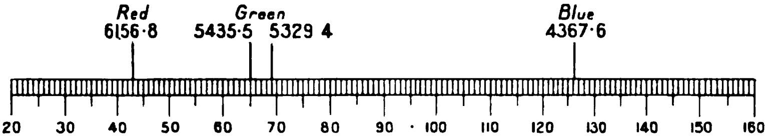

FIG. 4.—The Compound Line Spectrum of Oxygen in a Geissler's Tube.

(iii) The *continuous spectrum* appears at the lowest temperature at which oxygen becomes luminous. According to E. Becquerel, an excess of oxygen in the oxy-hydrogen flame produces a yellow colour probably due to the continuous spectrum of oxygen. (iv) The *negative-glow spectrum* was first observed by A. Wüllner in 1872, and is always seen in the glow surrounding the negative electrode in oxygen. It consists of five bands—three red, two green. The least refrangible red band is so faint that it may escape observation, and the two red bands are so close that with a small dispersion they appear as one line. With high optical powers the two green bands can be resolved into a series of lines. A. Schuster further described the appearance of a vacuum tube filled with pure oxygen as it is sparked while being gradually exhausted:

> At first the spark has a yellow colour, and the spectrum is perfectly continuous. Almost immediately, however, four lines are seen in the capillary part above the continuous spectrum. One of these lines is in the red, two are in the green, and one is in the blue. The discharge still passes as a narrow spark throughout the length of the tube. In the wide part the spectrum remains continuous, and it extends more towards the red than in the capillary part. It seems as if the four lines had taken away part of the energy of the continuous spectrum. As the pressure diminishes, these lines increase considerably in strength, the spark spreads out in the wide part of the tube, and the intensity of the continuous spectrum is, therefore, considerably diminished, while it still forms a prominent part in the spectrum of the capillary part. When the pressure is small the continuous spectrum decreases in intensity. At the same time the negative glow, with its own characteristic spectrum, gradually extends through the negative half of the tube into the capillary part. The continuous spectrum has now entirely disappeared; the bands of the negative pole and the four lines stand out on a perfectly black background. It is under these conditions that the change from the compound line spectrum to the elementary line spectrum is best studied. The mere insertion of the Leyden jar, I find, makes hardly

> any difference; the jar does not seem to be charged at all. If, in addition to the jar, we insert a movable air-break, which can be opened or closed at will, while we look through the spectroscope, we shall be able to see alternately two perfectly distinct spectra. If the air-break is closed, the four lines of the compound spectrum only are seen; if the air-break is opened, these four lines will disappear entirely, and the elementary line spectrum will come out.

The spectrum of oxygen is peculiar in that it does not show up clearly in the presence of other gases; for example, air in a vacuum tube gives the same spectrum as nitrogen. All carbonaceous impurities should be excluded from oxygen whose spark spectrum is under investigation, because the carbon is readily oxidized to carbon monoxide at the high temperature and the spectrum of the impurity may be the more brilliant, and entirely eclipse that of the oxygen. Several descriptions of the carbon monoxide spectrum have been published [19] which have been attributed to oxygen. C. Runge and F. Paschen [20] reduced the line spectrum of oxygen to two series of triplets and two series of doublets. All four series can be represented by formulæ of the type $\lambda^{-1}=a+bn^{-2}-cn^{-3}$, where a, b, and c are constants. J. J. Balmer's formula—*vide* hydrogen—is a special case of this more general expression. B. Reismann found that when a Geissler's tube of oxygen is excited by a direct current discharge the series, elementary line, and banded spectra appear at the cathode, and only the series spectrum at the anode. J. Stark and co-workers, and H. Wilsar have measured the spectrum of oxygen canal rays. The **Stark effect** with the spectrum of oxygen has been examined by U. Yoshida.

The **absorption spectrum of oxygen** has attracted some attention because certain dark lines of the solar spectrum—the so-called telluric lines—may be in part derived from the absorptive power of atmospheric oxygen. The absorption spectrum of oxygen is very feeble and it must be examined in a long tube, with the highly compressed or liquefied gas—since the two are practically identical. J. Janssen [21] used a tube 20 to 60 metres long, with the gas at 27 atm. pressure. There are two strong absorption bands in the red corresponding with the *A* and *B* Fraunhofer solar lines with wave-lengths from 6340 to 6225; a strong band in the yellow from 5820 to 5730; a feeble band in the green at 5350; and a feeble one in the blue at 4810. O. C. Lester found two series of absorption bands in the oxygen of the solar spectrum. J. Tyndall could scarcely detect any absorption of the invisible heat radiations by oxygen at atmospheric pressure. W. Burmeister found gaseous oxygen has no absorption bands in the infra-red.

The oxygen gas produced by heating potassium permanganate is positively electrified.[22] Liquid oxygen is virtually a non-conductor of electricity. For the phenomena associated with the ionization of oxygen, see hydrogen. The mean values of J. Zeleny's, A. P. Chattock's, and J. Franck's determinations of the velocity of the positive and negative oxygen ions when the electric discharge is in a field of 1 volt per cm. are respectively 1·32 and 1·83 cms. per second. The mean value of J. S. Townsend's and E. Salleo's determinations of the diffusion coefficient of the positive and negative ions per sq. cm. per sec. are respectively 0·0275 and 0·040. J. S. Townsend [23] gives $dn/dt=-3380n^2$, where n denotes the concentration of the ions, and dn/dt the velocity of combination of the ions to form ordinary molecules. A. Erickson and P. Philips have studied the effect of temperature on this reaction. The potential of the **oxygen electrode** is discussed later. The **discharge potential** has been discussed in connection with hydrogen. W. C. Röntgen found the minimum potential for a + point to be respectively 2402 and 1975 volts for pressures 205 and 110 mm., and J. Precht, 2800 volts for a + point, and 2350 volts for a − point with a pressure of 760 mm. A. L. Hughes and A. A. Dixon [24] found the **ionizing potential** is dependent on the least energy necessary to ionize the molecules of a gas by the impact of electrons, and amounts to 9·2 volts for oxygen; J. Franck and G. Hertz found 9 volts; F. M. Bishop, 9 volts; and the value calculated by K. T. Compton's formula $V=0{\cdot}194(K-1)^{-\frac{1}{2}}$ is 8·4 volts, where V denotes the ionizing potential, and K the specific inductive capacity.

The **dielectric constant** of liquid oxygen[25] lies between 1·465 and 1·491 at −182°. H. Rohmann gives the dielectric constant of oxygen gas at 0° and one atm. pressure as 1·000547; according to A. Occhialini, oxygen gas at 13·5° and compressed to a density of 35 has a dielectric constant 1·01831, and at a density 110, 1·05843. The results agree with Mossotti and Clausius' formula but not with $(K-1)/D=$constant. In 1847, M. Faraday's experiments indicated that oxygen gas is diamagnetic, but it was subsequently shown to be paramagnetic having a magnetic susceptibility of $+0{\cdot}12\times10^{-6}$ at 20° and 1 atm.; and $+6{\cdot}2\times10^{-6}$ at 16° and 40 atm. pressure (volume units). E. Becquerel noticed the magnetic qualities of oxygen—more particularly of wood charcoal saturated with adsorbed oxygen. The magnetic qualities are greatly enhanced when oxygen is condensed in the liquid state. Liquid oxygen then shares with iron, nickel, and cobalt the property of being magnetic. If the **magnetic moment** of iron be unity, that of liquid oxygen is 0·001. When a little liquid oxygen is placed in a cup between the poles of an electromagnet, the liquid leaps up to the poles, and remains attached until all has evaporated.[26] If the current is cut off while the oxygen is attached to the poles of the electromagnet, the oxygen detaches itself. A thin test tube of liquid oxygen, suspended by a long thread, will attach itself to an electromagnet, and fall away as the current is cut off. The **magnetic susceptibility** of liquid oxygen 304×10^{-6} volume units or 241×10^{-6} mass units at −182°; 280×10^{-6} at −208°. For the solid, at −253° the magnetic susceptibility is 375×10^{-6} (mass units), and at −259°, 436×10^{-6}. At its freezing point therefore the magnetic susceptibility of liquid oxygen is nearly 1·3 times as great as that of solid oxygen.

The solubility of oxygen.—The solubility of oxygen in water is small; 100 vols. of water absorb nearly 5 vols. of oxygen at 0°. The absorption coefficient was measured by R. W. Bunsen[27] in 1855. L. W. Winkler (1891) and C. Bohr and J. Bock (1891) measured the coefficient of absorption of water between 0° and 100°; L. W. Winkler's results are rather lower than C. Bohr and J. Bock's. The latter are here indicated along with ω, the weight of gas in grams taken up by 100 grams of solvent at the indicated temperature and a total pressure—gas plus the vapour of the solvent—of 760 mm.:

	0°	4°	8°	12°	16°	20°	24°
β . .	0·04961	0·04496	0·04098	0·03732	0·03425	0·03171	0·02954
ω . .	0·00704	0·00637	0·00578	0·00526	0·00481	0·00443	0·00411

L. W. Winkler represented his results for the absorption coefficient β at $\theta°$ between 0° to 30° by the empirical formula $\beta=0{\cdot}04890-0{\cdot}0013413\theta+0{\cdot}04283\theta^2-0{\cdot}0629534\theta^3$; J. J. Fox's formula (1909) is $\beta=0{\cdot}04924-0{\cdot}0013440\theta+0{\cdot}0428752\theta^2-063924\theta^3$; C. Bohr and J. Bock's values between 25° and 100° are:

	25°	30°	40°	50°	60°	80°	100°
β . .	0·02904	0·02676	0·02326	0·02070	0·01893	0·01726	0·01679
ω . .	0·00403	0·00368	0·00310	0·00263	0·00221	0·00135	0·00000

Unit volume of water increases 0·00115 unit by the absorption of one volume of oxygen. Water is easily supersaturated with oxygen, and the excess is given off with difficulty.[28] W. E. Adenby and H. G. Becker have studied the rate of solution of oxygen in water.

According to G. Geffcken,[29] the solubility λ of oxygen in acids solutions at 15° and 25°, when λ for oxygen in water is 0·0363 (15°) and 0·0308 (25°) is:

	Hydrochloric acid.		Nitric acid.		Sulphuric acid.	
	15°	25°	15°	25°	15°	25°
½*N*-acid . .	0·0344	0·0296	0·0348	0·0302	0·0338	0·0288
2*N*-acid . .	0·0299	0·0267	0·0315	0·0284	0·0335	0·0251

According to A. Christoff, the solubility λ of oxygen in 95·6 per cent. *sulphuric acid* is 0·03166 between 17° and 20°; in 0·06162 per cent. acid, 13·30; in 0·03582 per cent. acid, 15·61; and in pure water, 0·03046. The value of λ for *potassium hydroxide* in ½*N*-solutions is 0·0291 (15°) and 0·0252 (25°), and for normal solutions, 0·0234 (15°) and 0·0206 (25°); with $\frac{1}{2}N$-solutions of ***sodium hydroxide***, λ=0·0288 (15°) and 0·0250 (25°); with normal solutions of sodium hydroxide, λ=0·0231 (15°) and 0·0204 (25°). Similarly, with $\frac{1}{2}N$-solutions of ***potassium sulphate***, λ=0·0294 (15°) and 0·0253 (25°), and with normal solutions, λ=0·0237 (15°) and 0·0207 (25°). With $\frac{1}{2}N$-solutions of ***sodium chloride***, λ=0·0308 (15°) and 0·0262 (25°); and with normal solutions, λ=0·0260 (15°) and 0·0223 (25°). The solubility of oxygen in salt solutions diminishes regularly with an increase in the concentration of the salt. C. G. MacArthur measured the solubility of oxygen in solutions of lithium, sodium, potassium, rubidium, cæsium, ammonium, magnesium, calcium, and barium chlorides; sodium and potassium bromide; potassium iodide, nitrate, and sulphate; and in sodium sulphate. The density determinations also furnished data for calculating the degree of hydration of the salts. C. G. MacArthur says that allowing for the hydration of the ions, the results show that particular ions increase the solubility to a definite extent which is specific for a particular ion. ***Sea water*** was found by F. Clowes and J. W. H. Biggs to dissolve a little more than 70 per cent. of the amount of oxygen dissolved by distilled water; and the amount dissolved diminishes regularly with the salinity of the water. According to J. S. Maclaurin, the absorption coefficient of oxygen in aqueous solutions of ***potassium cyanide*** is

KCy in 100 grms. solution . .	1	10	20	30	50 grms
Absorption coefficient . . .	0·029	0·018	0·013	0·008	0·003

The solubility of oxygen in organic solvents.—Oxygen is a little less than five times as soluble in *ethyl alcohol* as in water. According to E. E. O. Libarsch, the solubility of oxygen in unit volume of water is 0·0289, and in aqueous alcohol at 20° and 760 mm.

Per cent. alcohol . .	9·09	16·67	28·57	33·33	50·00	66·67	80·0
λ	0·0278	0·0278	0·0249	0·0267	0·0350	0·0495	0·056

The solubility thus decreases with increasing concentration of the alcohol; reaches a minimum with nearly 28 per cent. solutions, and again increases with increasing concentration. The variation of the absorption coefficient with temperature for 99·7 per cent. solutions of ethyl alcohol is β=0·2337 (0°), 0·2301 (5°), 0·2266 (10°), 0·2232 (15°), 0·2201 (20°), and 0·2177 (24°); he represents the absorption coefficient β for temperatures, θ, between 0° and 23·4°, by $\beta=0{\cdot}23370-0{\cdot}0374688\theta+0{\cdot}053288\theta^2$; with methyl alcohol and acetone, the values of λ are:

	0°	5°	10°	20°	30°	40°	50°
λ (methyl alcohol) .	0·31864	0·30506	0·29005	0·25374	0·21569	0·21569	0
λ (acetone) . .	0·2997	0·2835	0·2667	0·2313	0·1935	0·1533	0

and M. G. Levi represents the values for ***methyl alcohol*** by $\lambda=0{\cdot}31864-0{\cdot}002572\theta-0{\cdot}042866\theta^2$; and for ***acetone***, $\lambda=0{\cdot}2997-0{\cdot}00318\theta-0{\cdot}0412\theta^2$. With ***petroleum***, the absorption coefficient at 10° is 0·229, and at 20°, 0·202. C. G. MacArthur measured the solubility of oxygen in solutions of ***sugar***, and he found signs of an oxidation of the sugar. C. Bohr has measured the absorption of oxygen by blood.

The solubility of oxygen in solids.—Solids adsorb, or occlude, oxygen in an analogous manner to hydrogen.[30] G. Neumann found that if the following metals be heated to 450° in oxygen,

	Silver.	Gold.	Platinum.
Volumes of oxygen occluded	4·1–5·4	32·8–48·5	63·0–77·0

per volume of metal. ***Palladium*** is oxidized[31] to Pd_2O, or a mixture of Pd_2O and PdO. According to C. Engler and L. Wöhler, ***platinum***, like palladium, forms a true compound or a mixture of compounds: PtO and PtO_2. According to E. Goldstein,[32] the platinum electrode of a Geissler's tube rapidly absorbs oxygen when red hot. R. Lucas attributes the absorption of oxygen by platinum to the presence of iridium; pure platinum, says he, absorbs no oxygen. The case of silver[33] is peculiar. Molten *silver* dissolves about ten times its volume of oxygen, and gives it up again on cooling. In cooling, a solid skin forms on the exterior surface; as the interior cools, the gas bursts through the solid crust, driving out a spurt of the still fluid metal—the phenomenon is called the *spitting* or *rockage* of silver. Molten *platinum* behaves in a somewhat similar way. A little oxygen still remains dissolved in the cold metal, and this can be recovered by heating it to redness in vacuo.

According to S. Kern,[34] *steel* dissolves from 0·025 to 0·05 vol. of oxygen. H. V. Regnault[35] said that *mercury* dissolves a little oxygen, but E. H. Amagat found no evidence of this between 0° and 100°, even at 420 atm. pressure. According to F. Leblanc, molten *litharge* dissolves oxygen which is rejected when the oxide solidifies. *Charcoal*[36] dissolves 9·25 its volume of oxygen at 12° and 724 mm. pressure, as shown by T. de Saussure in 1814 and according to L. Joulin, 26 vols. at 0° and 2·36 atm. pressure, and 230 vols. at —185°. According to J. L. Baerwald, with one volume of charcoal at 760 mm. pressure, the volume of oxygen absorbed at different temperatures is

	10°	0°	−10°	−50°	−100°	−150°
Oxygen absorbed	61·7	66·7	70·0	105·0	165·0	245·0 vols.

Neither platinum nor palladium show this remarkable increase in its own absorptive power at low temperatures. According to G. Craig, the coke from lignite which has been heated to redness and cooled with the exclusion of air, absorbs oxygen with the formation of water.

The **coefficient of diffusion** of oxygen into carbon dioxide is 0·136, and of hydrogen into the same gas, 0·538. T. Graham[37] has shown that oxygen travels through indiarubber, 2½ times as rapidly as nitrogen. Hydrogen travels 5½ times as fast as nitrogen. According to M. Berthelot, cold glass is impermeable to oxygen, but at 650° he found a glass bulb lost 8 per cent. of the gas in 2 hours, and Jena glass at 800° scarcely lost any gas in 1½ hours. Oxygen does not diffuse through cold silver, but it does if the metal be heated, say at 800°; and L. Troost showed that at this temperature about 1700 c.c. of gas will travel through a sq. metre of the metal 1 mm. thick per hour, and 3300 c.c. if the plate is ½ mm. thick. The permeability of hot silver to oxygen is connected with its power of occluding this gas. For the diffusibility of oxygen through rubber, see hydrogen.

Liquid oxygen at —190° dissolves about 380 times its volume of nitrogen and the boiling point is then changed to —188·8°. The suggested cause of the discrepancies in the boiling point determined by different investigators is probably due to the contamination of the liquid with nitrogen. Liquid oxygen indeed rapidly absorbs nitrogen from the air[38]—Fig. 25, Cap. XI. J. K. H. Inglis and J. E. Coates studied the densities and partial pressures of solutions of oxygen and nitrogen, and J. K. H. Inglis the isothermal distillation of nitrogen and oxygen. Liquid oxygen readily dissolves liquid fluorine.

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§ 9. The Chemical Properties of Oxygen

Oxygen, so to speak, is the central pivot round which the whole of chemistry revolves.—J. J. Berzelius.

Oxygen is entirely unmatched among the rest of the elements both as regards the number and the varied character of its compounds.—W. A. Tilden.

The great chemical activity of oxygen is well typified by the quaint remarks which J. Priestley made about the gas. When a glowing splint of wood is plunged into oxygen it bursts into flame; the carbon of the wood is oxidized to carbon dioxide (CO_2). The inflammation of a glowing splint is often used as a test for oxygen. A mixture of nitrogen and oxygen containing less than 28·29 per cent. of the latter does not re-ignite a glowing splint, and if the mixture contains less than about 16 per cent. of oxygen the splint will be extinguished. Oxygen alone has no visible action on clear lime-water; but after a splint has burnt in the gas, the clear lime-water becomes turbid. Oxygen combines directly with most other elements, particularly at elevated temperatures, forming **oxides**.

The direct combination of oxygen with some of the elements can be illustrated by placing small dry pieces in deflagrating spoons, heating them until combustion begins, and then plunging each into a jar of oxygen. The glowing piece of *charcoal* burns very brightly and forms a gaseous oxide—carbon dioxide, CO_2. *Sulphur* burns with a lavender-blue flame, forming gaseous sulphur dioxide—SO_2—which has the peculiar odour characteristic of burning sulphur. The reaction is symbolized: $S+O_2=SO_2$; sulphur dioxide is soluble in water forming sulphurous acid—H_2SO_3—which reddens blue litmus solution—$H_2O+SO_2=H_2SO_3$. *Phosphorus* burns in oxygen vigorously and brilliantly, forming a white cloud of phosphorus pentoxide—P_2O_5. The reaction is represented: $4P+5O_2=2P_2O_5$. The phosphorus pentoxide dissolves in water, forming phosphoric acid—H_3PO_4. The reaction is written: $P_2O_5+3H_2O=2H_3PO_4$. The phosphoric acid reddens blue litmus. Metallic *sodium* treated in a similar way (spoon dry) burns with a bright yellow flame and gives a white oxide which dissolves in water, forming a solution of *caustic soda*. The solution turns red litmus blue. *Calcium* behaves similarly, but it burns with an orange-red flame. A piece of burning *magnesium* ribbon plunged in oxygen burns with an exceptionally brilliant flame. The white solid obtained is slightly soluble in water, and the solution turns red litmus blue. To show the combustion of *iron* in oxygen gas, tie a tuft of steel wool to the end of a stout iron wire by means of a piece of steel wire. Heat the end of the wool in a Bunsen's flame, until incipient combustion begins, and quickly plunge it into a jar of oxygen on the bottom of which a layer of water, sand, or asbestos paper has been placed. The wool burns with dazzling scintillations, the product of the reaction—iron oxide—falls to the bottom of the jar in fused globules. When cold, the oxide of iron resembles a blacksmith's scale. It is called black or magnetic oxide of iron—Fe_3O_4. The reaction is usually written: $3Fe+2O_2=Fe_3O_4$. Experiments showing the combustion of iron in oxygen date from G. C. Lichtenberg (1782).[1] The oxide of iron so formed is insoluble in water and has no effect on red or blue litmus.

Iodine, bromine, chlorine, fluorine, gold, platinum, and argon and its companions do not combine *directly* with oxygen. The reaction between metals and oxygen does not as a rule take place at ordinary temperatures, and heat is required. If the oxide is unstable at the temperature necessary for reaction, it will not be formed directly even though much heat be evolved in the formation of the oxide. Mercury at a high temperature does not appear to react with oxygen since the oxide, if formed, is immediately decomposed. The temperatures of formation and decomposition of the oxide are not far apart; with the oxides of silver and palladium, the temperatures of formation and decomposition are probably much nearer even than with mercury. Similar remarks apply to iodine and platinum oxides. The elements, nitrogen, fluorine, chlorine, and bromine, absorb energy when they unite with oxygen, and oxides can be formed indirectly or in some cases directly if the temperature is very high—*e.g.* nitrogen oxide.

Oxygen combines *indirectly* with all the elements excepting the argon group, fluorine, and possibly bromine. "Oxygen," said C. L. Berthollet (1803), "seems to take the lead of all substances in the extent and energy of its affinities," and, with perhaps the exception of fluorine, these words are true to-day. The energy which is degraded as heat when the different elements combine with oxygen, is a distinctive characteristic. The amount of heat liberated in combining with a gram-atom of the element is a rough indication of the avidity of the element for oxygen. Table I shows the heat developed during the formation of a gram-molecule of an oxide;[2] and also per gram-atom of the element united with oxygen. If no remark is made as to the state of aggregation—solid, liquid, gas—a solid is to be understood. If the metals be arranged in the order of their avidity or readiness to combine with oxygen, cæsium, potassium, and sodium will be found at one end of the series, while platinum and the argon family will be found at the other end. If the heats of formation of the oxides of the elements be plotted against the atomic weights, a periodic curve is obtained, corresponding approximately with the periodic curve obtained when many of the other properties of the elements are plotted against the atomic weights.

The preparation of the oxides.—The methods for preparing individual oxides are described when dealing with the respective elements. The following are common enough to merit the designation *general methods* : (1) By calcining the metal while freely exposed to air, *e.g.* tin gives stannic oxide, $Sn+O_2 \rightarrow SnO_2$; (2) By calcining the nitrate strongly, and subsequently washing the residue to remove the undecomposed nitrate, *e.g.* with copper nitrate, $Cu(NO_3)_2$, the action is represented : $2Cu(NO_3)_2 \rightarrow 2CuO+4NO_2+O_2$; with chromium nitrate : $4Cr(NO_3)_3 \rightarrow 2Cr_2O_3 +12NO_2+3O_2$; (3) By calcining the carbonate, *e.g.* with calcium carbonate : $CaCO_3 \rightarrow CaO+CO_2$. With barium and strontium carbonates it is better to mix the carbonate with powdered carbon (lampblack) before calcination. (4) By pouring a solution of alkali hydroxide or aqueous ammonia into a solution of the salt, washing the precipitated hydroxide, and afterwards calcining it to drive off the water, *e.g.* with ferric chloride and sodium hydroxide : $FeCl_3+3NaOH=Fe(OH)_3 +3NaCl$; the subsequent calcination of the ferric hydroxide, $Fe(OH)_3$, furnishes the required oxide : $2Fe(OH)_3 \rightarrow Fe_2O_3+3H_2O$.

TABLE I.—HEAT EVOLVED OR ABSORBED IN THE FORMATION OF THE OXIDES.

Oxide.	Cals. per gram molecule.	Cals. per gram atom.	Oxide.	Cals. per gram molecule.	Cals. per gram atom.	Oxide.	Cals. per gram molecule.	Cals. per gram atom.
H_2O (gas)	58·1	29·0	B_2O_3	272·6	136·3	Bi_2O_3	139·2	69·6
H_2O (liquid)	69·0	34·5	Al_2O_3	392·6	196·3	SO_2 (gas)	69·3	69·3
H_2O (solid)	70·4	35·2	Tl_2O	42·8	21·4	SO_2 (liquid)	91·9	91·9
Li_2O	140·0	70·0	Tl_2O_3	87·6	43·8	SeO_2	57·1	57·1
Na_2O	100·9	50·4	CO (gas)	29·2	29·2	WO_3	65·5	32·7
K_2O	98·2	49·1	CO_2 (gas)	97·2	97·2	Cl_2O (gas)	17·9	−8·9
Rb_2O	94·9	47·4	SiO_2	180·0	180·0	I_2O_5	45·3	22·6
Cs_2O	99·98	50·0	TiO_2	97·8	97·8	PbO	50·3	50·3
AgO	7·0	3·5	ZrO_2	177·5	177·5	PbO	63·4	63·4
Cu_2O	43·8	21·9	N_2O (gas)	—17·5	−8·8	SnO	70·7	70·7
CuO	37·7	37·7	NO (gas)	21·6	−21·6	SnO_2	141·3	141·3
Au_2O_3	11·5	5·8	NO_2 (gas)	2·0	−2·0	FeO	65·7	65·7
CaO	131·5	131·5	P_2O_5	365·3	182·6	Fe_2O_3	195·6	97·8
SrO	131·2	131·2	As_2O_3	156·4	78·2	Fe_3O_4	270·8	90·3
BaO	133·4	133·4	As_2O_5	219·4	109·7	CoO	64·1	64·1
BaO_2	145·5	145·5	Sb_2O_3	166·9	83·4	NiO	61·5	61·5
MgO	143·4	143·4	Sb_2O_5	231·2	115·6	MnO	90·9	90·9
ZnO	84·8	84·8	HgO	21·5	21·5	Mn_3O_4	328·0	109·3
CdO	66·3	66·3	PdO	21·0	21·0	MnO_2	125·3	125·3
Hg_2O	22·2	11·1	PtO	17·0	17·0			

In reviewing the oxides of all the elements, it will be apparent that the proportions of combined oxygen are not always the same. The elements, indeed, can be arranged roughly into natural groups determined by the composition and properties of what D. I. Mendeléeff regarded as the different typical oxides they form. This has been done in Table II.

Many of the elements form a number of different oxides, and in that case the same element might fall into two or more different groups. This is well illustrated by the family : iron, manganese, cobalt, and nickel. The RO oxides of these elements are readily oxidized to sesquioxides of the type R_2O_3, and these same elements also form still higher oxides of the type, RO_2, and, in the case of manganese, there is evidence of a yet higher oxide, Mn_2O_7. Under a pressure of about 12 atmospheres, at 480°, oxygen [3] oxidizes the oxides of lithium, sodium, potassium, and barium to peroxides of the type R_2O_2 ; and a small proportion of a peroxide is formed with cobalt and nickel oxides ; lead oxide gives red lead Pb_3O_4 ; antimony oxide gives the tetroxide Sb_2O_4; chromium sesquioxide gives chromium chromate Cr_2O_4 or $CrCrO_4$. Beryllium, calcium, strontium, zinc, cadmium, aluminium, boron, thallium, silicon, zirconium, tin, bismuth, molybdenum, tungsten, uranium, and ferric oxides do not change.

TABLE II.—OXIDES OF THE ELEMENTS.

Oxide.	Corresponding group of elements.	Character of oxide.
M_2O	(H), Li, Na, K, Cu, Rb, Ag, Cs, Au	Basic
MO	Be, Mg, Ca, Zn, Sr, Cd, Ba, Hg	Basic
M_2O_3	B, Al, Sc, Ga, Y, In, La, Yb, Tl	The first oxide B_2O_3 is weakly acidic; the others are basic
MO_2	C, Si, Ti, Ge, Zr, Sn, Ce, Pb	The first two are acidic; the last one is basic; and the others are both basic and acidic, becoming more basic with increasing atomic weight
M_2O_5	N, P, V, Nb, Di, Er, Ta, Bi	These oxides are acidic; Bi_2O_3 is also basic
MO_3	O, S, Cr, Se, Mo, Te, W, U	Acidic and become less and less acidic as the atomic weight increases; VO_3 is also feebly basic
M_2O_7	F, Cl, Mn, Br, I	Acidic. The highest oxide is represented by M_2O_7. No definite oxide of Br or F is known
MO_4	Fe, Ni, Co; Ru, Rh, Pd; Os, Ir, Pt	The first triad forms feebly basic sesquioxides; RuO_4 and OsO_4 are the only representatives of the highest oxide. These are feebly acidic. The lower oxides are feebly basic

Oxygen is closely related to the elements of the sulphur, selenium, and tellurium family. The changes in the physical characters of the oxides show regular gradations with increasing atomic weight in harmony with the periodic classification. Regularities have been traced in the specific gravity, atomic volume, volatility, stability, reactivity with water, heats of formations, etc. According to G. H. Bailey [4] in the even series of Mendeléeff's table:

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Li_2O	BeO	B_2O_3	CO_2	N_2O_5	CrO_3	Mn_2O_7	FeO_4
K_2O	CaO	Sc_2O_3	TiO_2	V_2O_5	MoO_3	——	RuO_4
Rb_2O	SrO	Yt_2O_3	ZrO_2	Nb_2O_5	WO_3	——	OsO_4

The oxides of the first four groups are so stable that they undergo no decomposition at temperatures below 1750°; nitrogen pentoxide decomposes below 50°, and, further on, the oxides are more stable the higher the atomic weight—uranium oxide, UO_3, appears to be an exception. In the horizontal series, the stability of the oxides decreases from left to right as the atomic weight increases. The behaviour of the RO_4 oxides of the eighth group is also in keeping with these generalities. Osmium octoxide is more stable than ruthenium octoxide, and there is a doubt about the existence of the corresponding iron compound.

Many substances are oxidized at ordinary temperatures—*e.g.* nitric oxide, a colourless gas, oxidizes to reddish-brown nitrogen, peroxide, NO_2, in air at ordinary temperatures; the alkali metals; ferrous and manganous hydroxides; etc. In some cases the oxidation is so vigorous that the heat developed inflames the mass. This is the case, for instance, with hydrogen phosphide, P_2H_4; silicon hydride, Si_2H_6; zinc ethyl, $Zn(C_2H_5)_2$; etc. Some of the metals in a very fine state of subdivision are oxidized in air—*e.g.* pyrophoric iron, nickel, cobalt, etc. In some cases the oxidation is specially stimulated by exposure to sunlight—*e.g.* lead sulphide, PbS. becomes lead sulphate, $PbSO_4$; carbon chloride, C_2Cl_6, forms a mixture of carbonyl chloride, $COCl_2$, and trichloroacetyl chloride, $CCl_3.CO.Cl$; phosphorus trichloride, PCl_3, forms phosphoryl chloride, $POCl_3$; etc. The presence of the noble metals, and of cobalt, nickel, etc., in a fine state of subdivision, may enormously accelerate the speed of oxidation.

The influence of water in chemical reactions.—Water plays an important *rôle* in many reactions. If water be dropped on to a mixture of iodine with one-sixth of its weight of aluminium powder, the reaction proceeds so rapidly as to inflame the mass. There are, however, cases in which the minute trace of water vapour which is present in an imperfectly dried gas, controls the reactivity of the gas. For instance, H. B. Baker (1886)[5] showed that dry sulphur, dry phosphorus, and dry carbon burn with great difficulty or not at all in dry oxygen. Similarly, H. B. Dixon (1880) showed that carbon monoxide reacts with oxygen with greater difficulty, if it be thoroughly dried—*e.g.* if moist, a mixture of the two gases readily detonates, but not if dried. Numerous other reactions have been notified which are arrested if the reacting materials be dried. In fact, many **perfectly dried substances often appear to be chemically inert, whereas they react vigorously if a trace of moisture be present.**

The fact is quite old. Near the end of the eighteenth century, for instance, T. Bergmann[6] noticed that the "regulus of manganese" remains bright in dry air, but not in moist air; the illustrious C. W. Scheele also noted in 1786 that pyrophorus will not oxidize in air dried by quicklime, and he inferred that "the water usually present in the atmosphere is the chief cause of the burning of pyrophorus." Mrs. Fulhame, too, in her remarkable brochure, *An Essay on Combustion with a view to a new art of dying and painting* (London, 1794), showed "beyond the power of contradiction" that water is necessary for the reduction of the metallic oxides, and for the oxidation of the metals. She found, for example, that gold chloride cannot be reduced by hydrogen gas if moisture be excluded. The effect of moisture is not to promote the reduction by breaking up the salt into minute particles, nor by condensing the gas and so bringing the hydrogen into closer contact with the metallic oxide; for, if either of these views were correct, ethereal and alcoholic solutions of the metallic salt should prove as effective as water. This is not the case. Neither ether nor alcohol promotes the reduction if water be absent. Mrs. Fulhame believed that the reaction—oxidation or reduction—took place in two stages. In the first place, carbon monoxide decomposed the water, forming carbon dioxide and liberating hydrogen; thus—$CO+H_2O=CO_2+H_2$ (nascent); finally, the nascent hydrogen united directly with the free oxygen, reforming water—$2H_2$ (nascent)$+O_2=2H_2O$. Consequently, the oxygen which unites with the carbon monoxide to form carbon dioxide is not obtained directly from the oxygen gas mixed with the carbon monoxide, but from the water. H. B. Dixon[7] developed quite an analogous theory as a result of an important investigation on the oxidation of carbon monoxide, and he submitted that carbon monoxide is oxidized by steam with the liberation of hydrogen,[8] and that the hydrogen then unites with oxygen to reform steam. These results make it probable that steam does really undergo "a cycle of chemical reactions whereby it gives up oxygen to carbon monoxide and returns to its original state." H. B. Dixon also proved that other gases like hydrogen sulphide, ethylene, formic acid, ammonia, pentane, and hydrogen chloride will determine the explosion of carbon monoxide and oxygen; while sulphur dioxide, carbon disulphide, carbon dioxide, cyanogen, and carbon tetrachloride are quite ineffective. Hence, he inferred that *not only steam, but all substances which will form steam under the conditions of the experiment, are capable of determining the explosion.*

M. Traube (1882) observed that traces of hydrogen peroxide are generally formed during the oxidation of carbon monoxide, and he suggested that hydrogen peroxide, H_2O_2, is an intermediate product in the oxidation of hydrogen or carbon monoxide,; and that the water acts catalytically by acting as a link in the cyclic changes: $CO+H_2O+O_2=CO_2+H_2O_2$; and $CO+H_2O_2=CO_2+H_2O$. Dixon, however, showed that the hydrogen peroxide is most probably a by-product in the oxidation of moist carbon monoxide. In the oxidation of hydrogen, M. Traube supposed that the water acted catalytically :

$$\begin{matrix}H\\ \dot{H}\end{matrix}+\begin{matrix}HOH\\ HOH\end{matrix}+\begin{matrix}O\\ \dot{O}\end{matrix}=\begin{matrix}HOH\\ HOH\end{matrix}+\begin{matrix}HO\\ H\dot{O}\end{matrix}\ ;\quad \text{and}\quad \begin{matrix}HO\\ H\dot{O}\end{matrix}+\begin{matrix}H\\ \dot{H}\end{matrix}=\begin{matrix}HOH\\ HOH\end{matrix}$$

In reality we have not got much further than Mrs. Fulhame (1794) in working out the mechanism of this reaction. This gifted woman said :

> Water is essential both to the reduction and oxygenation of bodies, and is always decomposed in these operations. . . . In every instance of combustion water is decomposed, and one body oxygenated by the oxygen of the water, while another is restored to its combustible state by the hydrogen of the same fluid.

It must be added that the water as a catalytic agent does not necessarily accelerate the speed of all reactions. W. S. Millar, for example, found that the speed of decomposition of diazoacetic ester by picric acid in alcohol solutions is retarded in a marked degree if a small amount of water be present, and this the more with isobutyl alcohol than with ethyl or methyl alcohol as solvent.

The physiological action of oxygen.—In 1667, Robert Hooke[9] clearly demonstrated before the Royal Society that a continual supply of air is necesssary for the maintenance of life. In an experiment on a dog with its ribs and diaphragm removed, and described as "an experiment made by Mr. Hooke of preserving animals alive by blowing through their lungs with a bellows," he emphasized

> It was not the subsiding or movelessness of the lungs that was the immediate cause of death, or the stopping of the circulation of the blood through the lungs, but the *want* of a sufficient *supply of air*.

In 1674, J. Mayow showed that one constituent of air is alone active, and further that this constituent is the same as that on which ordinary combustion depends. He called the active constituent *spiritus nitro-æreus*, which was later identified with oxygen. From his experiments with mice, etc., he concluded :

> It is manifest that air is deprived of its elastic force—decreased in volume—by the breathing of animals very much in the same way as by the burning of a flame ; and, indeed, we must believe that animals and fire draw particles of the same kind from the air.

The importance of oxygen in the maintenance of animal life was emphasized by M. de Condorcet's term *l'air vital*—the life maintaining constituent of air.[10] It is the only gas capable of supporting respiration. There are, however, a few micro-organisms—*e.g.* the mould *mucor racemosus*, and the butyric acid ferment—which are killed by oxygen, and they are able to live and multiply without air. L. Pasteur called them *anaerobic organisms*. E. Weinland found that intestinal worms can normally exist in the absence of oxygen ; and A. Pütter found that the leech can live two days without oxygen.

The oxygen is carried by the blood to the various tissues in the body, and the waste products are carried away by the same liquid. The circulating blood is oxidized in the lungs of land animals, and in the gills of water animals. In insects, the blood is oxidized in a system of ramifying tubes called *tracheæ* in which the air is periodically changed by muscular movements and diffusion. Fish are dependent upon the air dissolved in water for the oxygen they need for respiration. According to E. A. Birge and C. Juday, the dissolved oxygen is deficient in the lower layers of water in 129 inland lakes of Wisconsin. This is attributed to the thermal stratification of the water owing to the greater specific gravity of the colder water hindering vertical circulation, and the depletion of the oxygen in the colder layers by the respiration of animals and plants, by the direct oxidation of dead organic matter, and by the decomposition due to the action of bacteria. A deficiency has also been noted in the lower layers of certain tidal waters which is similarly caused by stratification due to the greater specific gravity of the under-run of sea water hindering vertical circulation.

Warm-blooded animals die very rapidly in an atmosphere containing no oxygen. A man at rest becomes suddenly unconscious after about ten breaths of such an atmosphere; and very small animals, such as a mouse or a sparrow, in which the breathing is far more rapid than in a man, are killed within a few seconds, death being much faster than by drowning. When pure oxygen is breathed no noticeable effect is produced for many hours. As A. L. Lavoisier first showed, and many subsequent observers have also found, breathing pure oxygen causes no increase in the oxidation processes within the body. Paul Bert found, however, that oxygen at a pressure of over three atmospheres has a rapid poisonous effect on warm-blooded animals, accompanied by diminution of oxidation processes. This poisonous action is also produced in living organisms of all kinds. Pure air of which the pressure is raised so high as to give the same partial pressure of oxygen has the same effect. More recently, Lorrain Smith showed that exposure for two or three days to pure or nearly pure oxygen produces inflammation of the lungs; and the higher the partial pressure the sooner the inflammation appears. It was formerly supposed that poisonous organic matter is exhaled in the breath along with CO_2. All recent investigation has shown that this view is without foundation. "It has been often asserted," adds L. Hill, "that there is some organic poison exhaled with the breath. I have carefully sifted the evidence on which this assertion is based, and find that there is none worthy of evidence."

Air normally contains nearly 21 per cent. of oxygen by volume. When the oxygen is reduced to about 17·5 per cent. the flame of a candle or oil-lamp is extinguished. A man or animal is, however, not appreciably effected by so small a diminution in the oxygen percentage. On the other hand, if the atmospheric pressure, and consequently the partial pressure of oxygen, be diminished to a third the man or animal is greatly affected and soon dies, while the flame continues to burn almost as well as before. Roughly speaking, the flame responds to the *percentage* of oxygen in the air, while the animal responds to the *partial pressure* of oxygen. H. C. Dallwig, A. C. Kolls, and A. S. Lowenhart (1915) found that the flame of a candle is just extinguished when the partial pressure of oxygen is 116·4 mm. of mercury when this lowering is produced by adding nitrogen to air, whereas the flame is first extinguished at 19·8 mm. if the lowering is effected by reducing the total pressure of the atmosphere. Pure oxygen can be breathed for many hours without harm, and is used in a pure state in mine-rescue apparatus and in resuscitating persons poisoned by carbon monoxide. During the war the continuous administration of air containing an increased percentage of oxygen was used with striking success in the treatment of lung-inflammation caused by poison-gas; and similarly enriched air is now coming into extensive use in medical cases of other kinds.

Uses of oxygen.—Mixtures of liquid oxygen and petroleum are violently explosive. It is said that a lighted candle falling into a bucket of liquid oxygen in 1903 "sent G. Claude to the hospital in a very pitiable condition." Liquid air, or rather liquid air rich in oxygen, furnishes an explosive—called *oxylignite*—when mixed with charcoal, or cotton wool. 3-cm. cartridges charged with one part of carbon, one part of petroleum, and eight parts of liquid oxygen were tried experimentally in cutting the Simplon tunnel. The cartridges were exploded by an electric fuse, or a mercury fulminate cap. The chief objection is that the cartridges must be used within a few minutes after being charged, or the oxygen will evaporate. This objection might be an advantage under some circumstances, since a mis-fired shot becomes harmless in a very short time. The cartridges must also be prepared immediately before use, so that there are no dangers during transport.

The temperature of the hydrogen flame burning in air at 0° is, according to P. Mahler,[11] 1960°; of the carbon monoxide flame, 2100°; and of the acetylene flame, 2350°. Oxygen is used in conjunction with hydrogen for the *oxy-hydrogen blowpipe*, and with acetylene for the *oxy-acetylene blowpipe* used in welding, metal-cutting, etc. Thick steel plates can be cut by directing a stream of oxygen on the heated metal. Metal cutting or welding by the oxy-acetylene or oxy-hydrogen blowpipe has proved to be a remarkable labour-saving process. It has been estimated that 70 per cent. of oxygen consumed in the United Kingdom is used in cutting metals in shipbuilding and repairing yards, steel works, and engineering shops. Oxygen is used in the ventilation of submarines, etc., and for medical purposes; it is employed in the oxidation and thickening of oils to be used in making varnishes and linoleum. It is sometimes used to hasten the maturing of spirits; and the oxidation of alcohol by *mycoderma aceti* in vinegar manufacture. Oxygen has been recommended in the bleaching of paper-pulp, etc., where a fine stream of oxygen is said to effect a saving in the consumption of bleaching powder.[12] It has also been proposed to use carburetted oxygen—a safe mixture of oil and oxygen—as a motive gas for engines, for illuminating purposes,[13] in organic "combustion analyses," etc.

The determination of oxygen in a gas.—The property of rekindling a glowing splint is possessed by only one other gas—nitrous oxide—and the two gases are distinguished by a bubble of nitric oxide—oxygen gives red fumes, nitrous oxide does not. The methods for measuring the amount of oxygen in a gas depend on its absorption by various liquids and solids. For instance: (1) a solution of cuprous chloride in hydrochloric acid. The colourless solution becomes greenish-brown owing to the formation of cupric oxychloride. The exhausted solution is restored by keeping it in contact with copper shavings away from air. (2) An alkaline solution of pyrogallol freely absorbs oxygen forming a dark brown liquid—if the solution be saturated with oxygen, some carbon monoxide may be formed. This solution was used by J. von Liebig in 1851.[14] (3) Clean moist copper absorbs oxygen. The absorption soon ceases owing to the formation of a film of oxide; this can be washed off by an ammoniacal solution of ammonium carbonate. The gas containing oxygen is introduced into a vessel containing copper shavings and the ammoniacal solution, the liquid is displaced and the copper absorbs the oxygen, the return of the ammoniacal liquid displaces the gas. (4) Clean sticks of phosphorus are sometimes employed for absorbing the gas. (5) A solution of chromous chloride in hydrochloric acid; and (6) an alkaline solution of ferrous tartrate, also absorb oxygen.

The atomic weights of hydrogen and oxygen.—The early determinations of the combining ratios of hydrogen and oxygen by H. Cavendish (1781), A. L. Lavoisier and M. Meunier (1788), M. Monge (1788), J. Dalton (1803), and W. H. Wollaston (1814) are of great historical interest; but the results are not considered accurate enough to be worthy of consideration in deducing best representative values of these data. Several methods have been used in evaluating the ratio H : O. The accurate determination of this ratio has proved to be of extreme difficulty. The subject has been well discussed by B. Brauner,[15] J. Sebelien in his *Beiträge zur Geschichte der Atomgewichte* (Braunschweig, 1884), and by F. W. Clarke in his *A Recalculation of the Atomic Weights* (Washington, 1910).

I. *Gravimetric methods.*—In these methods of determining the ratio H : O, the hydrogen and oxygen may each be weighed separately, and the water also weighed. More usually two of these three quantities are determined, and the third estimated by difference. The various methods include: (i) Those in which the hydrogen and oxygen are weighed, and the water estimated by difference;[16] (ii) those in which the oxygen and water are weighed, and the hydrogen estimated by difference;[17] (iii) those in which the hydrogen and water are weighed, and the oxygen estimated by difference;[18] and (iv) those in which the hydrogen, oxygen, and water are all weighed—*synthèse complète.*[19] According to F. W. Clarke, the best representative value is O=15·8779 if H=1; and H=1·00769 if O=16.

II. *Volumetric methods.*—Volumetric methods include those in which the volumes of the hydrogen and oxygen are measured and the water estimated by difference; and those in which either the volume of the oxygen or of the hydrogen, or both are measured and the resulting water weighed. Determinations of the ratio of the combining volumes of hydrogen and oxygen[20] (Cap. III), give as the best representative value of the ratio H : O=1·0077 : 16.

. III. *Gas densities.*—Determinations of the relative densities of hydrogen and oxygen[21] furnish for hydrogen the atomic weight 1·00777 ; and for oxygen, 15·8767.

IV. *Physico-chemical methods.*—A number of other methods[22] have been employed. For example, *the method of critical constants* by A. Leduc and P. Sacerdote, Lord Rayleigh, A. Jaquerod and O. Scheuer, and by D. Berthelot furnished H : O=1·00777 : 16 ; *the method of limiting densities* by P. A. Guye, D. Berthelot, and A. Leduc furnished H : O=1·00775 : 16 ; and *the method of molecular volume* by A. Leduc furnished H : O=1·0076 : 16.

V. *Indirect determination.*—J. Thomsen determined the amount of ammonia required to saturate a given amount of hydrogen chloride, then, given the atomic weights of nitrogen and chlorine (O=16), the atomic weight of hydrogen can be computed.

Dry hydrogen chloride was passed into a weighed flask containing water coloured with litmus and weighed—5·0363 grms. of hydrochloric acid were absorbed ; dry ammonia was passed in until the liquid was almost neutral and the flask again weighed. The excess of ammonia or acid was determined by titration with standard acid or alkali—2·3523 grms. of ammonia were used to neutralize 5·0363 grms. of hydrogen chloride. Hence, $HCl : NH_3 = 5·0363 : 2·3523$. If the atomic weight of chlorine be 35·457 and of nitrogen 14·044, the atomic weight of hydrogen is 0·9989. The uncertainty as to the value of the atomic weight of nitrogen here affects that of hydrogen.

J. S. Stas[23] determined the relation of silver to ammonium chloride and bromide. Given the atomic weights of nitrogen, chlorine, and bromine (O=16), the atomic weight of hydrogen follows. The mean of Stas' results with the chloride and bromide gave H : O=1 : 15·9229 ; or 1·00598 : 16. J. Dewar and A. Scott (1887) tried to use the substituted ammonias—*e.g.* triethylamine, $N(C_2H_5)_3$—in place of ammonia, but the difficulties involved in purifying the triethylamine make the method undesirable.

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§ 10. The Origin of the Terms: Acid, Alkali, Base, Salt

> However convenient the classification of oxides into acids and bases might be for an elementary presentation of chemistry, a glance from the vantage ground of facts not usually referred to in elementary courses, shows such classifications to be imperfect and arbitrary to a degree.—D. CARNEGIE (1894).

The early chemists appear to have gradually learned to arrange certain substances into two groups according as these substances possessed certain qualities in common with vinegar or with wood ashes. The former were called **acids** (*acidus*, acid) and the latter **alkalies** (Arabian, *alkali*, ashes of a plant), because the alkalies were generally obtained by calcining various materials and reducing them to ashes. The word *acid* was probably first used in a concrete sense for vinegar, and it then came to be used for certain substances which tasted " sharp " or sour like vinegar—

the acid of soured wine; the term *alkali* was used for crude potash; and *salt* has been used from the earliest times for culinary salt. Aristotle employed the term *salt* for the evaporated lixivium of wood ashes.[1] Disocorides and Pliny employed the same term for crude soda, and generally for substances which could be recovered from their solution in water by evaporation. About the time the works of "Basil Valentine" were written, the *vitriols* were regarded as metallic salts, and the term salt came to be employed for that constituent of a substance which could not be destroyed by calcination, and among the alchemists the term was used to represent the principle of solidity. H. Boerhaave, T. Bergmann, and R. Kirwan used solubility in water as one criterion for salts, but this led to the separation of substances of a similar nature into separate groups.

Although the three terms—acid, alkali, and salt—were first applied to specific substances, their meanings have changed so that they no longer designate the names of things, but are employed as generic or class names to indicate what certain things will do; otherwise expressed, they are the names of certain chemical functions. The generic term only becomes specific when an adjective is affixed—*e.g.* sulphuric acid.

The great solvent or corrosive action of the acids was well known to the ancients. This is emphasized by Pliny's story of Cleopatra and the pearls; and Livy's and Plutarch's fantastic story of Hannibal cutting a passage through the Alps by dissolving limestone rocks by means of vinegar. In his *Reflections upon the hypothesis of alcali and acidum* (London, 1684), Robert Boyle summarized the properties of acids as substances which (1) have a sour taste; (2) dissolve many substances (corrosive); (3) precipitate sulphur from alkaline solutions of sulphur; (4) change the tint of many vegetable blue colours (*e.g.* blue litmus) red; and (5) lose their acid characteristics when brought into contact with the alkalies. H. Boerhaave (1732)[2] divided the acids into *acida vegetantia*, or those derived from plants; and *acida fossilia*, or those derived from mineral substances. Soon afterwards, J. van Helmont (1736) called the latter, *acides minéraux*, and included them in the class containing sulphuric, hydrochloric, and nitric acids.

J. B. van Helmont (1640), F. Sylvius de la Boé (1659), N. Lemery (1675) and H. Boerhaave (1732), at first, applied the term *alkali* to bodies which effervesced with acids, but R. Boyle recognized as alkalies certain substances which do not act in this manner. R. Boyle considered the alkalies to be substances which (1) possessed detergent and soapy properties; (2) dissolved oils and sulphur; (3) restored vegetable colours reddened by acids; and (4) had the power of reacting with acids to produce indifferent substances. The idea connoted by the term **base** is much older than the word; *base* stands in generic relations with *alkali*. F. Sylvius de la Boé recognized the distinction between acids and bases in 1659, although the idea was familiar to chemists before his time; this is emphasized by the fact that acids and alkalies have a strong disposition to unite chemically. In 1744, G. F. Roulle employed the word base for any substance which unites with an acid to form a salt, and which gives to the salt *une forme concrete ou solide;* the term is now usually applied to oxidized bodies with properties which are complementary to the acids; the term includes the earths, alkalies, metallic oxides (calces), and all substances which produce salts by reacting with acids. It was soon found that some substances with alkaline qualities did not melt or change when heated, did not effervesce with acids, and were almost insoluble in water—these substances were called **earths**.

With these criteria, it is possible to classify the oxides formed by burning carbon, sulphur, phosphorus, sodium, iron, etc., in oxygen into acidic, basic, or neutral oxides:

ACIDIC OXIDES.	BASIC OXIDES.	NEUTRAL OXIDES.
Carbon	Sodium	Iron
Sulphur	Calcium	Copper
Phosphorus	Magnesium	Tin

The properties of acids and alkalies or bases were thus opposed to one another; for when mixed together, the one neutralized the activity of the other. Although each component of the mixture is itself pungent or corrosive, the final product is usually mild and inoperative. J. B. van Helmont, about 1640, used the term **saturation,** and a few years later, O. Tachen gave one of the first rational definitions of a **salt,** for he said that all salts can be resolved into an acid and an alkali, and very soon, the term *salt* came to be used for the products of the interaction of acids and alkalies or bases. John Mayow, in his essay *On the combination of contrary salts* (Oxford, 1669), recognized the dual nature of salts, and showed that although the acid and alkali, when they meet, unite together to form a salt, yet they do not destroy one another since both may be afterwards recovered from the salt. According to N. Lemery (1675), during saturation, the base is "cloyed or filled with acid," and a *sel sale* was defined as an alkali charged with an acid. G. E. Stahl (1723) called the substance which united with the acid to form sodium chloride, *materia illa quæ sali corpus præbet.* H. Boerhaave (1732) stated that an alkali is understood to be saturated with an acid when a point is reached at which the product is neither acid nor alkaline; the resulting product was called a **neutral salt**—*salia, sic dicta jam neutra.* H. Boerhaave also spoke of *salia alcalina,* and of *salia acida;* and he regarded the vitriols as semi-metals.

It was soon recognized that many substances could not well be grouped with the acids and bases although they possessed qualities characteristic of acids or bases. Thus *aluminium ammonium sulphate*—alum—forms a solution with water which has a sour taste, deprives sodium hydroxide of its alkaline qualities, and turns blue litmus red; copper sulphate reddens blue litmus; *sodium carbonate* and *sodium borate* turn red litmus blue, etc. Conversely, substances may be grouped as acids and bases, even though they have no action on litmus, *e.g. silicic acid,* H_2SiO_3, has no action on blue litmus, and yet it is an acid; similarly, *copper oxide,* CuO, is a base without action on red litmus.

What is the source of the acidity of acids ?—Otherwise expressed, why are the acids acidic, and the bases alkaline ? J. J. Becher (1669), G. E. Stahl (1723), and other early chemists postulated the presence of a principle of acidity—all acids in common were supposed to be impregnated with more or less of a *primordial or primitive acid.* For example, F. Sylvius de la Boé and J. F. Meyer [3] supposed both acids and alkalies owed their peculiar properties to the presence of a common principle which the former termed *fiery matter* and the latter *acidum pingue.* When the alkalies came to be divided into caustic and effervescent, it was assumed that the transformation of caustic into effervescent lime was due to the effervescent lime transferring its *acidum pingue* to the effervescent alkali. G. E. Stahl assumed that acids, alkalies, and salts contained one common ingredient—namely, the primitive acid; and that the three were transmutable *inter se* by adding or subtracting primitive acid. The alkalies were supposed to contain less primitive acid than acids or salts. T. Bergmann postulated a *principle of acidity* and a *principle of alkalinity,* but he admitted that while "chemistry was not able to extract these two universal principles, there is not the least doubt that they are different and opposite to each other." Not till 1755 did J. Black [4] demonstrate qualitatively and quantitatively that the loss of fixed air changes an effervescent into a caustic alkali, and the union with fixed air changes a caustic into an effervescent alkali. N. Lemery considered it to be self-evident that the ultimate particles of acids had sharp edges or hooks which gave the acids their peculiar properties. His proof was:

> I hope nobody will dispute whether an acid has points or not, seeing that it is demonstrated by every one's experience, that an acid pricks the tongue like anything keen and finely cut; but a demonstration and convincing proof that an acid consists of pointed parts is that not only all acid salts do crystallize with edges, but all dissolutions of different things caused by acid liquors, do assume this figure in their crystallization.

This argument is invalid, for the crystals of nearly all compounds—whether acidic alkaline, or neutral—have sharp edges. The lesson is obvious. What is self-evidently an hypothesis must not be advanced as if it were an inviolable fact.

A. L. Lavoisier, following J. Mayow (1669) and C. W. Scheele (1777), renounced the peculiar fancies involved in the terms primordial acid, principle of acidity, etc., and ascribed acidity to the universal presence of oxygen, the acid-producer. Consequently, Lavoisier's *oxygen* is the acidifying principle under another guise. J. Mayow got very near to the same theory of acidity in 1669. This hypothesis can now be tested.

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§ 11. Acids

Acid is rather the name of a function than the name of a substance.—MILLS.

In his study of the properties of oxygen, A. L. Lavoisier noticed that when certain elements were burnt in oxygen, the resulting oxide forms an acid with water—*e.g.* carbon, sulphur, and phosphorus. Hence, Lavoisier jumped to the conclusion (1777) that " oxygen is an element common to all acids, and the presence of oxygen constitutes or produces their acidity." He also considered oxygen to be the essential constituent of all acids. The very name *oxygen*, given to this element, was derived from Greek words signifying " the generative principle of acids "—ὄξυς, sour, and γείνομαι, I produce—because " one of the most general properties of this element is to form acids by combining with many different substances ; " hence also the German term for oxygen *Sauerstoff*, meaning " acidifying stuff." In his *Considérations générales sur la nature des acides*, and his *Mémoire sur l'existence de l'air dans l'acide nitreux* (1777), A. L. Lavoisier considered that the difference in the various acids depended on the nature of the substance or substances united with the oxygen ; he called the non-oxygenated part of an acid a simple or a compound *acidifiable base*. The mineral acids are usually oxygenated compounds of simple acidifiable bases—carbon, sulphur, nitrogen, phosphorus—the vegetable and animal acids—tartaric and oxalic acids—are oxygenated compounds of the compound acidifiable bases. Lavoisier's theory of acidity made him unprepared to find water or oxidized hydrogen exhibiting no signs of acidity, and there is a possibility that his hypothesis prevented his discovering the composition of water. *L'analogie*, said Lavoisier,[1] *m'avait porté invinciblement à conclure que la combustion de l'air inflammable devoit également produire un acide.* The difference between analogy and fact, added Berthollet, is just the difference between probability and certainty. For a time, *le principe oxygène* was almost a fetish with the French chemists ; but, with increasing knowledge, it was found that **Lavoisier's oxygen theory of acids** led to confusion and error, and it was gradually abandoned by chemists when it was recognized that :

1. **Some oxides form alkalies, not acids, with water.**—*E.g.* sodium, potassium, and calcium oxides. As Humphry Davy expressed it, " the principle of acidity of the French nomenclature might now likewise be called the principle of alkalescence."

2. **Some acids do not contain oxygen.**—In 1785, J. C. de la Métherie [2] had maintained as a paradox that oxygen does form a necessary constituent of acids.

This idea was ridiculed by A. L. Lavoisier, but C. L. Berthollet showed, in 1787, that hydrocyanic (prussic) acid is a compound of carbon, nitrogen, and hydrogen, but contains no oxygen; and he also came to a similar conclusion with regard to hydro-sulphuric acid. But for some time Lavoisier's reputation had more weight than Berthollet's facts. In 1810–11, Humphry Davy proved that hydrochloric acid is a compound of hydrogen and chlorine and that no oxygen could be detected in the compound. In 1813, H. Davy also proved that hydriodic acid contained hydrogen and iodine, but no oxygen. Hence, added H. Davy, "acidity is not connected with the presence of any one element;" and he appears to have regarded the acidity of a substance as a kind of resultant whose direction is hydrogen.

It must be added, however, that when these substances are thoroughly dried so as to remove all traces of water they do not show acidic qualities. Water is always present when these substances manifest their acidic properties, and water is itself a compound of hydrogen and oxygen. Hence, a very good case might be made out for an extension of Lavoisier's hypothesis, but solutions of ammono-bases and ammono-acids in liquid ammonia would then have to be considered because this solvent has no oxygen.

As a result of H. Davy's work, the acids came to be classed as **hydracids**—acids containing no oxygen; and **oxyacids**—acids formed from acidic oxides. In 1815, H. Davy suggested the possibility that hydrogen, not oxygen, gives the acid characters to the acids; but he did not rush to the other extreme and say that all hydrogen compounds are necessarily acids. In the same year, 1815, P. L. Dulong's study of oxalic acid led him to the view that there is no essential difference between oxygenated and non-oxygenated acids. He supposed oxalic acid to be a compound of oxygen with carbon dioxide, and salts of oxalic acid to be formed by replacing the hydrogen of the acid by the metals. In this way, hydrogen and the metals were opposed to the salt-forming radicles.

There is no one property which we can use as an absolute criterion or decisive test of acidity. In a crude sort of way, it can be said that *acids usually have a sour taste, are usually corrosive, redden the blue colour of vegetable substances* (*e.g. litmus*) ; *and contain hydrogen, part or all of which can be replaced when the acid is treated with a metal, metallic oxide, hydroxide, or carbonate.* Acids are known which have a sweet taste—*e.g.* amidophosphoric acid; acids are known which are not corrosive; and alkalies have hydrogen replaceable by a metal as is shown when, say, aluminium is treated with alkali lye. *Alum*, as indicated above, does not contain replaceable hydrogen, and it would not therefore be classed as an acid, although it is sour, corrosive, and colours blue litmus red. Sodium bisulphate has a sour taste, is corrosive, reddens blue litmus, and contains replaceable hydrogen, but it is not usually regarded as an acid because of its mode of formation. Again, methane, CH_4, is not considered to be an acid although it has hydrogen replaceable by a metal, and the resulting compound is not called a salt, *e.g.* zinc methide, $Zn(CH_3)_2$.

However, we are yet far from a satisfactory definition of acids, although, as we shall see later, a fair definition can be made in terms of the ionic hypothesis in spite of the fact that so far as *practical applications* are concerned, definitions in terms of the ionic hypothesis are not very different from those under consideration, the difference is then rather a question of nomenclature.

Naturally the student delights in clear, sharp-cut definitions, and teachers of science have many temptations to frame definitions and draw boundary lines which do not exist in nature. "Definitions," said R. Hunter, "are the most accursed of all things on the face of the earth."

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§ 12. Salts

The relation of acid and base in a salt is one of the main grounds of all theoretical reasonings (on chemical combination).—W. WHEWELL.

There is perhaps no inquiry which has thrown so much light on a multitude of combinations which the want of method had permitted to be confounded, as Rouelle's observations on the characters of the salts.—C. L. BERTHOLLET (1803).

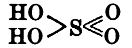
In modern chemistry the term *salt* is a descriptive term applied to a distinct class of substances, and not to any particular individual. A salt is produced by replacing all or part of the hydrogen of an acid by a metal or basic radicle. For instance, zinc displaces the hydrogen of sulphuric acid: $Zn+H_2SO_4=ZnSO_4+H_2$, forming the salt zinc sulphate. C. Gerhardt[1] regarded salts as *corps binomé*, liable to double decomposition; and J. J. Griffin regarded them as compounds of two radicles. Hence J. von Liebig (1838), and C. Gerhardt (1843) defined acids to be "salts of hydrogen":

SO_4—BIVALENT RADICLE.		Cl—UNIVALENT RADICLE.	
Hydrogen sulphate (sulphuric acid)	H_2SO_4	Hydrogen chloride (hydrochloric acid)	HCl
Zinc sulphate	$ZnSO_4$	Zinc chloride	$ZnCl_2$
Sodium sulphate . . .	Na_2SO_4	Sodium chloride	NaCl

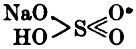
Salts of the **binary acids** (*i.e.* acids compounded of two elements like hydrochloric acid, etc.) are usually named by dropping the prefix *hydro* and changing the termination *-ic* into *-ide*. Thus the acids just named furnish chlorides, fluorides, etc. To show what chlorides, etc., are in question, the name of the corresponding element (or elements) is introduced in an adjectival sense. Thus we have sodium chloride, potassium chloride, calcium chloride, etc. The names of the elements are thus used adjectivally in the same sense that the words stone, brick, and wood prefixed to house are adjectival, and indicate the kind of house in question. Some radicles free from oxygen, *e.g.* CN or Cy, behave as if they were single elements. Thus hydrocyanic acid—HCN—is treated as if it were a binary acid, and its salts are accordingly named *cyanides*.

The salts of the **ternary acids** (*i.e.* acids with three elements) are named by changing the *-ic* termination of the acid into **-ate,** or the *-ous* termination of the acid into "**-ite,**" and adding the word so obtained to the name of the base or bases forming the salt. The sulphuric acid forms *sulphates*—*e.g.* sodium sulphate; nitric acid, *nitrates*—*e.g.* calcium nitrate; sulphurous acid, *sulphites*—*e.g.* ammonium sulphite; perchloric acid, *perchlorates*—*e.g.* potassium perchlorate; hypochlorous acid, *hypochlorites*—calcium hypochlorite; carbonic acid, *carbonates*—*e.g* calcium carbonate, etc. Hence, some years ago, the name of the basic element used to be modified to give it an adjectival form: hydric chloride; potassic chloride; calcic chloride; etc. This system has been abandoned unless it is desired to distinguish between -ous and -ic compounds—*e.g.* ferrous chloride and ferric chloride, etc. Consonant with the definition that acids are salts of hydrogen, nitric acid, HNO_3, has been called hydrogen nitrate; hydrochloric acid, HCl, hydrogen chloride; sulphuric acid, H_2SO_4, hydrogen sulphate.

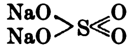
In **normal salts** all the displaceable hydrogen of the acid is replaced by the base. For instance, sodium sulphate—Na_2SO_4—is a normal salt because all the replaceable hydrogen of sulphuric acid is displaced by sodium. In **acid salts** only part of the replaceable hydrogen has been displaced, acid sodium sulphate—$NaHSO_4$—contains half the replaceable hydrogen of sulphuric acid, and half as many equivalents of sodium as normal sodium sulphate. If an acid contains two or more replaceable hydrogen atoms, it does not follow that all need be displaced by the same element. These ideas can be illustrated graphically—sulphur sexivalent:


$\begin{matrix}HO\\HO\end{matrix}>S\ll\begin{matrix}O\\O\end{matrix}$

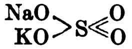
Sulphuric acid.


$\begin{matrix}NaO\\HO\end{matrix}>S\ll\begin{matrix}O\\O\end{matrix}$

Acid sodium sulphate.


$\begin{matrix}NaO\\NaO\end{matrix}>S\ll\begin{matrix}O\\O\end{matrix}$

Normal sodium sulphate.


$\begin{matrix}NaO\\KO\end{matrix}>S\ll\begin{matrix}O\\O\end{matrix}$

Sodium potassium sulphate.

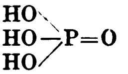
About 1754, F. G. Rouelle[2] distinguished the *neutral salts* of a given base from the *acid salts* with an excess of acid, and basic salts with an excess of base, and he showed the action of some of these salts on vegetable dyes. A. Baumé (1770) objected to F. G. Rouelle's classification—neutral, acid, and basic salts—for he maintained that the neutral salts are the only true salts, and that the basic and acid salts are mixtures of neutral salts respectively with an excess of bases or acids. The question was discussed later, whether the proportion of acid and base in the two salts is constant so that there are but two combinations—those with a maximum and those with a minimum proportion of acid—or whether combinations exist with intermediate proportions dependent on the circumstances under which the salts are formed. C. L. Berthollet (1803) advocated the latter alternative, but this was not generally accepted, and guided by the law of multiple proportions the two salts are usually considered to be combinations of acid and base in two definite and fixed proportions. When deviations from these proportions are observed, it is supposed that a *mixture* of normal and acid salts, or of the normal or acid salt with an excess of uncombined acid or base, is in question.

Sometimes the term "hydrogen" is used in place of "acid" for the acid salts, and sometimes the prefix bi- or di- is appended to the term for the acid in the salt. Thus, acid sodium sulphate is also called sodium hydrogen sulphate, sodium bisulphate, as well as mono-sodium sulphate, etc. Originally, the Latin prefixes bi-, etc., were applied to the name of the acidic and the Greek prefixes di-, etc., to the name of the basic part of a salt, so that sodium disulphate would not mean the same as bisulphate. Colloquially, the prefixes bi-, etc., are used for the acid salt—*e.g.* sodium bicarbonate, $NaHCO_3$; sodium bisulphite, $NaHSO_3$, etc.—possibly because a term like sodium hydrogen carbonate appears to be pedantic outside the lecture room.

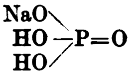
The normal salts are sometimes called **neutral salts** in the sense that all the hydrogen has been neutralized or displaced from the acid. These salts, however, are not necessarily *neutral* to litmus—thus normal zinc and copper sulphates react towards litmus as if they were acids; borax, sodium nitrite, and normal sodium carbonate react as if they were alkalies. The confusion in the use of the term *acid* may also be noted. It can be used as a noun to denote a particular class of compounds now under discussion; and also as an adjective to represent a certain quality or property—*e.g.* the behaviour towards blue litmus—characteristic of the class acids. Accordingly, some acid salts are *acid* to litmus, *e.g.* sodium hydrogen sulphate; others are *alkaline*, *e.g.* sodium hydrogen carbonate, acid potassium tellurate; others again are *neutral*, *e.g.* disodium hydrogen phosphate. Usually the normal mercurous, mercuric, cupric, chromic, ferric, stannous, stannic, antimonious, and bismuthous salts with the common acids have an acid reaction—redden blue litmus; while the borates, carbonates, chromates, hypochlorites, nitrites, phosphates, silicates, sulphides, and sulphites have an alkaline reaction—turn red litmus blue.

The mode of defining a neutral salt as a compound obtained by mixing an acid with a base until the product is neutral to litmus is ambiguous and therefore objectionable; the close relation between salts which are and salts which are not neutral to litmus does not allow them to be distinguished from one another. Hence, J. J. Berzelius proposed to retain the term *neutral* for those salts like potassium and sodium sulphates which are neutral to litmus, and to take no account of the behaviour of the other metallic salts towards litmus, but rather be guided by their analogy with the salts which are neutral to litmus. This extension of the term neutral is not free from objections. When the term neutral salt is now employed, it is usually understood to be synonymous with normal salt.

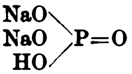
It is sometimes necessary to use the prefixes mono-, di-, tri- . . . to discriminate between the different salts of one acid. Thus with phosphoric acid—phosphorus quinquevalent:



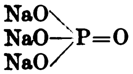
Phosphoric acid.



Monosodium phosphate.



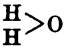
Disodium phosphate.



Normal or tri-sodium phosphate.

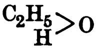
It would be a mistake to assume that all the hydrogen of an acid is replaceable by a base. Thus, so far as we know, hypophosphorous acid—H_3PO_2—has only one of its three hydrogen atoms replaceable by a metal. No one has ever prepared Na_2HPO_2. Following the recommendation of J. von Liebig (1857): **The number of atoms of hydrogen in one molecule of an acid which are replaceable by a metal, or a radicle, is termed the basicity of the acid.** Thus hydrochloric acid—HCl—is monobasic because each molecule of hydrochloric acid contains one replaceable hydrogen atom; sulphuric acid—H_2SO_4—is dibasic; phosphoric acid—H_3PO_4—is tribasic; and ferrocyanic acid—H_4FeCy_6—is tetrabasic because the four hydrogen atoms can be replaced by equivalent atoms of the basic elements—say four of potassium, two of calcium, etc. Hypophosphorous acid—H_3PO_2—is monobasic because only one of the three hydrogen atoms can be replaced by a metal.

Alcohols and ethers.—The normal alcohols, *methyl alcohol*, CH_3OH; *ethyl alcohol*, or simply alcohol, $C_2H_5.OH$; etc., are related to water in that one hydrogen atom of water is replaced by a univalent hydrocarbon radicle. When both hydrogen atoms of water are replaced by univalent hydrocarbon radicles, the so-called *ethers* are formed; thus, $(CH_3)_2O$ represents *methyl ether* or *methyl oxide*; and *ethyl ether* or ethyl oxide or simply *ether* is represented by $(C_2H_5)_2O$; and *methyl ethyl ether*, by $(CH_3)(C_2H_5)O$. Graphically,



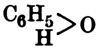
$\begin{matrix}H\\H\end{matrix}\!>O$

Water.



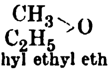
$\begin{matrix}C_2H_5\\H\end{matrix}\!>O$

Ethyl alcohol.



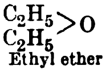
$\begin{matrix}C_6H_5\\H\end{matrix}\!>O$

Phenol.



$\begin{matrix}CH_3\\C_2H_5\end{matrix}\!>O$

Methyl ethyl ether.



$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}\!>O$

Ethyl ether.

The hydrogen of the residual OH-group in the alcohols can be replaced by a metal —*e.g.* sodium dissolves in ethyl alcohol with evolution of hydrogen. When the solution is heated to 200° in a current of hydrogen to drive off the excess of alcohol, the white powder which remains is *sodium alcoholate*, $C_2H_5.ONa$, which seems to suggest that water and alcohol have acidic properties in that they contain replaceable hydrogen. These compounds are included in the subject matter of organic chemistry.

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[1] J. J. Griffin, *The Radical Theory in Chemistry*, London, 1858; C. Gerhardt, *Compt. Rend.*, 17. 312, 1843; J. von Liebig, *Liebig's Ann.*, 26. 113, 1838.

[2] F. G. Rouelle, *Mém. Acad.*, 347, 1731; 97, 1744; 572, 1754; A. Baumé, *Chymie expérimentale et raisonnée*, Paris, 1773; C. L. Berthollet, *Essai de statique chimique*, Paris, 1803.

§ 13. Neutralization

Neutrality measured by means of a colouring matter is but a hypothesis.—J. S STAS (1865).

A solution of sulphuric acid, like other acids, colours blue litmus red; and a solution of sodium hydroxide, like other alkalies, colours red litmus blue. It is possible to mix the acid with the alkali so as to furnish a solution which neither tastes nor reacts towards litmus like sulphuric acid or like sodium hydroxide. If too much acid be present the litmus will be coloured red, and blue if too much alkali be present. The mixture on evaporation furnishes a crystalline solid which neither colours blue litmus red nor red litmus blue. The colour of a violet solution of litmus is not affected. The product of the reaction is said to be **neutral,** and the process of neutralization consists in adding an acid to an alkali, or an alkali to an acid, until a neutral substance is obtained. The result of the reaction is called a **salt.** The salt contains the metal of the alkali, and the radicle of the acid. The litmus used to determine the point of neutralization is called the **indicator.** Several other indicators besides litmus are available; *e.g.* phenolphthalein furnishes a pink coloration with alkaline solutions, and is colourless with acids and neutral solutions;

methyl orange is yellow with alkalies, pink with acid, and orange with neutral solutions. Poirrier's soluble blue gives a blue colour with acids and with carbonates, and red with alkalies. The petals of white flowers usually change to yellow when placed in alkaline solutions and back to white when placed in acids ; red and purple flowers usually become green or greenish-blue in alkaline solutions, and back to the original or a brighter red colour in acids ; yellow flowers are usually not affected by acids or alkalies. Yellow turmeric becomes reddish-brown in alkaline solution. Litmus and phenolphthalein solutions can each show the presence of about 1·8 parts of hydrochloric acid per million parts of solution, while methyl orange will show 3·7 parts of this acid per million.

It will be observed that the determination of the neutral point is here referred arbitrarily to the behaviour of litmus, because when compounds are arranged into classes, acidic, alkaline, and neutral, the members of the different classes are not the same when different indicators are used. For instance, salts of the heavy metals—alum, ferric chloride, ferrous sulphate, etc.—are usually acid to both litmus and phenolphthalein as indicators, and neutral to methyl orange ; borax, sodium and potassium bicarbonates, and sodium citrate are alkaline to litmus and methyl orange, but neutral to phenolphthalein ; while sodium phosphate is neutral to litmus and phenolphthalein, and alkaline to methyl orange. When free phosphoric acid is titrated with sodium hydroxide, it appears to be a monobasic acid if methyl orange (*i.e.* the commercial dimethylaminoazobenzene sulphonate) be used as indicator ; to be a dibasic acid with litmus or phenolphthalein ; and to be a tribasic acid with Poirrier's soluble blue. Again, free boric acid does not affect methyl orange, but it reacts acid with both litmus and phenolphthalein after adding an equal volume of dilute sodium chloride solution ; and an aqueous solution of potassium sulphite is neutral to phenolphthalein, but it turns violet litmus blue. It therefore follows that **acids and alkalies have only a relative existence.** This was emphasized by J. Freind[1] in 1709, for he pointed out that the corrosive and colorimetric properties of acids are often shared alike with the alkalies, so that a substance which is termed an alkali if referred to one body, might be called an acid by the very same writers if referred to another body ; and added : " In vain we endeavour to fix the boundaries which separate each kind."

Other properties of acids and alkalies have been employed to determine the neutral point and also the point where a normal salt is formed when an acid is treated with an alkali and conversely. The index of refraction, electrical conductivity, and the freezing point may be cited in illustration. E. Cornec (1909)[2] showed that when the lowering of the freezing point of a solution is plotted with the composition for all proportions of acid and base, the minimal points in the curve correspond with sharply defined salts and bends occur where partly stable compounds occur. Thus, when $\frac{1}{2}N$-sodium hydroxide is added in gradually increasing quantities to $\frac{1}{2}N$-hydrochloric acid, the lowering of the freezing point falls regularly from 1·885° to 0·890° when equivalent proportions are present, and then regularly rises to 1·705°, the value for sodium hydroxide. The curve, Fig. 5, thus consists of two straight lines which intersect at a point corresponding with sodium chloride. Sulphuric acid and sodium hydroxide give a well-defined minimum corresponding with Na_2SO_4, but there is no sign of the formation of an acid salt, $NaHSO_4$, in the solution. Hence, it is inferred that the acid sulphate dissociates completely in solution into the normal sulphate and free acid : $2NaHSO_4 \rightarrow Na_2SO_4 + H_2SO_4$. Phosphorous acid, H_3PO_3, behaves like a dibasic acid giving a minimum point with Na_2HPO_3 ; hypophosphorous acid, H_3PO_2, behaves like a monobasic acid ; arsenic and phosphoric acids with sodium hydroxide give minima corresponding respectively with Na_3PO_4 and Na_3AsO_4, and bends or terraces in the curve for phosphoric acid correspond with the partial formation of NaH_2PO_4 and Na_2HPO_4 ; analogous bends in the arsenic acid curve. These two acids with ammonia give curves with minima corresponding respectively with $(NH_4)_2HPO_4$ and $(NH_4)_2HAsO_4$. Chloric acid, $HClO_3$, and perchloric acid, $HClO_4$, give graphs characteristic of monobasic acids ; selenious acid, H_2SeO_3, dithionic acid, $H_2S_2O_6$, and carbonic acid, H_2CO_3, all behave as dibasic acids ; hypophosphoric acid, $H_4P_2O_6$, and pyrophosphoric acid, $H_4P_2O_7$, behave like tetrabasic acids.

As a corollary from Richter's law of proportionality that acids and alkalies unite in constant proportions to form salts, it follows that **when two neutral salt solutions mutually decompose one another, the newly formed products are also neutral,** because the amount of base neutralized by a certain weight of one acid is also neutralized by an equivalent weight of another acid. In illustration, when a neutral aqueous solution of sodium chloride is added to an equivalent solution of silver nitrate, the solution remains neutral after the precipitation of the silver chloride. It also follows from Richter's law that if one metal be precipitated by another metal from a neutral salt, the neutrality is maintained. T. Bergmann (1785) knew that when one metal is precipitated by another from a neutral salt solution, the neutrality is not disturbed, which he interpreted in terms of the phlogiston theory by assuming that the quantities of two metals which are united with the same amount of acid contain the same amount of phlogiston. **Richter's law of neutrality**—*Neutralitätsgesetz*—is obviously a special case of the law of reciprocal proportions which, as previously shown, was recognized a few years later. J. J. Berzelius (1827) unfortunately confused the work of Wenzel and Richter on this subject, and the mistake was continued by later writers up to about 1841.

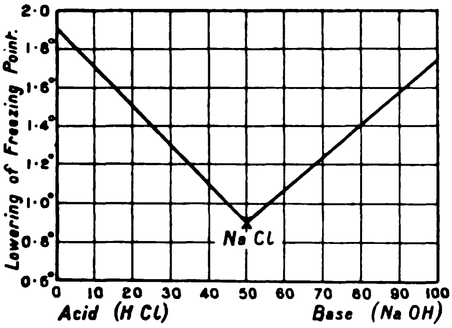

Fig. 5.—Lowering of the Freezing Point of Solutions of Sodium Hydroxide and Hydrochloric Acid.

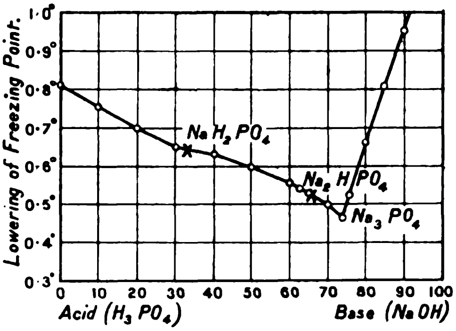

Fig. 6.—Lowering of the Freezing Point of Solutions of Sodium Hydroxide and Phosphoric Acid.

Neutralization versus hydrolysis.—The process of neutralization of a basic hydroxide by an acid is attended by the formation of a salt and water. We shall find later that some salts—*e.g.* zinc sulphate, sodium carbonate, potassium cyanide, etc.—are partially decomposed—*i.e.* hydrolyzed—by water into acid and base. The action of water on such a salt or base is thus an example of an opposing reaction ; hydrolysis is opposed to neutralization :

$$\underset{\text{Neutralization}\longrightarrow\qquad\qquad\longleftarrow\text{Hydrolysis.}}{H_2SO_4+Zn(OH)_2=ZnSO_4+2H_2O}$$

In some cases, however, the amount of hydrolysis is inappreciable, and the process of neutralization is so complete that it can be employed for measuring the quantity of acid or base in a given solution. Hence, the chemical action of water as a solvent can be neglected in many chemical reactions, but in other cases the solvent is of prime importance, when it determines the nature of the compound formed. Probably most of the examples of normal salts, which furnish acid or alkaline solutions, are hydrolyzed by water, and the acidic or alkaline properties of the aqueous solutions are due to the corresponding products of hydrolysis.

Acidimetry and alkalimetry.—A **standard solution** containing a known amount of acid or base per litre is prepared, and just sufficient of this solution is added to neutralize a solution of a given base or acid. The volume of the standard solution required for the purpose is noted. It is possible to calculate the amount of "chemically pure" substances present in the given solution from the volume of the standard solution required for the neutralization. **A solution containing one equivalent weight of the acid or base element or compound expressed in grams per litre is called a normal solution,** written "N-solution," and a solution containing one-tenth the concentration of a normal solution is called a **decinormal solution,** written "$\frac{1}{10}N$-solution." **The equivalent weight of a base is that quantity which just completely neutralizes one molecular weight of a monobasic acid; and the equivalent weight of an acid is that quantity which contains unit weight of replaceable hydrogen.** Thus 36·47 grams of HCl per litre gives a normal solution of hydrochloric acid; and 49·04 grams of H_2SO_4 per litre gives a normal solution of sulphuric acid. Here the molecular weight of the latter acid is 98·08, and the acid is dibasic, for it contains two replaceable hydrogen atoms; and, by definition:

$$\text{Equivalent of acid} = \frac{\text{Molecular weight of acid}}{\text{Basicity of acid}}$$

that is, the equivalent of sulphuric acid is $98·08 \div 2 = 49·04$. A normal solution of sodium hydroxide contains 40 grams of NaOH per litre, and a litre of a normal solution of any acid so far considered will just neutralize a litre of normal solution of any base.

EXAMPLES.—(1) Suppose that a 50 c.c. burette be charged with a normal solution of sodium hydroxide, and suppose that the amount of HCl in 500 c.c. of a dilute solution of hydrochloric acid be in question—acidimetry—pipette 50 c.c. of the acid into a beaker and add a few drops of litmus. The alkali solution is run from the burette into the beaker until the addition of but one more drop of acid is needed to change the red litmus to blue. Suppose that 42 c.c. of the normal sodium hydroxide has been run from the burette. The argument runs: The neutralization $NaOH + HCl = NaCl + H_2O$ shows that 40 grams of sodium hydroxide correspond with 36·47 grams of HCl; and 1000 c.c. of NaOH has 40 grams of sodium hydroxide, which is equivalent to 36·47 grams of HCl. Consequently 42 c.c. of the standard sodium hydroxide solution is equivalent to 1·53 grams of HCl per 50 c.c. of the given acid, or 15·3 grams of HCl are present in 500 c.c. of the given acid.

(2) Suppose that 42 c.c. of a decinormal solution of sulphuric acid were required to just neutralize 50 c.c. of a solution of potassium hydroxide, how many grams of potassium hydroxide would be contained in a litre of solution? A normal solution of sulphuric acid—H_2SO_4, molecular weight 98—contains 49 grms. of the acid per litre, and a $\frac{1}{10}N$-solution contains 4·9 grms. per litre, and this is equivalent to 5·6 grms. of potassium hydroxide per litre. Hence 52 c.c. of the $\frac{1}{10}N$-H_2SO_4 are equivalent to 0·235 grm. of KOH per 50 c.c. of the given solution. Ansr. 4·7 grms. of potassium hydroxide per litre.

Similar remarks apply to the determination of alkalies—alkalimetry—by standard solutions of the acids. This process of analysis is called *volumetric analysis* in contradistinction to *gravimetric analysis*, which involves several weighings during each determination. In volumetric analysis, the preparation of the stock of standard solution may involve one or two weighings; the stock of standard solution may serve a great number of analyses. Experimental details are discussed in laboratory text-books.

W. Ostwald employed the term **mol** as an abbreviation for **gram-molecule**, that is, a weight of a compound equivalent to the molecular weight expressed in grams—*e.g.* one gram-molecule or one mol of sulphuric acid, H_2SO_4, is 98 grms.; and 147 grms. of absolute sulphuric acid contains $147 \div 98 = 1·5$ mols or gram-molecules. F. Fichter (1914) proposed **val** for a **gram-equivalent**, that is, a weight of a compound numerically the same as the equivalent weight expressed in grams—*e.g.* one gram-equivalent or one val of sulphuric acid is 49 grms. A **millimol** is equivalent to a milligram molecule; and a **millival** to a milligram equivalent, etc. The term mol is in fairly common use, but val is not used in place of equivalent weight.

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[2] E. Cornec, *Compt. Rend.*, **149**. 676, 1909; **153**. 341, 1911; *Bull. Soc. Chim.*, (4), **5**. 1081, 1121, 1909.

§ 14. Bases

> We maintain that hydrogen is an essential not an accidental constituent of all acids and alkalies.—J. P. COOKE (1876).
>
> Philosophically, acids and bases ought to be regarded as salts.—A. NAQUET (1864).

The term base—Greek βάσις, a base—was originally intended to express the idea that the metal or metallic oxide was the more important constituent, the foundation, or base so to speak, of a salt. This idea was dropped when it was recognized that the acidic constituent of a salt is just as important as the basic constituent. The idea persists in chemistry text-books where the salts are described under the basic element.

As a first approximation to a satisfactory definition, it was said that **a base is a substance which reacts with an acid to produce a salt and water.** For instance, zinc oxide reacts with sulphuric acid to produce zinc sulphate and water : $ZnO+H_2SO_4=H_2O+ZnSO_4$. Sodium hydroxide reacts with sulphuric acid to produce sodium sulphate and water: $2NaOH+H_2SO_4=2H_2O+Na_2SO_4$. The oxides of the non-metallic elements are usually but not always acidic, and the oxides of the metals are usually but not always basic.

H. Zeitler (1917)[1] illustrates the formation of water during the union of an acid and base to form a salt by placing a stick of dry alkali hydroxide in a jar of dry hydrogen chloride. After a short time, the glass is bedewed, and the alkali is covered with crystals of the alkali chloride.

As a rule, the bases include the oxides and the hydroxides of the metals, but for convenience, certain groups of elements are called bases, although they form salts by direct addition or combination without the separation of water, *e.g.* ammonia—NH_3, hydroxylamine—NH_2OH, hydrogen phosphide—PH_3, etc. Thus, gaseous ammonia and hydrogen chloride form ammonium chloride: $NH_3+HCl=NH_4Cl$. Liquid ammonia dissolves but does not colour phenolphthalein, and it is an open question whether it should be called a base. However, the aqueous solution of ammonia probably forms ammonium hydroxide, NH_4OH, which does behave like the regular bases in this respect: $NH_4OH+HCl=NH_4Cl+H_2O$.

The definition of a base indicated above is highly unsatisfactory because it involves the definition of an acid, and we have just acknowledged that a satisfactory definition of an acid is not yet possible. Hence the definition of a base defines the unknown in terms of the unknown—*ignotum per ignotum.* Alkali and base are not synonymous terms. Every alkali is a base, but every base is not an alkali. The alkali oxides form very soluble hydroxides with marked basic properties, *e.g.* potassium hydroxide. The oxides of the alkaline earths form sparingly soluble hydroxides with less marked basic properties, *e.g.* calcium hydroxide. The other oxides, as a rule, do not react directly with water, and the hydroxides are made indirectly. **An oxide cannot be classed as acidic or basic unless it can be shown to produce corresponding salts.** These facts are sometimes summarized in a scheme resembling:

				Examples.
Bases	Metal oxides and hydroxides	React directly with water	Very soluble	Alkali oxides
			Sparingly soluble	Alkaline earth oxides
		Do not react directly with water		Iron and copper oxides
	Hydrides of certain non-metals and their derivatives			Ammonia, phosphine

The process of synthesizing a salt from an acid and base can be reversed. In 1803, J. J. Berzelius and W. Hisinger[2] showed that aqueous solutions of the salts are resolved into their proximate constituents—acids and bases—by the passage of an electric current; and they demonstrated that during the electrolysis of an aqueous solution of a salt, the acid accumulates about the positive and the base about the negative pole. This is readily illustrated by electrolyzing an aqueous solution of a neutral salt in a U-tube. The liquid is coloured violet with litmus. In a short time, the liquid about the negative pole becomes blue, and that about the positive pole red.

Peroxides.—We have seen how barium oxide, BaO—barium bivalent—when heated under certain conditions forms barium peroxide—BaO_2. The peroxides contain a higher proportion of oxygen than the normal oxides. Barium oxide with sulphuric acid forms barium sulphate and water: $BaO+H_2SO_4=BaSO_4+H_2O$. It is therefore a base. Barium peroxide forms barium sulphate, water, and oxygen when likewise treated with sulphuric acid: $2BaO_2+2H_2SO_4=2BaSO_4+2H_2O+O_2$. The hypothetical salt, $Ba(SO_4)_2$, not $BaSO_4$, corresponds with barium peroxide. Hence, barium peroxide is not a basic oxide. If $Ba(SO_4)_2$ or a related salt could be prepared, then barium peroxide would, by definition, be a basic oxide.

G. H. Bailey[3] showed that the tendency of the typical oxides of Mendeléeff's table is to form higher oxides—peroxides—without regard to the stability of the oxide; with the *even* series, this tendency is greater in a given (vertical) family of elements the higher the atomic weight; and in the horizontal series, also, there is a tendency to associate with oxygen in passing from left to right, *i.e.* with increasing atomic weight. In the *odd* series, taken vertically, there is less tendency to form peroxides as the atomic weight of the positive element increases, and the attraction for oxygen grows feebler as the atomic weight increases in passing from left to right, although there is a disposition for the attraction to become more marked as the extreme right of the period is reached. The constitution and properties of the peroxides is discussed later.

Amphoteric oxides.—Lead dioxide or peroxide, PbO_2—lead quadrivalent—can be regarded as a basic oxide because it forms the corresponding salt—$PbCl_4$—with hydrochloric acid. But PbO_2 also forms salts—plumbates—with bases, *e.g.* potassium plumbate, $O=Pb=(OK)_2$. Hence, a substance may be both acidic and basic according to circumstances. Aluminium hydroxide—aluminium tervalent—is a base, because, when treated with an acid, it forms a salt—aluminium chloride, $AlCl_3$—and water:

$$Al(OH)_3+3HCl=AlCl_3+3H_2O$$

But aluminium hydroxide when treated with a base, say, sodium hydroxide, also forms a salt—sodium aluminate, $Al(ONa)_3$—and water:

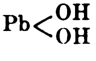
$$Al(OH)_3+3NaOH=Al(ONa)_3+3H_2O$$

Hence, aluminium hydroxide acts towards an acid like a base, and towards a base like an acid. Such oxides can be called **intermediate oxides,** or **amphoteric oxides**—from the Greek ἀμφότερος, both. Zinc oxide is an intermediate oxide. Stannic oxide, $O=Sn=O$—tin quadrivalent—forms stannic sulphate, $SO_4=Sn=SO_4$, and also sodium stannate, $O=Sn=(ONa)_2$; hence, stannic oxide is also an intermediate oxide.

Basic salts.—On comparing the graphic formulæ of the hydroxides of sodium (univalent), lead (bivalent), and bismuth (tervalent):

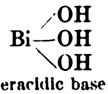
$Na-OH$

Uniacidic base.



$$Pb<\begin{matrix}OH\\OH\end{matrix}$$

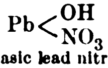
Biacidic base.



$$Bi\begin{matrix}/OH\\-OH\\\backslash OH\end{matrix}$$

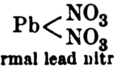
Teracidic base.

with the graphic formula for mono-, di-, and tri-basic acids we naturally inquire if the OH or hydroxyl group can be replaced by acid radicles one by one so as to furnish what would be called uni-, bi-, and ter-acidic bases. In the particular examples just selected, salts corresponding with $Pb(OH)NO_3$ and with $Pb(NO_3)_2$; or



$$Pb<\begin{matrix}OH\\NO_3\end{matrix}$$

Basic lead nitrate.



$$Pb<\begin{matrix}NO_3\\NO_3\end{matrix}$$

Normal lead nitrate.

are known. The former is called *basic lead nitrate*, the latter *normal lead nitrate*, or simply lead nitrate. Similarly, $Bi(OH)_2NO_3$, *basic bismuth nitrate*, and normal bismuth nitrate, $Bi(NO_3)_3$, are known. The basic salts are thus intermediate in composition between the normal salts and the basic oxides; they are usually derived from the more feeble bases—MgO, ZnO, PbO, CuO, Bi_2O_3, Al_2O_3, etc. As a rule, the basic salts unite readily with other salts to form complexes or double salts (*q.v.*).

The basic salts are usually prepared by the action of water or of bases—potassium hydroxide, aqueous ammonia, etc.—on solutions of the normal salts. Some basic salts form well-defined crystals, others are more or less amorphous, ill-defined, mud-like precipitates about which doubts can be raised whether they are really homogeneous chemical individuals, for their composition varies with the conditions under which they are formed, with the amount of washing the precipitate has suffered, and even with the way the solutions have been mixed. A great many basic salts have been reported which are probably mixtures or partially decomposed compounds. Accordingly, there have been many differences of opinion as to the basic salts of many of the elements; as one writer has expressed it, "the principle employed in selecting which are true individuals and which are mere mixtures has been left to individual taste." The phase rule, to be described later, furnishes a rational basis which can often be employed in deciding which precipitates are mixtures and which are compounds.

There is need for a clear understanding of the term *basic*: Na_2O represents a basic compound (oxide); HNO_3 represents a monobasic compound (acid); and $BiO.NO_3$ represents a basic compound (salt). Similarly, HNO_3 represents an acid; $CuSO_4$ has an acid reaction; $NaHCO_3$ represents an acid salt; and NaOH represents a monoacid base. Two of these have an acid and two an alkaline reaction.

The basic salts are usually, not always, less soluble in water than the corresponding normal salts.

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[2] W. Hisinger and J. J. Berzelius, *Gehlen's Journ.*, **1.** 147, 1803.
[3] G. H. Bailey, *Journ. Chem. Soc.*, **65.** 315, 1894.

§ 15. Hydroxides and Anhydrides

> Acids and alkalies are compounds having the same general molecular structure, and the differences between acids and alkalies, and, we might add, the differences between individual acids and individual alkalies, depend on the nature of their radicles.—J. P. COOKE (1876).

We have seen that sulphur dioxide and phosphorus pentoxide form acids with water:

$$\underset{\text{Sulphur dioxide.}}{SO_2} + H_2O = \underset{\text{Sulphurous acid.}}{H_2SO_3}; \text{ and } \underset{\text{Phosphorus pentoxide.}}{P_2O_5} + 3H_2O = \underset{\text{Phosphoric acid.}}{2H_3PO_4}$$

The water in these compounds has completely lost its identity, and it is generally supposed to produce a new class of bodies called **hydroxides.** Every element, excepting fluorine and the argon family, appears to form one or more hydroxides, directly or indirectly. The heats of formation of a few hydroxides[1] from their elements and water are indicated in Table III. If the heat of formation of the oxide, Table I, be deducted from these values, the heat of conversion of the oxide into the hydroxide will be obtained. For the formation of these hydroxides from these elements add on the heat of formation of the corresponding amount of liquid water, *viz.* H_2O—68·36 Cals., and $\frac{1}{2}H_2O$—34·18 Cals.

TABLE III.—HEATS OF FORMATION OF SOME HYDROXIDES.

Hydroxide.	Cals.	Hydroxide.	Cals.	Hydroxide.	Cals.
KOH	68·99	$Tl_2O_3.xH_2O$	86·34	$Mn(OH)_2$	94·77
NaOH	67·69	$Sn(OH)_2$	68·09	$MnO(OH)_2$	116·33
$Cu(OH)_2$	37·52	$SnO(OH)_2$	133·50	$Fe(OH)_2$	68·28
$Au_2O_3\,xH_2O$	13·19	$Pb(OH)_2$	125·16	$Fe_2O_3.xH_2O$	191·15
$Ca(OH)_2$	146·47	H_3PO_4	200·06	$Co(OH)_2$	63·40
$Sr(OH)_2$	146·14	H_3AsO_4	113·09	$Co_2O_3.xH_2O$	149·38
$Ba(OH)_2$	146·50	H_3SbO_4	114·39	$Ni_2O_3.xH_2O$	120·38
$Mg(OH)_2$	148·96	$Sb(OH)_3$	83·71	$Pd(OH)_2$	22·71
$Zn(OH)_2$	82·68	$Bi(OH)_3$	68·87	$PdO(OH)_2$	30·43
$Cd(OH)_2$	65·68	H_3PO_3	125·16	$PtO(OH)_2$	17·88
$Al_2O_3.xH_2O$	388·92	H_2SO_4	124·56	$Pt(OH)_2$	19·22
Tl(OH)	22·73	$TeO(OH)_2$	77·18		

The oxides from which the acids are produced do not contain the elements of water. They are called **anhydrides,** or **acid anhydrides**—from the Greek *α*, without; ὕδωρ, water. Thus SO_2 is not only called sulphur dioxide, but also sulphurous anhydride; and P_2O_5 is not only phosphorus pentoxide, but phosphoric anhydride. An anhydride can be regarded as the residue left when the elements of water are removed from the oxyacids. Thus sulphuric acid, H_2SO_4, less water, gives sulphuric anhydride—SO_3—also called sulphur trioxide; sulphurous acid, H_2SO_3, less water, gives sulphurous anhydride—SO_2. It is generally supposed that sulphurous anhydride in combining with water forms a compound containing quadrivalent sulphur and two univalent hydroxyl—OH—groups, that is, $SO(OH)_2$. The reaction is symbolized:

$$O{=}S{=}O + H-OH \rightarrow O{=}S{<}{}^{OH}_{OH} \quad \text{(sulphurous acid)}$$

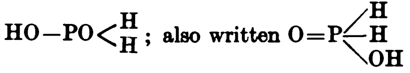
and sulphuric acid is considered to be a compound containing sexivalent sulphur and two hydroxyl groups, $SO_2(OH)_2$. The reaction is symbolized:

$$\genfrac{}{}{0pt}{}{O}{O}{\gg}S{=}O + H-OH \rightarrow \genfrac{}{}{0pt}{}{O}{O}{\gg}S{<}{}^{OH}_{OH} \quad \text{(sulphuric acid)}$$

If the acids be regarded as salts of hydrogen, it can be argued that water is a basic oxide which unites with an acid anhydride to form a salt, *e.g.* SO_3 (acidic oxide) $+H_2O$ (basic oxide)$=H_2SO_4$ (salt), by analogy with $SO_3+K_2O=K_2SO_4$. Isaac Newton called water a salt. It is easy to show that with the regular definitions of acid and base, the fame of venerable sulphuric acid—the mother of acids—can be attacked. Representing sulphuric acid as just indicated, the two hydroxyl groups can be replaced one by one with other acid radicles, *e.g.*

$$\genfrac{}{}{0pt}{}{O}{O}{\gg}S{<}{}^{OH}_{Cl} \qquad\qquad \genfrac{}{}{0pt}{}{O}{O}{\gg}S{<}{}^{Cl}_{Cl}$$

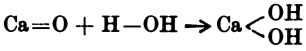
where the hydrogen of the hydrochloric acid, HCl, is displaced by the bivalent radicle SO_2, "analogous with the formation of magnesium chloride, $MgCl_2$, by the substitution of the hydrogen of hydrochloric acid by the bivalent atom Mg" in magnesium hydroxide, $Mg(OH)_2$. This shows how the definitions of acid and base, if not applied with care, may lead into a bewildering labyrinth. Enough has been said to show that **an acid anhydride with water forms an acid, and with a base it forms a salt:** $ZnO+SO_3=ZnSO_4$ (zinc sulphate). Sulphurous acid can also be regarded as sulphurous hydroxide—$SO(OH)_2$; and phosphoric acid—phosphorus quinquevalent—as phosphoric hydroxide—$PO(OH)_3$. The basicity of an acid is generally supposed to correspond with the number of hydroxyl groups it contains. The hydrogen of the hydroxyl groups is supposed to be the *displaceable hydrogen* referred to in the definition of acids. Monobasic hypophosphorous acid—H_3PO_2—is supposed to be $H_2PO(OH)$; or



$$HO-PO\begin{matrix}<H\\<H\end{matrix}\text{; also written } O=P\begin{matrix}\diagup H\\ -H\\ \diagdown OH\end{matrix}$$

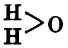
because there is only one displaceable hydrogen atom per molecule. The hydrogen atoms directly united to the phosphorus atoms are not supposed to be replaceable by the bases, but the hydrogen of the single hydroxyl group is displaceable.

The basic oxides are sometimes called **basic anhydrides,** and they too form hydroxides with water, *e.g.* calcium oxide, CaO—calcium bivalent—with water forms calcium hydroxide, $Ca(OH)_2$:



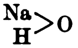
$$Ca=O + H-OH \rightarrow Ca\begin{matrix}<OH\\<OH\end{matrix}$$

From this point of view water can be regarded as hydrogen hydroxide, H—OH, analogous with K—OH, potassium hydroxide, and Na—OH, sodium hydroxide. Water itself behaves in some respects as if it were an acid, and in others as if it were a base. In view of the regular definition, it could be reasonably argued that if water be an acid, sodium hydroxide, NaOH, is an acid salt, and sodium oxide, Na_2O, a normal salt



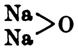
$$\begin{matrix}H\\H\end{matrix}>O$$

Water.



$$\begin{matrix}Na\\H\end{matrix}>O$$

Sodium hydroxide.



$$\begin{matrix}Na\\Na\end{matrix}>O$$

Sodium oxide.

Excluding certain carbon compounds, the hydroxides of the non-metallic elements are usually but not always acids, and the hydroxides of the metals are usually but not always bases. The term *hydroxide* is generally reserved for compound of the basic oxides with water; and the term *anhydride* is usually reserved for the acid anhydrides. The compounds of the basic anhydride with water (hydroxides) were once called **hydrates**—*e.g.* potassium hydroxide was called potassium hydrate, etc. The term **hydrated salt** is applied more or less vaguely to compounds which contain the elements hydrogen and oxygen in the proportion required to form water—combined water.

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§ 16. The Polar Theory of Chemical Combination.

Strife between opposite tendencies is the parent of all things.—HERACLEITUS (*c.* 450 B.C.).

Nature is constantly labouring after repose by the balance and neutralization of contrary tendencies; and so far as polar forces enter into her economy, she seeks harmony by means of discord, and unity by opposition.—W. WHEWELL (1840).

Every chemical action is fundamentally an electrical phenomenon. . . . Electricity is the first cause of all chemical action.—J. J. BERZELIUS (1812).

In some early conjectures on chemical affinity, Isaac Newton (1714) assumed that electrical and chemical phenomena were both due to attractive forces acting at insensibly small distances. He said:

> The attraction of electricity reaches to sensible distances and so has been observed by vulgar eyes; but there may be others which reach to so small distances as to have hitherto escaped observation. Possibly electrical attraction reaches to small distances, even without being excited by friction.

Newton seems to have regarded the intensity of chemical affinity to be inversely proportional to the composition of compound particles. The more complex the aggregates the weaker their affinity. Newton, however, did not consider that the facts were sufficiently well known to justify further conjectures, for he said:

> We must learn from the phænomena of nature what bodies attract one another, and what are the laws and properties of the attractions before we inquire the cause by which the attraction was performed.

H. Davy's electrical theory of chemical affinity (1807).—After W. Nicholson and A. Carlisle (1800) had decomposed water, and J. J. Berzelius and W. Hisinger (1803) had decomposed salts by the electric current, chemists began to suspect that electrical and chemical forces were closely related. H. Davy took up the subject about 1806, and in his paper *On some chemical agencies of electricity* (1807), he showed that sulphur and copper can be charged with opposite electricities by friction—the former negatively, the latter positively—just as A. Volta (1792) proved that when two metals touch one another, they develop electricity—each assuming an electric charge of opposite sign to the other. H. Davy tried to show that the chemical activity of a substance is dependent upon its electrical condition, for he said:

> As the chemical attraction between two bodies seems to be destroyed by giving one of them an electrical state different from that which it naturally possesses; that is, by bringing it artificially into a state similar to the other, so it may be increased by exalting its natural energy. Thus, whilst zinc, one of the most oxidizable of metals, is incapable of combining with oxygen when negatively electrified in the circuit, even by a feeble power; silver, one of the least oxidizable, easily unites to it when positively electrified; and the same thing might be said of other metals.

Davy argued that in the act of combination, the reacting substances by contact acquire electrical charges of opposite signs; and that chemical combination is accompanied by a neutralization or exchange of electricities of opposite signs between the combining substances. Thus, an acid unites with an alkali because the former acquires an electronegative and the latter an electropositive charge; oxygen acquires an electronegative charge, and it unites with metals which acquire an electropositive charge; similarly, electronegative sulphur unites with electropositive copper producing electrically neutral sulphide. When the quantity of electricity which is neutralized in the act of combination is restored, the compound is decomposed, and the original products are reproduced. As a climax, H. Davy virtually said that chemical affinity is nothing but electrical energy; for example, in his *Elements of Chemical Philosophy* (London, 1812), he said:

> Electrical effects are exhibited by the same bodies when acting as masses, which produce chemical phenomena when acting by their particles; it is not therefore improbable that the primary cause of both may be the same, and that the same arrangement of matter, or the same attracting powers which place bodies in the relations of positive and negative—*i.e.* which render them attractive of each other electrically, and capable of communicating attractive powers to other matter—may likewise render their particles attractive, and enable them to combine when they have full freedom of motion.

Davy did not follow up his ideas about the relations between electrical disturbance and chemical decomposition, on the theoretical side, but he applied the principle as an instrument of decomposition, and solved some questions of the very greatest importance to the growing science, for it led him to the isolation of the alkali metals—potassium and sodium.

The idea of acidity involves two concepts—(*a*) an antagonistic force which is reciprocated by the alkalies; and (*b*) a great tendency to unite with bodies generally. In 1809, A. Avogadro published a paper entitled, *Idées sur l'acidité et l'alkalinité*.[1] H. Davy's experiments on electrolysis suggested to A. Avogadro the idea of a chemical force which is polar at the moment of action, and which not only determines the union of an acid and alkali, but also chemical changes generally. According to Avogadro:

> All the phenomena are easily explained if we consider acid and alkali antagonism as purely relative properties, only becoming somewhat absolute when referred to a middle

substance A which has the acid antagonism with reference to B, and which may possess the alkaline antagonism with reference to a third substance C. What are then termed acids and alkalies are merely bodies which have the acid or alkali antagonism in respect of certain other bodies whose position in the scale is approximately indicated by certain properties, such as inability to affect vegetable blues. . . . The degree of acidity or alkalinity of a compound depends upon the degree of those properties in its constituents. . . . Of two substances in the act of combination, one always plays the part of acid, and the other of alkali; and it in this antagonism which constitutes the tendency to combination, or affinity properly so called.

Accordingly, said A. Avogadro, different substances can be arranged in series, the position of each marking its true affinity to any predecessor or successor. Oxygen and sulphur would come first in the series, hydrogen and carbon last, with the neutral salts in the middle of the series. The measure of chemical antagonism is electric heterogeneity or oxygenicity. A substance is the more oxygenic the less it is oxidizable.

The essence of polarity is the contrast of opposing qualities such as is exhibited by the so-called north and south poles of a magnet where unlike poles attract and like poles repel one another; by the two states of static electricity—positive and negative; and by the phenomena of electrolysis—as interpreted by C. J. T. von Grotthus (1805), H. Davy (1806), and M. Faraday (1834)[2]—where the atoms or radicles have opposite polarities to that of the electrode about which they accumulate. Atoms with opposite polarities combine readily, while those with the same polarity have little or no tendency for union. "In every part of nature," said R. W. Emerson, "we meet with polarity. . . . An inevitable dualism besets nature so that each thing is a half, and suggests another to make it a whole." J. J. Berzelius considered that "the form of crystalline substances presupposes an effort on the part of the atoms to touch one another by preference at certain points, and this shows that the particles probably exhibit an electric or magnetic polarity."

J. J. Berzelius' electrochemical theory (1819–48).—J. J. Berzelius further expressed his view that the electrical charges on the particles were the controlling factors in chemical reactions. Berzelius' views were described in his *Essai sur la théorie des proportions chimiques et sur l'influence chimique de l'électricité* (Paris, 1819), and he took quite a different view from H. Davy as to the way the electrical charges on the particles produce chemical action. While H. Davy considered the electrical charges to be the consequence of contact or of mutual action between heterogeneous particles, Berzelius believed that each elementary atom is endowed with two kinds of electricity and has in consequence two electrical poles; these poles differ in strength so that the resultant effect is to make each atom appear as if it were positively or negatively electrified. Thus, Berzelius distinguished electropositive and electronegative elements according to which charge prevailed; the kind of charge carried by an element was determined by the appearance of the element at the positive or negative pole when a compound of the element was electrolyzed. The varying degrees of chemical affinity were supposed to imply that different substances were charged with varying quantities of electricity. Consequently the elements were arranged in series according to the magnitude of the charge, and Berzelius thus obtained an electrochemical series with the alkali metals at one end of the series, and oxygen at the other:

Potassium
Sodium
. . . .
Zinc
Lead
Gold
. . . .
Fluorine
Nitrogen
Sulphur
Oxygen

Oxygen was supposed to be the most electronegative substance of all, and was assumed to be always electronegative. In order to explain the variations of chemical affinity with temperature, the electric polarity was further supposed to vary with temperature. To explain why sulphur has a greater affinity for oxygen than for, say, gold, when both oxygen and sulphur are electronegative, Berzelius assumed that the absolute quantity of positive electricity on sulphur is much greater than on gold, and since elements attract one another by their contrary poles, sulphur exerts a stronger attraction for oxygen than for gold. Thus, an element might be positively polar with some elements, and negatively polar with others—sulphur, for instance, is positive with oxygen, and negative with hydrogen and the metals. In the case of the caustic alkalies, too, said J. J. Berzelius, water plays the part of an acid ; and when it unites with an acid (anhydride), it plays the part of a base.

According to J. J. Berzelius, chemical combination consists in the attraction of the dissimilar poles of the reacting units, and, in consequence, the neutralization of opposite electric charges. If opposite electrical charges be exactly balanced, an electrically neutral compound, chemically inactive, is supposed to be formed. Berzelius explained double decomposition by his electrochemical theory in these words :

> Every chemical action is an electrical phenomenon dependent upon the electrical polarity of the particles, and everything which appears to be the result of chemical affinity is really due to the electrical polarity of some bodies being stronger than that of others. When the compound AB is decomposed by a substance C, the affinity of C for A is greater than that of B for A, and C must possess a stronger electrical polarity than B. . . . If two bodies AB and CD react so as to produce two new bodies AD and BC, it follows that the electric polarities in the latter pair of bodies are better neutralized than in the former.

These statements may or not may be true, but the argument is not sound, for it is assumed that because B is displaced by C from its combination with A, the affinity of C for A is greater than that of B for A ; it is further assumed that affinity and electrical polarity are the same, and to state that this proves that the electrical polarity of C for A is greater than B for A is arguing in a circle.

When, say, sodium unites with oxygen to form the base sodium oxide, Na_2O ; or sulphur with oxygen to form the acid anhydride sulphur trioxide, SO_3, primary compounds, or **compounds of the first order**, are formed ; these primary compounds are made up of atoms having opposite polarities, thus :

$$\overset{+}{Na}_2\overset{-}{O} \qquad \overset{+}{Ca}\overset{-}{O} \qquad \overset{+}{S}\overset{-}{O}_3 \qquad \overset{+}{C}\overset{-}{O}_2$$

The electrical attractions are not supposed to be always exactly neutralized during the formation of these primary compounds ; the basic oxides were supposed to have an excess of positive electricity and the acid anhydrides an excess of negative electricity ; the excess causes a further attraction between the acidic and basic radicles resulting in the formation of **compounds of the second order,** for example ·

$$\overset{+}{H_2O}+\overset{-}{SO_3} \qquad \overset{+}{Na_2O}+\overset{-}{SO_3} \qquad \overset{+}{CaO}+\overset{-}{CO_2} \qquad \overset{+}{K_2O}+\overset{-}{Cl_2O_5}$$

and these again might similarly form **compounds of higher orders,** for example, said Berzelius, alum must be looked upon as the product of a reaction between aluminium and potassium sulphates, the former acting as a negative, the latter as a positive radicle :

$$\overset{+}{K_2SO_4}+\overset{-}{Al_2(SO_4)_3}=K_2SO_4.\overset{+}{Al}_2(SO_4)_3$$

similarly the union of an anhydrous salt with water may be regarded as a combination of the positively charged anhydrous salt with negatively charged water :

$$\overset{+}{K_2SO_4.Al_2(SO_4)_3}+24\overset{-}{H_2O}=K_2SO_4.Al_2(SO_4)_3.24H_2O$$

Similarly, potassium chloride, KCl, acts as a base towards platinum tetrachloride, $PtCl_4$, and these two salts unite to form a compound with a composition corresponding with $2KCl.PtCl_4$. Berzelius' ideas were embodied in the chemical formulæ in use about 1820. For example :

	Present formulæ.	Berzelius' formulæ.
Sodium sulphate	Na_2SO_4	$Na_2O.SO_3$
Sulphuric acid	H_2SO_4	$H_2O.SO_3$
Calcium carbonate	$CaCO_3$	$CaO.CO_2$
Potassium chlorate	$KClO_3$	$K_2O.Cl_2O_5$

The idea of compounds of different orders is fairly old, for, as previously shown, Isaac Newton had as clear ideas on this subject as Berzelius. Joseph Black has told us in his *Lectures on the Elements of Chemistry* (Edinburgh, **1.** 281, 1803) :

> The older chemists gave the name *mixt* to chemical compounds consisting of two ingredients which we have never been able to reduce to simpler ingredients. Particles of a mixt compound with particles of another mixt formed particles of a *compound ;* the union of two compounds formed a *decompound ;* the union of two decompounds formed a *supercompound ;* etc.

Chemists did not long use the terms indicated by J. Black, although there is a tendency to retain the idea of J. J. Berzelius' compounds of different orders, *e.g.* A. Werner (1893) used the idea in his theory of the ammino-compounds.

The main objections to Berzelius' hypothesis are as follows : In the first place, contrary to Berzelius' assumption that different substances are charged with *varying quantities* of electricity, M. Faraday proved that on electrolysis, *definite and fixed quantities* of electricity are associated with the atoms of matter, although the atoms of the same kind of matter in different compounds, on electrolysis, might be charged with different yet definite quantities of positive or negative electricity. Secondly, after Avogadro's hypothesis had been established, Berzelius' theory was thought to be incompatible with such a comparatively simple reaction as $2H_2+O_2\rightarrow 2H_2O$, for the compound nature of oxygen is due to different electrical charges on the component atoms of the molecules; at first sight this does not agree with the supposed identity of the resulting two molecules of water. Berzelius accordingly denied the diatomic nature of the elementary gases. Thirdly, J. B. A. Dumas (1834) showed that the hydrogen atoms in compounds like CH_4 can be replaced one by one by atoms of chlorine. J. J. Berzelius had postulated that hydrogen is an electropositive element, and chlorine an electronegative one, as exemplified by hydrogen chloride. Here in Dumas' substitutions, a negative element can be exchanged for a positive element without fundamentally altering the chemical character of the resulting compounds. It would be easy to modify Berzelius' theory to meet these difficulties.

J. J. Berzelius entangled his electrochemical theory with other hypotheses as to the structure of compounds which ultimately brought about its fall ; but the electrochemical theory should be considered on its merits apart from the subsidiary hypotheses. "There is life after death in the case of a good doctrine," said I. Remsen in 1903 ; "and the spiritual part of the electrochemical hypotheses of Berzelius, so to speak, lives to-day as the doctrine that atoms of the elements carry electric charges which are the cause of their chemical activity." H. Davy himself pointed out that his statement of the mode of action of the electrical forces is so general that half a dozen essentially different schemes might be devised, each in agreement with the hypothesis that "the forces termed chemical affinity and electricity," as Faraday expressed it, "are one and the same ; " or that "chemical affinity is a consequence of the electrical attractions of particles of different kinds of matter." This hypothesis, developed by H. von Helmholtz (1881), R. Abegg (1906), J. Stark (1908), and J. J. Thomson (1914), is that which is generally accepted to-day, and will be described later.

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§ 17. Binary and Unitary Theories of the Constitution of Acids and Salts

> We understand a phenomenon historically when we are clear in our minds concerning the external conditions and habits of thought from which it sprung; and when its mainsprings of action and its purposes, as well as the effects which have proceeded from it, are distinctly traceable.—P. CARUS (1892).

The fundamental idea in Lavoisier's system is the dualism or polarity of compounds. The acids were regarded as compounds of the acidifiable bases with oxygen, and salts were compounds of acids with oxygenated compounds of the metals or radicles. Lavoisier's oxygen theory was accepted by J. J. Berzelius (1815), and by J. L. Gay Lussac (1816). The former adapted the dualistic theory to his electrochemical hypothesis of chemical combination. He said:

> Assuming that every chemical compound is solely dependent upon two opposing forces —positive and negative electricity—every compound must be composed of two parts held together by their mutual electrical forces. Hence, every compound body, whatever be the number of its constituents, can be separated into two parts one of which is positively and the other negatively electrified. Sodium sulphate, for example, is obtained not from sulphur, oxygen, and sodium, but from sulphuric acid and soda each of which can itself be separated into positive and negative constituents.

All acids and salts were accordingly supposed to have a binary or dualistic structure. Berzelius assumed that there is no redistribution of the atoms during the formation of sulphuric acid by the action of water, H_2O, on sulphur trioxide, SO_3; and accordingly he represented the constitution of sulphuric acid by the formula $H_2O.SO_3$. J. J. Berzelius (1815) did not at first accept Davy's demonstration (1810–15) that some acids—*e.g.* hydrochloric acid—are free from oxygen, because it disturbed the uniformity of his dualistic or binary system of chemical combination, but between 1820–5, he abandoned this prejudice, and recognized the existence of non-oxygenated acids, although he fought for his dualistic or binary hypothesis to the end of his life. He died on August 7th, 1848.

T. Graham's theory of acids (1833).—In his *Ueber die neueren Gegenstände der Chymie* (Breslau, 1796), J. B. Richter described some experiments which pointed to the generalization: The same constant weight of *Lebensluftstoff* (oxygen) is combined with those weights of metal which are required to saturate a constant amount of acid; otherwise expressed, the quantities of the various bases required to saturate a constant amount of acid contain the same weights of oxygen. J. J. Berzelius substantiated "this discovery of the meritorious investigator J. B. Richter" by experiments described in his paper entitled, *Versuch die bestimmten und einfachen Verhältnisse aufzufinden nach welchen die Bestandtheile der anorganischen Natur mit einander verbunden sind* (1811–2); and about 1826, chemists generally held the opinion that the metal oxides contain one atom of the metal to one atom of oxygen, and that one molecule of the metal oxide united with one molecule of the acid to form a molecule of neutral salt. T. Graham, however, proved that this hypothesis is erroneous, for in his *Researches on the arseniates, phosphates, and modifications of phosphoric acid* (1833), he demonstrated the existence of three distinct acid hydrates of phosphoric oxide, P_2O_5—then written PO_5. Keeping to the modern notation, the three hydrates had respectively 3, 2, and 1 molecules of water per molecule of phosphoric oxide, and corresponded with the formulæ:

$P_2O_5.3H_2O$	$P_2O_5.2H_2O$	$P_2O_5.H_2O$
Orthophosphoric acid.	Pyrophosphoric acid.	Metaphosphoric acid.

These hydrates were respectively regarded as "terphosphate, biphosphate, and phosphate of water." Graham further showed that the molecules of water in these three acids could be replaced one by one with basic oxides so that three sodium salts of orthophosphoric acid, with its three molecules of basic water, are possible; two with pyrophosphoric acid, with its two molecules of basic water; and one with metaphosphoric acid, which has only one molecule of basic water. He exhibited the constitution of the phosphoric acids and their salts of soda in tabular form:

		Oxygen in the		
		Soda.	Water.	Acid.
First class	Phosphoric acid	0	3	5
	Biphosphate of soda	1	2	5
	Phosphate of soda.	2	1	5
	Subphosphate of soda	3	0	5
Second class	Pyrophosphoric acid	0	2	5
	Bipyrophosphate of soda	1	1	5
	Pyrophosphate of soda	2	0	5
Third class	Metaphosphoric acid	0	1	5
	Metaphosphate of soda	1	0	5

The result of Graham's work was to show (i) that acids may contain the equivalent of *n* molecules of water which can be replaced by basic radicles to form salts; and (ii) the number of molecules of acid required to form a neutral salt is not necessarily equal to the number of molecules of the base, as was supposed to be the case from the experiments of Richter and Berzelius.

J. von Liebig's theory of polybasic acids (1838).—J. von Liebig followed up Graham's work, and in a paper entitled, *Ueber die Constitution der organischen Sauren* (1838), he adduced examples proving that the molecules of all acids are not equivalent to one another; in other words, acids may be mono-, di-, tri-, . . . basic, according as the acid contains one, two, three, . . . molecules of water which can be replaced by the corresponding number of molecules of the base. This is sometimes called Liebig's theory of polybasic acids. Liebig also said when two and more than two molecules of the base combine with one molecule of the acid, and only one molecule of water is separated during the operation (that is, fewer than the number of equivalents of the fixed base), a **basic salt** is produced. J. von Liebig proved that the products of decomposition of organic acids and salts are different under different conditions, and thus demonstrated the fallacy of the then prevalent assumption that the products of decomposition of a compound prove that they are present as such in the original compound. Every theory based on processes of decomposition, said J. von Liebig, is incomplete and insufficient.

Again, J. von Liebig showed that when lime is neutralized with sulphuric or hydrochloric acid, the same amount of water is formed. According to Berzelius' dualistic theory, in the one case water was present in the sulphuric acid ready formed; and in the other case, the water is produced during the reaction. It cannot be supposed that there is any essential difference between these two reactions, because in both it is most probable that the metal of the lime replaces the hydrogen of the acid, and the hydrogen of the acid combines with the oxygen of the lime to form water. Hence, there is no difference in kind between the action of the so-called oxyacids and hydracids. J. von Liebig thus brought the reactions between most of the acids and bases under one common scheme: Acid+base=salt+water. Acids, said J. von Liebig, are particular compounds of hydrogen in which the latter can be replaced by the metals.

> Neutral salts are those compounds of the same class in which the hydrogen is replaced by an equivalent of the metal. Those substances at present called anhydrous acids acquire the property of forming salts with metallic oxides, for the most part, only on the addition of water; or they are compounds which decompose the oxides at a high temperature. . . . At ordinary temperatures no salt can be produced without water, and the constitution of the salts is analogous to that of the hydrogen compounds which we call acids. The principle of Davy's theory is that the capacity of saturation of an acid is dependent upon the hydrogen, or upon part of the hydrogen, which it contains, so that if the other elements of the acid are

collectively called the radicle, the composition of the radicle does not possess the slightest influence on this capacity.

On grounds of probability and convenience, J. von Liebig thus advocated a hydrogen theory of acids analogous to that previously suggested by H. Davy and P. L. Dulong. To recast the words of J. J. Berzelius, sodium sulphate is a compound of sulphur, oxygen, and sodium, but there is nothing to show that it is composed of a basic oxide, Na_2O, with an acid anhydride, SO_3. Acids are regarded as combinations of simple or compound radicles with replaceable hydrogen; and salts are derivatives of the acids formed by replacing the hydrogen of the latter by metals or equivalent radicles. This form of the hydrogen theory of acids was opposed by J. J. Berzelius to the end of his life (1848), because he saw in it evidence against his own dualistic view of the composition of acids and salts. J. von Liebig's theory is strictly dualistic in that the replaceable hydrogen in acids is contrasted with the acidic radicle.

A. Laurent and C. Gerhardt's unitary hypothesis.—While the hydrogen theory of acids was developing, Berzelian dualism was fighting a losing battle with organic chemistry, as described previously; and it received its severest blow with the advent of A. Laurent and C. Gerhardt's unitary hypothesis, where it was shown that the molecules of a compound are to be regarded as simple edifices, as J. B. A. Dumas expressed it, and not double buildings; molecules are capable of modification by the exchange of one of their constituent elements for another. The unitary hypothesis denies the existence of separate and opposing components in any particular compound; it represents acids and salts by similar formulæ to the hydrogen theory, but it does not insist upon their containing any definite compound, radicle, or their being composed according to any particular type; although it does place compounds with analogous properties in the same class to express the influence of each element on the united properties of the compound.

CHAPTER IX

WATER

§ 1. The Cycle of Water in Nature

> I am the daughter of Earth and Water
> And nursling of the Sky ;
> I pass through the pores of the Ocean and Shores ;
> I change, but I cannot die.—THE CLOUD.

WATER is widely distributed in nature in its three states of aggregation—steam or aqueous vapour, liquid water, and solid ice or snow. It has been estimated that three-fourths of the surface materials on the crust of the earth is water. Animals and plants contain a large proportion of combined water—*e.g.* fish contains the equivalent of about 80 per cent. ; beef, 60–62 per cent. ; the human body, 70 per cent. ; aquatic plants between 95 and 99 per cent. ; and ordinary land plants, 50–75 per cent. A great many rocks contain water—combined and absorbed. Clay, for example, contains up to 14 per cent. of combined water.

Water plays a vital part in the nutrition of animals and plants ; indeed, it is absolutely indispensable to animal and vegetable life. It is universally employed as a solvent, and it is utilized as a thermal agent in refrigeration and heating, where it is valuable on account of the magnitude of its heat of fusion, and its specific heat ; it is also similarly used in steam engines. In short, water is employed for countless purposes by man ; and it is the cause of the most striking phenomena in nature.

The circulation of water in nature—the water cycle.—All the water on the earth passes through a remarkable cycle of changes. The heat of the sun leads to the evaporation of water from the seas, etc. ; water vapour is only 0·62 times as heavy as an equal volume of air, and consequently it rises into the upper regions of the atmosphere, as well as diffuses into and mixes with the atmospheric air. The temperature of the ascending vapour gradually decreases, and consequently a plane must be reached where the air is saturated with moisture. The vapour will then condense in the form of fine drops of water—mist or clouds. The fine drops coalesce into larger drops. Ultimately, the condensed water must descend again to the earth as dew, rain, snow, or hail. The wind distributes the vapour. The heat given up during the condensation of the vapour is distributed or carried from the hotter regions—where evaporation is fastest—to the colder regions—where the vapour is condensed—thus helping to stretch the temperate regions nearer to the poles. The water which is sprayed, as rain, etc., on the surface of the globe, does a certain amount of physical and chemical work. On the chemical side, water helps in the decomposition and weathering of rocks ; and on the physical side, it transports matter in suspension from the higher to the lower levels. The soluble matters ultimately collect in the seas.

Thus the water cycle involves : (1) evaporation from the oceans, seas, lakes, etc. ; (2) condensation in the upper regions of the atmosphere as a fine mist of distilled water where it collects as clouds ; (3) further condensation followed by rain ; (4) percolation of the rain-water through the soil and its accumulation on an impervious bed of rock, whence it is forced to the surface, as spring water, by the pressure of the superincumbent water ; and (5) the collection of spring and surface waters by the streams and rivers to be forwarded to the sea. The river thus returns the water whence it came to commence anew the never-ending cycle. P. B. Shelley has described the idea in a charming manner in his well-known poem—*The Cloud.* It must be added that a relatively small proportion of the water which finds its way into the ground is "fixed" by reacting with certain silicates and other minerals forming hydrated silicates, hydrated alumino-silicates, etc.—*e.g.* kaolinite, $Al_2O_3.2SiO_2.2H_2O$; selenite, $CaSO_4.2H_2O$; etc.

Rain-water.—When rain falls on the surface of the earth, part of it sinks deeply underground to reappear as spring water; about 25 per cent. drains off directly into streams and rivers; a part is retained as the ground water of soils; and a part returns by evaporation directly to the atmosphere. Rain, in its journey through the air, dissolves oxygen, nitrogen, carbon dioxide, chlorides, and ammoniacal and nitrate nitrogen. It also carries down dust—organic and inorganic. Rain-water, particularly if collected near the sea in high winds, contains sodium chloride; and if collected near towns, contains sulphur compounds—sulphur dioxide and sulphuric acid—derived from the products of combustion of coal. When evaporated to dryness, 10,000 parts by weight of rain-water will give about 0·34 part of solid matter; most of this consists of sodium chloride and organic matter. Rain-water contains in solution 0·013 per cent. of dissolved nitrogen; 0·0064 per cent., oxygen; and 0·0013 per cent., carbon dioxide. The rain which falls at the end of a shower is less contaminated than that which falls at the beginning, because the atmosphere is washed, so to speak, during the earlier part of the shower. According to F. W. Clarke's important work, *The Data of Geochemistry* (Washington, 1916),

> As a carrier of ammonia, nitric acid, sulphuric acid, and chlorine, rain-water performs a function of the highest significance to agriculture, but whose geological importance has not been generally recognized. Rain and snow collect these impurities from the atmosphere in quantities which vary with local conditions, and redistribute them on the soil.

The average of a number of analyses of rain-water at Rothamsted (England) [1] gave 2·71 lbs. of ammoniacal nitrogen per acre per annum, and 1·13 lbs. of nitric nitrogen. In most cases ammonia is in excess, but in the tropics the reverse seems to obtain. At Barbados,[2] 1·009 lbs. of ammoniacal nitrogen and 2·443 lbs. of nitric nitrogen were annually deposited per acre. Similarly, 14·87 lbs. of chlorine as chlorides were deposited annually per acre at Rothamsted, and 180·63 lbs. at Ceylon.

Spring and mineral water.—Directly the rain-water strikes the ground, it begins to attack and dissolve various rocks, decaying organic tissue (humic compounds), etc., forming *surface and ground water.* It is estimated that between 25 and 40 per cent. of the rainfall, in temperate regions, soaks into the ground. In its journey underground the percolating water—*underground water*—loses most of its organic matter and dissolves more or less mineral matters—compounds of calcium, magnesium, and sodium; carbon dioxide; etc. The greater the depth to which the water sinks the greater the amount of solid matter it can dissolve. Water under great pressure is a powerful solvent. Sooner or later the water which has percolated underground will be forced to the surface as *spring water.* If the spring water holds an unusual amount of some particular constituent in solution which gives it a marked taste, or some specific property, the term *mineral water* is applied. Mineral waters do not necessarily contain a large excess of mineral matters in solution. The water from mineral springs is often named according to some special constituent dissolved in the water, or from the locality of the spring. *Fresh water* is a vague term applied to a natural water which does not contain much dissolved impurity; to natural water as distinct from salt or sea water; etc.

Chalybeate waters contain ferrous carbonate—*e.g.* Tunbridge; Buxton; the Excelsior Spring, Saratoga, N.Y.; the Hot Springs of Arkansas; Homberg; etc. *Sulphur waters* contain hydrogen sulphide and other sulphur compounds, alkaline sulphides, etc., *e.g.* Baden; Carlsbad; Harrogate; Bath; Aachen; the Red Sulphur Spring, Sharon, N.Y.; etc. The water of the Steamboat Springs in Nevada has borates and deposits a sinter containing arsenic, antimony, mercury, lead and copper sulphides, as well as traces of gold and silver. *Saline waters* contain salts of various kinds, for instance, magnesium sulphate and chloride which give the water a bitter taste—*e.g.* Bath; Epsom; Seidlitz; Friedrichshall, Ofen; Cheltenham; etc. *Sodium sulphate and sodium carbonate*—*e.g.* Marienbad; Carlsbad; etc. *Carbon dioxide* (*acid reaction*)—*e.g.* Apollinaris (imitations of this and other mineral waters are made artificially; the natural water is bottled and exported). *Carbon dioxide with sodium carbonate* (alkaline reaction.)—*e.g.* Vichy; Neuenahr; etc. *Carbon dioxide with sodium chloride*—*e.g.* Ems; Neider-Selters; etc. *Sodium* and other chlorides—*e.g.* Homberg; Aachen; Baden Baden; Congress Spring, Saratoga, N.Y.; etc. Some waters contain *iodine and bromine compounds*—*e.g.* Congress Spring, and Excelsior Spring, Saratoga, N.Y.; Woodhall Spa; etc. *Arsenic*—*e.g.* Roncegno; Levico; etc. *Lithia*—*e.g.* Congress Spring, Saratoga, N.Y.; etc. *Boric acid*—*e.g.* Yellowstone Park; Chaguarama Valley (Venezuela); Tuscany; etc. *Silica*—*e.g.* the Hot Springs of Iceland, New Zealand, Yellowstone Park, etc. *Hard waters* have calcium and magnesium carbonates and sulphates in solution. The waters of some springs, particularly in volcanic districts, issue at an elevated temperature, hence the term *thermal waters, e.g.* the Hot Springs of New Zealand (about 60°); Teplitz (39°–49°); Vichy (32°); San Bernardino, California (40°–78°); etc. For an extensive bibliography on the different natural waters, see C. Doelter, *Handbuch der Mineralchemie*, Dresden, **3**. i, 889, 1918; and H. von Fehling, *Neues Handwörterbuch der Chemie*, Braunschweig, **11**. 745, 1915. For a bibliography of British mineral and chemical waters, see W. H. Dalton, *B. A. Rep.*, 859, 1888.

River water.—Spring water collects in rivers and streams. Of the total rainfall on all the land of the globe per annum—29347·4 cubic miles—J. Murray[3] estimates that the rivers of the world discharge about a quarter—or 6524 cubic miles—into the sea per annum. Rivers contain not only the dissolved and solid matters in suspension furnished by spring waters, but also organic matter derived from plants growing on the sides and bottom of the river, and also drainage from the villages and towns through which the river passes. The river, in virtue of its greater volume and force, carries along a considerable amount of suspended solids. River water also contains in solution matter dissolved from the land which it drains, and this the more the further the river is away from its source. Thus, the Irwell near its source has about 0·008 per cent. of dissolved solids, and at Manchester nearly 0·056 per cent. The waters of the Dee (Scotland), draining slate and sandstone rocks, contains about 0·0056 per cent. of solid matter, about one-fourth of this being calcium salts; the Thames, draining chalk rocks, contains about 0·03 per cent. of solid matter, two-thirds of which are calcium salts. F. W. Clarke estimates that 2,735,000,000 tons of solid matter in solution are annually carried to the ocean by rivers. This does not include suspended matter.

Sea-water.—Just as spring water flows into the rivers, the rivers flow into the sea carrying their dissolved salts, and suspended matters which have not been deposited in transit. Consequently, the salts in sea-water have probably been all derived from the land, and hence it has been said that sea-water holds the *débris* of ancient continents in solution. Indeed, attempts have been made to estimate the age of the sea from the time required for the accumulation of the salt it contains. For example, it has been estimated that the rivers of the world discharge some 160 million tons of salt into the sea every year, and that the seas hold in solution some 144 billion tons or 120 million tons per cubic mile, enough to cover the whole of the present dry land with salt to a depth of 400 ft. Consequently, if these estimates be somewhere near the mark, and if present conditions are not very different from those which prevailed in former times, it must have taken at least 90 million years to accumulate the amount of salt now present in the seas.[4] Estimates of the volume of the water of the ocean vary from 302,000,000 to 323,722,150 cubic miles.

The vapour which rises from the sea by evaporation is almost pure water; hence, unless the dissolved matters are continuously removed, sea-water must be gradually getting more and more salty. The sea in regions where there is a large rainfall has less soluble salts than elsewhere. Sea-water contains a relatively large proportion of soluble salts—the Atlantic contains from 3·301 to 3·737 per cent. of solids in solution. The composition of the dissolved solids in a number of lakes and seas is indicated in connection with NaCl. Where the evaporation is greatest we naturally expect to find the greatest proportion of salts in solution. The water on the surface, for example, usually contains more salt than water deeper down; similarly, the Mediterranean contains from 3·836 to 4·115 per cent. and the Indian Ocean from 3·553 to 3·668 per cent. of solids in solution; whereas the White Sea contains 2·598 to 2·965 per cent.; the Black Sea, 1·826 to 2·223 per cent.; and the Baltic, with its numerous fresh-water tributaries, and less evaporation, contains between 0·3 and 0·8 per cent. of solids in solution. Salts accumulate in land-locked or partially land-locked seas and lakes much faster than in the sea. In illustration, the Red Sea contains from 5·085 to 5·854 per cent. of solids in solution; Owens Lake (California), 7·2 per cent.; the Dead Sea contains 19·215 to 25·998 per cent.; the Great Salt Lake (Utah), 14·994 to 23·036 per cent.; the Caspian Sea, 12·67 to 28·50 per cent.; and the Elton Lake (Russia), 26·5 per cent. These masses of water behave as if they were exposed in a large evaporating basin, for the salts accumulate in the water and are deposited in crystalline masses on the shores of the lakes as the water evaporates. Average spring water contains ten times as much silica as sea-water. If all the salts in sea-water are derived from the land, it might be asked: Where have the silica and calcium salts gone? The deficiency is said to be adequately explained by the abstraction of these substances from sea-water by the marine animals and plants. Diatoms and sponges, for example, use silica to make their skeletons and shells; while corals and shell fish use calcium carbonate for making their skeletons and shells. It has been estimated that a single oyster requires the lime in about 50,000 times its weight of sea-water to make its shell. So that while fresh supplies of silica and lime salts are being continuously poured into the sea, the store is being steadily removed.

Potable and drinking water.—It is claimed that the natural waters in particular localities contain impurities specially favourable to certain industries, and conversely in other localities. Hence, "in the brewing of malt liquors," said T. Bergman (1778), "the baking of bread, the bleaching of linen, dyeing, the preparing of hides and skins, and in a number of other arts, the quality of the water employed is of no small consequence, that unless one be chosen fit for the purpose, the whole process fails." Potable water—that is, water fit for human consumption—is obtained principally from rivers and lakes, and also from wells—artesian and otherwise. The inorganic or mineral matters usually found in solution in natural water are not directly injurious to health. The purification of water for towns and cities is a very important practical problem for the chemist. The best process can be adopted only after a careful study of the local conditions, and the nature of the impurities. Water should be freed from pathogenic (disease-producing) bacteria, and from suspended impurities. This is generally done by filtration through large filter beds made from layers of sand and gravel, extending in some cases over an acre of ground. In special cases, a Pasteur-Chamberlain's bougie (candle), made of unglazed and porous earthenware, and shaped like a hollow candle, is arranged to screw on to the water tap. The water is forced through the earthenware by the pressure of the main and trickles through the aperture below. Bacteria, organic matter, etc., collect on the inside of the bougie as a slimy layer which clogs the filter. The bougie must be frequently cleaned or replaced (1) to permit the free passage of water; and (2) to remove the layer of slimy organic matter which serves as a medium for the growth of bacteria. In some cases the living organisms in water are killed by the addition of minute traces of poison—ozone, sodium hypochlorite, copper sulphate, etc. The salt last named also prevents the growth of green algæ which are sometimes very troublesome.

To maintain the purity of the water supply up to the proper standard, it is necessary to make (1) a periodical critical examination of the source from which the water is obtained; (2) regular bacteriological examinations for pathogenic germs; and (3) chemical examinations for nitrogenous organic matter—albumenoids, etc.—upon which bacteria feed; and for the products of bacterial life—free ammonia, ammonium nitrate, and nitrate. The presence of these substances in water throws it under suspicion.

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§ 2. The Purification and Distillation of Water

Water is purified on a small scale by distillation. The water is boiled in a flask or boiler, and the steam is condensed back to the liquid condition by passage through a tube, about which a continual steam of cold water flows. To economize space, the condensing tube is generally coiled as a spiral—called the worm—and kept in a tank through which cold water continually flows. It might be added that the counter-current principle applied to condensers did not originate with J. von Liebig, but was employed by a French chemist in 1770, by C. Weigel in 1771, and by J. Gadolin.[1] The form of apparatus sometimes employed in the laboratory with the ordinary Liebig's condenser for distilling small quantities of liquid, is easily modified so as to prevent the steam coming in contact with rubber or cork stoppers, etc. —nothing but glass. The condenser is fitted to the distilling flask by ground joint; rubber or cork stoppers are not used. Much more compact condensing arrangements[2] are available with some of the more recent vertical condensers. The form illustrated in Fig. 1, for example, has been recommended for preparing water for bacteriological purposes. Water as free as possible from ammonia should be employed; river water is therefore objectionable. A small amount of volatile organic matter if present will be carried over with the first rush of steam, and soluble matters derived from the glass receiver and condenser may be found in the distillate. Tubes of quartz glass, block-tin, or silver for the condenser are better than glass, since the water acts very much more vigorously on glass than it does on quartz, tin, or silver. Distilled water which has been kept some time in a glass bottle cannot be used satisfactorily in the analysis of silicates, because it contaminates the silicate undergoing analysis with some of the constituents to be determined. In very special cases silver, gold, and platinum vessels have to be used as condensers and receivers. J. S. Stas[3] obtained water free from volatile organic matter by mixing 4 or 5 per cent. of potassium permanganate or manganate with the water in the boiler. Some potassium hydroxide was also added to keep the solution *très alcalin*. The distillate was mixed with aluminium sulphate, or with potassium or sodium hydrogen sulphate, and again distilled to eliminate ammonia, etc. G. A. Hulett recommended distilling the water twice—once after the addition of sulphuric acid and potassium permanganate; and the second time, after the addition of baryta water so as to get rid of carbon dioxide. According to W. R. Bousfield,[4] potassium hydrogen sulphate gives very satisfactory results in keeping back ammonia and traces of basic impurities; and according to

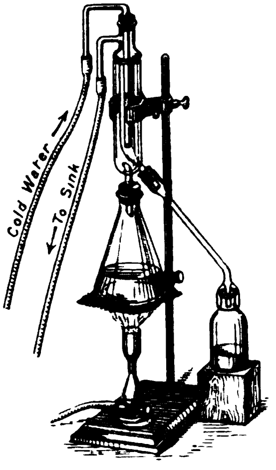

FIG. 1.—Distillation Apparatus

R. Bourdillon, phosphoric acid acts very much the same—about 0·5 per cent. of potassium hydrogen sulphate will suffice.

The purest water so far prepared has an electrical conductivity of $0{\cdot}043 \times 10^{-6}$ reciprocal ohms at 18°, and for ordinary conductivity experiments, **conductivity water**—water with a conductivity of 10^{-6} to 3×10^{-6} reciprocal ohms—is considered satisfactory. The former can be prepared only by distillation in vacuo, and it cannot be kept without absorbing impurities—carbon dioxide, ammonia, etc.—from the air, and these quickly increase the conductivity of the water. Thus, F. Kohlrausch and A. Heydweiller [5] found that a freshly prepared sample of water distilled in vacuo had a specific conductivity of $0{\cdot}05 \times 10^{-6}$ to $0{\cdot}11 \times 10^{-6}$; and after prolonged exposure to air, $0{\cdot}66 \times 10^{-6}$. Water which has been distilled in air always contains carbon dioxide, and F. Kohlrausch says that such water can be freed from much of this gas by passing through it a current of air which has been scrubbed in a tower of soda-lime. It is now usual to pass a stream of scrubbed air through the condenser in which the water is being condensed. The flask or bottle in which the conductivity water is stored should be made of good Jena glass; it should be fitted with a paraffined cork; it should be arranged with a stoppered syphon for draining off the water as required; and the air entering the bottle as the water is removed should pass through a tube packed with soda-lime.

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§ 3. The Effect of Temperature and Pressure on the Volume of Water

> Not only in the matter of solutions, but in other more strictly physical relations, it is a misfortune that the *rôle* of a typical liquid was assigned to water.—G. F. STRADLING (1901).

Although at ordinary temperatures water is a clear limpid liquid, it forms a crystalline solid—ice—at temperatures below 0°, under atmospheric pressures, and it forms a gas—steam—at temperatures exceeding 100°. In 1803, J. Southern [1] made some measurements to determine how much water was required to furnish one cubic foot of steam at various pressures. A litre of liquid at 100° occupies 1696 litres when it is changed to saturated vapour; and at 0°, a litre of liquid forms 205,093 litres of saturated vapour. The great expansion experienced when water passes into steam has been suggested as a substitute for gunpowder for discharging projectiles; and in 1824, J. Perkins constructed a steam gun which gave results rivalling those obtained with gunpowder.

A. Winkelmann measured the relative density of water vapour, standing in equilibrium with the liquid, when the density of air is taken as unity:

Pressure	0·5	1·0	2·0	3·0	4·0 atm.
Temperature	81·7°	100·0°	120·6°	133·90°	144·0°
Density	0·63357	0·64026	0·64838	0·65400	0·65860

The theoretical density on the assumption that the molecular weight of water is 18·02 is 0·6224; the observed densities agree with the assumption that the molecular weight of water is between 18·33 and 19·06. This means that a small fraction of the molecules in water vapour are polymerized.

O. Knoblauch, R. Linde, and H. Klebe [2] have calculated the specific volume of water vapour, if it obeyed the ideal gas laws, to be

$$v_0=\frac{82{\cdot}1}{18{\cdot}016}\cdot\frac{760}{p}T$$

and the percentage deviations from the calculated (v_0) and observed (v) values, when p is constant, are

Temperature .	100°	110°	120°	130°	140°	150°	160°	170°	180°
v-v_0 . . .	1·6	2·0	2·5	3·1	3·5	4·5	5·1	6·0	6·8

The ice and water molecule theory of W. C. Rontgen.—The physical properties of water differ widely from those of most liquids, and the list of anomalous properties is a long one. In order to explain these, W. C. Röntgen (1891) [3] assumed that water is a mixture of two kinds of molecules which he called **ice molecules** and **water molecules.** The ice molecules were supposed to form a mass more complex but less dense than water molecules. Similarly, in I. Traube's theory of liquids, the existence of what he called *gasogenic molecules* and *liquidogenic molecules* is postulated. The former would be represented by steam molecules, and the latter by water molecules. If $(H_2O)_n$ represents the ice molecules, $(H_2O)_m$ the water molecules, and H_2O the steam molecules, then

$$\underset{\text{Ice mols.}}{m(H_2O)_n}\rightleftharpoons\underset{\text{Water mols.}}{n(H_2O)_m}\rightleftharpoons\underset{\text{Steam mols.}}{(m+n)H_2O}$$

Increase of temperature⟶ ⟵Decrease of temperature
Increase of pressure⟶ ⟵Decrease of pressure

The diminution in volume which occurs when ice changes into liquid water corresponds with the passage of ice into water molecules, because the ice molecules have the less density and occupy a greater volume than the sum of the volumes of the corresponding water molecules.

The following hypotheses enable most of the so-called abnormal properties of water to be explained: (1) Liquid water contains at least two kinds of molecules—respectively called ice molecules and water molecules; (2) Low temperatures favour the accumulation of ice molecules; (3) High pressures favour the accumulation of water molecules; pressure dissociates the more complex molecules; and the greater the pressure, the less the proportion of ice molecules in the liquid; (4) The passage of ice into water molecules is accompanied by a contraction, and conversely; (5) The passage of ice into water molecules absorbs heat and is therefore said to be an endothermal reaction, and conversely for the reverse change; (6) In spite of the heterogeneous character of liquid water, this liquid freezes at a constant temperature because there is a definite equilibrium concentration for each molecular species at each temperature; and (7) The proportion of ice molecules in the liquid is reduced when a salt is dissolved therein. The anomalous properties of water are thus referred to the presence of special kinds of molecules in liquid and solid water; these molecules, too, are invested with special properties to fit the facts. This is a dangerous method of investigation, but there is an overwhelming mass of evidence to justify the procedure.

There is a definite equilibrium concentration between the ice molecules and the water molecules at each temperature, and C. S. Hudson [4] represents this by the curve *C*, Fig. 2; the solubility of the ice molecules will also vary with temperature, as represented by the curve *S′*, Fig. 2. Above the freezing temperature, the solubility of the ice molecules in the water molecules is greater than the equilibrium concentration and the solution is not saturated; at temperatures below the freezing point the liquid is supersaturated with ice molecules and the water can freeze; at the freezing point, the equilibrium concentration of the ice molecules is equal to their solubility. The addition of soluble salts to the liquid lowers the equilibrium concentration and solubility of the ice molecules, and thus lowers the maximum density and freezing point of the liquid.

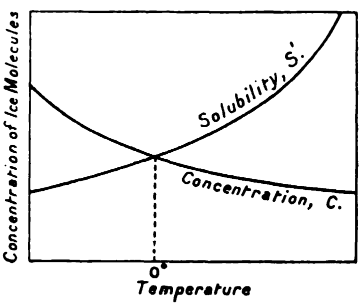

Fig. 2.—Equilibrium Concentration and Solubility of Ice Molecules at Different Temperatures (Diagrammatic).

The thermal expansion of water.—It was known to the Arabian writer Al-Khazini in the twelfth century that water contracted when cooled, and expanded when heated, and that ice was specifically lighter than water. His measurements were so accurate that they are quite in accord with those adopted at the present day. He found ice to have a specific gravity of 0·965, and hot water 0·958 when water at ordinary temperatures is taken as unity. G. Galilei also discussed the expansion which occurs when water is heated, and the contraction which occurs when water is cooled.

The coefficient of thermal expansion α, or $(dv/dt)_p/v$—that is, the increase in volume per unit volume per degree rise of temperature at a constant pressure—of water, and of a few other liquids for comparison, is

	Water.	Mercury.	Sulphuric acid.	Alcohol.	Ether.	Benzene.	CS_2.
α . . .	0·00048	0·00018	0·00063	0·00113	0·00155	0·00125	0·00119

The coefficient increases with a rise of temperature. J. Meyer found for water,

	20°	40°	60°	100°	140°	180°	200°
α . . .	0·000110	0·000217	0·000305	0·000452	0·000584	0·000722	0·000788

These numbers agree with the values of G. A. Hirn, and G. Tammann and K. Zepernick between 100° and 143°. The observed expansion of water with rise of temperature is assumed to be the joint effect of (*a*) a decrease in volume due to the change of ice into water molecules; and (*b*) the normal expansion due to the further separation of the molecules. The higher the temperature the less the proportion of ice molecules to be changed into water molecules, and the thermal expansion becomes proportionally greater.

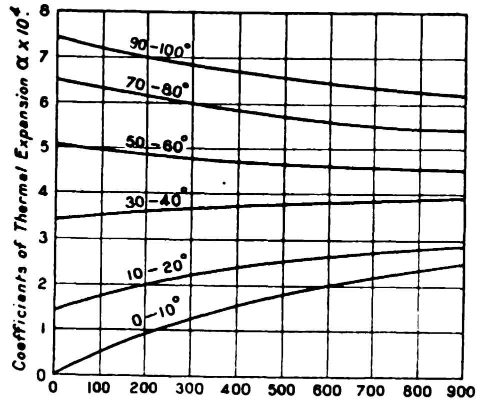

Fig. 3.—Coefficients of Thermal Expansion of Water at Different Temperatures and Pressures.

Excluding water, the coefficients of thermal expansion of about eleven liquids—including alcohol, carbon sulphide, etc.—which have been tried, diminish the higher the pressure. For example, E. H. Amagat (1893)[5] found the following values for the coefficient of expansion of ether ($\times 10^6$) at different temperatures and pressures:

Pressure (atmospheres) . .	50	100	200	600	800	1000
$\alpha \times 10^6$ from 0° to 20° . .	1511	1445	1319	1045	958	900
$\alpha \times 10^6$ from 138° to 198° .	—	—	2156	1165	1008	890

With water, E. H. Amagat found that the coefficient of thermal expansion at a constant temperature for temperatures up to 50° increases with increasing pressures as indicated in the first five vertical columns of Table I; about 50°, the reverse obtains, for the coefficient of expansion decreases with an increase of pressure, and water then behaves like other liquids which have been tried. Consequently, *water behaves like a normal liquid at temperatures exceeding* 50°. E. H. Amagat's and F. Auerbach's values for the effect of pressure on the mean coefficient of thermal expansion of water are illustrated by Fig. 3. The horizontal lines, Table I, represent the coefficient of thermal expansion at different temperatures when the pressure is constant. Up to a pressure of 3000 atm., the coefficient steadily increases as the temperature rises, no matter what be the pressure provided it be constant. E. H. Amagat's and G. Tammann's results for the effect of pressure on the volume of water at different temperatures are illustrated in Fig. 4—volumes are denoted by ordinates, temperatures by abscissæ

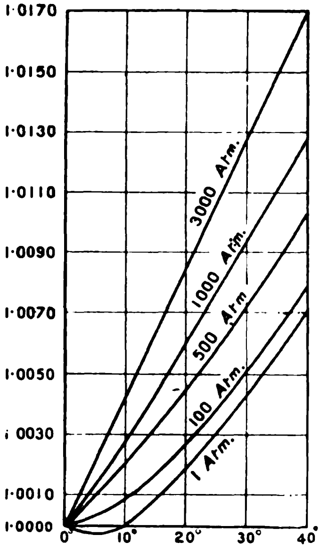

Fig. 4.—The Effect of Pressure on the Volume of Water at Different Temperatures.

J. H. Vincent found the linear coefficient of expansion of ice between —10° and 0° to be 0·0000507 ; and J. Dewar found the mean coefficient of expansion of ice between 0° and —188·7° to be 0·00008099—about a quarter of the value between 0° and 10°, and half the value between 4° and 100°.

The Florentine Academicians discovered in 1670, that there is a certain temperature at which liquid water possesses a maximum density, but the temperature at which water acquires this state was not determined with any degree of precision until J. A. Deluc[6] noticed that the anomaly obtained when water is used as a liquid in thermometers corresponds with 5° as the temperature of maximum density. Count Rumford (1805), J. G. Tralles (1807), G. C. Hällström (1827), and C. M. Despretz (1836) made careful measurements of this constant, and the more recent work of P. Chappius (1897) and L. C. de Coppet (1904) gives numbers ranging from 3·980° to 3·983° for the **temperature of maximum density of water;** while, according to J. D. van der Waals, the temperature of maximum density is 4·18° in vacuo, and 4·08° under the normal pressure of one atmosphere. E. H. Amagat found the temperature of maximum density was lowered to 3·3° by a pressure of 41·6 atm., to 2·0° by a pressure of 93·3 atm., and to 0·6° by a pressure of 144·9° atm. According to S. Lussana, the temperature of maximum density is lowered to 4·10—0·0225(p—1), by a pressure of p atm.

Table I.—The Coefficient of Thermal Expansion of Water at Pressures ranging from 1 to 3000 Atm.

Pressure in atmospheres.	Mean coefficient of thermal expansion × 10^6.									
	0°-10°.	10°-20°.	20°-30°.	30°-40°.	40°-50°.	50°-60°.	60°-70°.	70°-80°.	80°-90°.	90°-100°.
1	14	149	267	334	422	490	556	—	—	—
100	43	165	265	345	422	485	548	—	—	—
200	72	183	276	350	426	480	539	600	—	—
400	125	221	298	363	429	478	527	575	626	673
600	169	250	319	372	429	484	520	557	605	650
800	213	272	339	378	439	480	518	546	595	630
1000	259	293	343	396	437	474	512	554	581	610
2000	364	356	416	423	469	—	—	—	—	—
3000	391	420	433	440	469	—	—	—	—	—

The water molecules *en masse* have a relatively greater density than ice molecules, and hence occupy a smaller volume. During the melting of ice, however, only a certain fraction of the ice molecules are changed into water molecules, and the resulting liquid is a solution of ice molecules in water molecules. Any further application of heat results in (*a*) a decrease in volume arising from the transformation of the ice into water molecules; and (*b*) an increase in volume due to the joint thermal expansion of both the ice and water molecules. The observed effect is the difference between these two opposite effects. In passing from 0° to 4°, the expansion due to the thermal expansion is masked by the contraction due to the breaking down of a definite proportion of the ice molecules; from 4° upwards, thermal expansion overbalances the contraction due to the changing molecules; while at about 4°, the two effects just balance one another. The temperature of the maximum density of water is reduced by increasing the pressure, because the proportion of ice molecules in water is reduced.

C. M. Despretz's study of the effect of salt solutions on the temperature of maximum density led him to the conclusion that *the lowering of the temperature of the point of maximum density of water caused by the addition of a soluble salt is directly proportional to the concentration of the solute.* F. Rosetti did not succeed in finding any definite relation between the lowering of the temperature of maximum density and the lowering of the freezing point produced by a dissolved salt, for although a definite ratio was obtained for a given solute at different concentrations, a different ratio was obtained with a second solute. Consequently, while the lowering of the freezing point depends only on the concentration of the solute, *the lowering of the temperature of maximum density depends on the nature as well as on the concentration of the solute.* L. C. de Coppet noticed that for solutions of salts of a given family of metals, the lowering of the temperature of maximum density is sensibly the same for a given acid radicle. Each acidic and each basic radicle produces its own effect, and the joint effect is the sum of the separate effects. R. Wright has established a similar rule for the salts of the dibasic acids, and the salts of the alkaline earths.

TABLE II.—THE VOLUME OF WATER BETWEEN —10° AND 320° (VOLUME AT 4° UNITY).

Temperature.	Volume occupied at θ° by one c c. at 4°.									
	0	1	2	3	4	5	6	7	8	9
−1	1·00019									
0	0013	0021	0031	0042	0055	0070	0088	0108	0131	0157
0	0013	0007	0003	0001	0000	0001	0003	0007	0012	0019
1	0027	0037	0048	0060	0073	0087	0103	0102	0104	0157
2	0177	0189	0221	0244	0268	0294	0320	0347	0375	0404
3	0435	0465	0497	0530	0563	0598	0633	0669	0706	0743
4	0782	0821	0861	0901	0943	0985	1028	1072	1116	1162
5	1207	1254	1301	1349	1398	1448	1498	1548	1600	1652
6	1705	1758	1813	1867	1923	1979	2963	2093	2152	2210
7	2270	2330	2390	2452	2514	2576	2639	2703	2768	2833
8	2899	2965	3032	3099	3168	3237	3306	3376	2447	2518
9	3590	3663	3737	3810	3884	3959	4035	4111	4188	4265
10×1	0433	0505	0601	0693	0794	0902	1019	1145	1279	1429
10×2	1590	177	195	215	236	259	283	308	34	38
10×3	42	46	51	—	—	—	—	—	—	—

The variation of the volume of water with temperature has been the subject of researches extending from the beginning of the nineteenth century up to the present time. The more recent determinations are due to K. Scheel (1892),[7] W. Kreitling (1892), P. Chappius (1897), and to M. Thiesen, K. Scheel, and H. Dieselhorst (1900) of the Physikalisch Technischen Reichsanstalt. The results obtained by the latter, between 0° and 40°, are indicated in Tables II and III. The numbers in the sixth and seventh decimal places are deleted, and the fifth decimal raised one unit when the deleted figures exceed 50. The data from 40° to 100° are by M. Thiesen (1904); those from 0° to —10° are mean values of data by J. J. Pierre (1845), H. Weidner (1866), and F. Rosetti (1871); and those from 100° to 320° are mean values from measurements by W. Ramsay and S. Young (1893), J. J. Waterston (1863), and G. A. Hirn (1867).

TABLE III.—THE SPECIFIC GRAVITY OF WATER BETWEEN —10° AND 320° (SPECIFIC GRAVITY AT 4° UNITY).

Temperature θ	Specific gravity at θ° when the specific gravity at 4° is unity.									
	0	1	2	3	4	5	6	7	8	9
—1	0·99985									
—0	9987	9979	9970	9958	9945	9930	9912	9892	9896	9843
0	9987	9993	9997	9999	—	9999	9997	9993	9988	9981
1	9973	9963	9952	9940	9927	9913	9897	9880	9880	9843
2	9823	9802	9780	9752	9752	9707	9681	9654	9626	9597
3	9567	9537	9505	9473	9440	9406	9371	9335	9299	9262
4	9224	9186	9147	9107	9066	9025	8982	8940	8896	8852
5	8807	8762	8715	8669	8621	8573	8525	8475	8425	8375
6	8324	8272	8220	8167	8113	8059	8005	7950	7894	7830
7	7781	7781	7723	7666	7607	7489	7429	7368	7307	7245
8	7183	7121	7057	6994	6930	6865	6800	6734	6668	6601
9	6534	6467	6399	6330	6261	6192	6122	6051	5981	5909
10×1	9585	9510	9434	9352	9264	9173	9075	8973	8866	8750
10×2	6828	850	837	823	809	794	779	765	75	72
10×3	70	68	66	—	—	—	—	-	—	—

The volume v of water for a temperature θ between 0° and 33° can be represented by K. Scheel's formula $v=v_0\ (1-0{\cdot}46427\theta+0{\cdot}0585053\theta^2-0{\cdot}0_7 67898\theta^3+0{\cdot}0_9 50024\theta^4)$. The coefficient of expansion of ice is 0 04375. J. Duclaux assumed that the expansion of water for temperatures between —10° and 150° is a composite effect of two opposing forces: (1) the relation between the temperature and the expansion of a liquid constituted of simple molecules which can be represented by a parabolic formula $a+b\theta+c\theta^2$; and (ii) the increase in the volume due to the polymerization of the constituent molecules whereby the volume of the liquid becomes specifically greater as the number of polymerized molecules increases on the falling temperature. Assuming that the expansion is almost proportional to the number of polymerized molecules, it can be represented by Kn/T, where K and n are constant, and T is the absolute temperature. Consequently, the observed expansion is the sum of the two separate effects. The constants a, b, c, n, and k can be evaluated from M. Thiesen, K. Scheel, and H. Dieselhorst's data, so that the volume v of the water at θ°, when $T=273+\theta$, is

$$v=0{\cdot}991833+0{\cdot}000225208\theta+0{\cdot}0000028447 5\theta^2+\frac{0{\cdot}061695711}{273+\theta}$$

A. Hess found the specific volume of ice at 0° to be 1·0236; and J. Dewar calculates that at absolute zero, the specific volume of ice will be 0·9584.

M. Thiesen (1904) represented the relation between the specific gravity D of water and the temperature θ, between 25° and 100°, by the empirical formula:

$$D=1-\frac{(\theta-3{\cdot}982)^2}{466{,}700}\cdot\frac{(\theta+273)\ (350-\theta)}{(\theta+67)\ (365-\theta)}$$

while M. Thiesen, K. Scheel, and H. Dieselhorst have modified an older formula of D. I. Mendeléeff, and have represented the specific gravity of water by the expression:

$$D=1-\frac{(\theta-4)^2}{118{,}932+1366\cdot75\theta-4\cdot13\theta^2}$$

for temperatures between 0° and 30°. If the water contains air in solution, its specific gravity is reduced; but above 20°, the effect is negligibly small; the difference rises steadily from 0·0000025 at 0° to a maximum 0·0000034 at 8°, and then steadily falls to 0·0000004 at 20°.

Both H. Kopp and I. Traube[8] have shown that the **molecular volumes** of liquids—that is, the molecular weights divided by the respective specific gravities—are additive properties in that they can be represented as the sum of the molecular volumes of their components, and the results computed on this assumption agree with the observed values. Water is exceptional in that the observed molecular volume is larger than the computed result; it is therefore inferred that the molecular weight is larger than that represented by the simple formula H_2O, and I. Traube has shown that a molecule corresponding with $(H_2O)_3$ or H_6O_3 gives a better agreement between theory and observation. According to D. Berthelot, the molecular v of a liquid at the absolute temperature T is related with the critical temperature T_c and critical pressure P_c (atm.) by the expression $v=11\cdot4\,T_c/P_c(2T_c-T)$. When applied to water at 16°, the molecular volume appears to be 25 in place of 18; hence, the molecule is more condensed than corresponds with the formula H_2O.

The curve, Fig. 7, was obtained by plotting the volume of a given mass of water at different temperatures; it shows that water above 4°, like most liquids, expands when heated and contracts when cooled; but for temperatures below 4° the curve is abnormal, for the water expands when cooled, and contracts when heated. If the specific gravity of water at 4° be taken as unity, it follows that water becomes specifically lighter when the temperature is raised or lowered beyond this point. The temperature of maximum density of water, 4°, is often taken as a standard, or unit of reference for specific gravity, etc.

The expansion of water when cooled from 4° to 0° is very small, but that minute quantity has a very important bearing in nature. When the water on the surface of, say, a lake is cooled, it contracts. The heavier cold water sinks, and the warm water rises. This circulation cools the temperature of the whole body of water down to 4°; any further cooling results in the formation of specifically lighter water. Accordingly, this remains on the surface, and circulation ceases. Finally, as a result of this remarkable and abnormal property, when the temperature of the atmosphere falls to 0°, a surface film of ice is formed. *Ground ice* or *anchor ice* may be formed at the bottom of the more shallow rapidly moving streams when the cooling water is thoroughly mixed, and not allowed to settle in layers. If the water did not expand as the temperature falls to 0°, the whole body of water would freeze from below upwards and produce profound climatic changes, since the larger amount of ice formed in winter would materially affect the temperature for the rest of the year. The remarks do not apply to salt (sea) water which contracts as the temperature is lowered down to the freezing point, but sea water shows a temperature of maximum density at −3·21°. Indeed, C. M. Despretz (1839) showed that the temperature of maximum density of salt (sodium chloride) solutions is lowered almost proportionally with the amount of salt in solution; thus,

Per cent. sodium chloride . . .	0	0·05	0·1	0·4	0·8
Temperature maximum density . .	4°	3°	1·8°	−5·6°	−16·6°

Similar results have been obtained with other salts, and S. Lussana (1895) has shown that the effect of an increasing pressure is to still further reduce the temperature of maximum density. Thus, with solutions containing 0·5 per cent. of sodium chloride, the temperature of maximum density is $3\cdot35-0\cdot0177(p-1)$, where p

denotes the pressure in atmospheres ; and with 1·44 per cent. solutions of the same salt, the temperature of maximum density is $0·77-0·011(p-1)$.

In the act of freezing, water expands so that 100 c.c. of liquid water at 0° gives approximately 110 c.c. of ice at the same temperature. In 1665, Robert Boyle[10] found the specific gravity of ice to be 0·903 because he observed that the volume of water on freezing expanded 11·12 per cent. This result has no pretension to exactitude because of the uncorrected errors due (i) to strains in the containing glass during freezing ; (ii) to the probable presence of minute cracks in the artificially frozen ice ; and (iii) to the presence of varying amounts of dissolved gases. Similar remarks apply to the early determinations indicated by L. Playfair and J. P. Joule, who found a mean value of 0·9184. A more accurate determination was made by C. Brunner (1845), who found the specific gravity of ice at 0° is 0·9180 ±0·000039 ; G. Duvernoy gave 0·922 ; R. Bunsen (1870) gave 0·9165±0·00003 ; A. Leduc (1906), 0·9176. J. Plücker obtained 0·91580±0·000008 ; H. Kopp's not very exact value (1855) is 0·907 ±0·0007 ; L. Dufour's value (1860) is 0·9178±0·0005 ; J. von Zakrzewsky's (1892), 0·916710 at −0·7°. E. L. Nichols (1899) emphasized the difference of the order of 1 or 2 parts in 1000 in the results obtained between artificial ice 0·91615 and natural ice 0·91807. This does not mean that the two forms of ice are different, but that the differences are due to strains set up in the artificial ice in the act of freezing ; E. L. Nichols believes that these disappear in time, and the specific gravity then attains its final value. In 1901, H. T. Barnes and H. L. Cooke found the specific gravity of natural ice from the St. Lawrence river to be 0·91661±0·00007 ; J. H. Vincent (1902) obtained 0·9160. According to J. Dewar, the specific gravity of ice at −188·7° is 0·92999 ; and he calculates that at absolute zero, the specific gravity would be 0·9368 so that ice can never be cooled until it has the same specific gravity as water has at 100°.

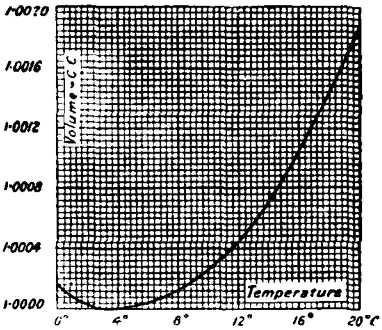

FIG. 5.—Relations between the Volume and Temperature of Water.

The specific gravity of ice at 0° varies with its mode of formation from 0·9159 to 0·9182 ; the specific gravity of water at 0° is 0·999867. Accordingly, ice floats on the surface of water. The expansion of water during freezing is an important factor. The expansion may burst the intercellular tissue of plants by freezing the cell-sap ; the expansion may disrupt the fibres of flesh, so that the frozen meat appears rather more pulpy than ordinary meat. If water freezes in pipes, the expansion of water in the act of freezing may burst the pipe, and water will leak when the ice thaws ; water freezing in the surface crevices of rocks, splits and widens the fissures so that the surface crust of the rock appears to disintegrate during a thaw. The *débris* collects as *talus* at the foot of the rocks, ready to be transported by water to lower levels. Hence this simple force plays an important part in the weathering and decay of rocks, building stones, etc., in countries exposed to alternate frost and thaw ; and, adds J. Tyndall : "The records of geology are mainly the history of the work of water."

In an old experiment of Rumford's usually cited to illustrate the low thermal conductivity of water a piece of ice was weighted to keep it at the bottom of a cylinder of water. It was then possible to boil the water by heating the cylinder near the top, and this without melting the ice. The experiment further illustrates what would happen if water did not exhibit the anomalous expansion on freezing. Instead of the ice being buoyed up to the surface it would sink to the bottom of lakes, etc. The warmer water would remain on the surface in summer so that the ice would increase in winter and persist in summer until a great portion of the water on the surface of the earth would be permanently frozen. As it is, the temperature at the bottom of a body of fresh water cannot get below the temperature of maximum density, for if the water be cooled further it rises to the surface and is there frozen. The ice thus hinders the further cooling of the water which remains in the liquid state.

The change in volume of water with increasing temperatures above 40° is represented by a curve concave towards the temperature axis, while with salt solutions this curve is flatter, approximating to a straight line with highly concentrated solutions. The curves for solution and solvent thus cross each other as illustrated in Fig. 6. According to P. de Heen,[11] for lithium, sodium, potassium, and ammonium chlorides the points of intersection are respectively 30°, 55°, 50°, and 35°; for calcium, barium, magnesium, and aluminium chlorides, respectively 45°, 50°, 35°, and 37°; for sodium and potassium sulphates, 60°; for sodium and potassium carbonates, respectively 67° and 65°; and for potassium and ammonium nitrates, 70°.

The compressibility of water.—In 1620, Francis Bacon subjected water to pressure, by squeezing it in a lead sphere; the water passed through the pores of the metal. The Florentine Academicians tried a similar experiment with a gold vessel in 1667, and came to the conclusion that water is incompressible. J. Canton,[12] in 1762, was probably the first to establish the compressibility of rain-water, sea-water, mercury, spirit of wine, and oil of cloves; and, in 1764, he showed that the compressibility decreases as the temperature is raised. J. Perkins, in 1826, also showed that the compressibility decreases as the pressure is increased—quickly at first, and afterwards more slowly. Experiments on this subject were made by H. C. Oersted (1822), D. Colladon (1827), and by H. V. Regnault (1848), and have been continued from that time to the present day.

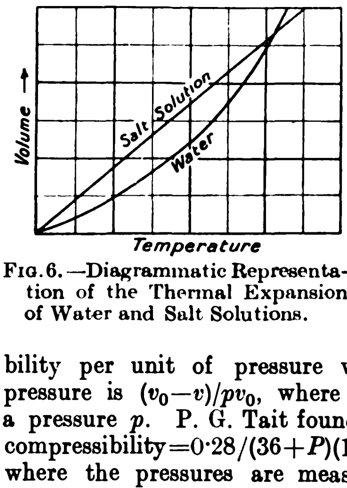

FIG. 6.—Diagrammatic Representation of the Thermal Expansion of Water and Salt Solutions.

The compressibility of a liquid is the fractional change in volume, dv/v, which occurs per unit change of pressure. The **coefficient of compressibility,** $\beta=-dv/vdp$, is numerically equal to the decrease in volume per unit volume produced by unit change of pressure. The average compressibility per unit of pressure which occurs on the application of p units of pressure is $(v_0-v)/pv_0$, where v_0 is the initial volume, and v the volume at a pressure p. P. G. Tait found for fresh water the empirical formula: Average compressibility$=0·28/(36+P)(150+\theta)$. Some results are shown in Table IV where the pressures are measured in tons per sq. in., showing that the compressibility decreases: (*a*) with an increase of pressure; (*b*) with a rise of temperature; and (*c*) when the water has salts in solution—the ratio of the compressibility of sea water and fresh water is nearly 0·92. The coefficient of compressibility of water per atmosphere, near 0°, is given in the following table with that of a few other liquids for comparison:

Water.	Mercury.	Alcohol.	Ether.	Benzene.	Carbon disulphide.
0·000050	0·0000038	0·000093	0·000164	0·000085	0·000078

T. W. Richards and his co-workers find a compressibility of $42·1\times10^{-6}$ at 20° between 100 and 500 megabars; $43·3\times10^{-6}$ between 100 and 300 megabars; and $40·9\times10^{-6}$ between 300 and 500 megabars. G. A. Hulett and T. Peczalsky have also measured the compressibility of water. Liquids in general are but slightly compressible. The volume of water is reduced but 0·00005th part of its volume per atmosphere pressure at 0°. According to P. G. Tait,[13] this small compressibility means that if sea-water were quite incompressible the average level of the sea-water would be raised 116 feet higher than it is to-day, and about 4 per cent. of the present land surface would be submerged. The compressibility of liquids, including water, decreases with rising pressure, temperature constant; because the compressibility decreases faster than the volume. The compressibility of liquids other than water increases with rise of temperature, that is, the thermal expansion decreases with rise of pressure as shown by the vertical column, Table V, for water above 50°. This is the behaviour which would be expected from a liquid composed of particles of constant volume, but separated by spaces which can be changed in size by pressure and temperature. With water the compressibility first decreases with a rise of temperature up to about 50°. This is shown by the vertical columns in Table V below 50°—at a higher temperature, the compressibility of water increases with rise of temperature as is the case with other liquids. The minimum temperature is but slightly affected by a change of pressure, but it becomes less and less pronounced with a rise of pressure until it has almost disappeared at a pressure of 3000 kilograms per sq. cm. Again, according to E. H. Amagat (1877), the compressibility of ether at 13·7° under 11 atmospheres pressure is 0·000168, and at 100°, 0·00056 of its volume per atmosphere. With water, the reverse obtains, and the compressibility falls to a minimum at about 63°, and then increases. Thus, C. Pagliani and G. Vicentini (1884)

TABLE IV.—COMPRESSIBILITY OF WATER.

Temperature	Fresh water.			Sea-water.		
	1 ton.	2 tons.	3 tons	1 ton.	2 tons.	3 tons.
0·4°	0·00004770	0·00004617	0·00004510	0·0000435	0·0000420	0·0000410
3·4°	4671	4521	4395	427	413	403
11·8°	4415	4276	4163	404	392	3835
15·0°	4338	4219	4102	398	387	378

TABLE V.—THE VOLUME OF WATER AT DIFFERENT TEMPERATURES AND PRESSURES.

Pressure kilograms per sq. cm.	Volume (c c. per gram); volume at 0° unity.									
	−20°	−15°.	−10°.	−5°.	0°.	5°	10°.	15°.	20°.	25°.
0			1·0017	1·0006	1·0000	0·9999	1·0001	1·0007	1·0016	1·0028
500			0·9800	0·9783	0·9776	9782	0·9791	0·9800	0·9812	0·9825
1000			9606	9592	9584	9596	9609	9623	9638	9654
1500		0·9401	9413	9404	9407	9420	9435	9451	9467	9483
2000	0·9233	9240	9248	9257	9265	9281	9298	9315	9332	9349
2500	9083	9092	9102	9115	9131	9148	9166	9185	9203	9222
3000	8957	8966	8978	8999	9009	9026	9044	9063	9081	9100
3500	—	8860	8872	8884	8903	8923	8944	8964	8984	9005
4000	—	8764	8772	8784	8805	8823	8842	8860	8878	8897
4500	—	—	8680	8691	8713	8721	8749	8767	8785	8802
5000	—	—	8593	8604	8626	8643	8661	8678	8696	8714
5500	—	—	—	—	8548	8565	8582	8599	8616	8633
6000	—	—	—	—	8480	8496	8513	8529	8545	8561
6500	—	—	—	—	8414	8429	8444	8460	8475	8490
7000	—	—	—	—	8356	8370	8384	8398	8412	8426
7500	—	—	—	—	—	8309	8321	8334	8346	8358
8000	—	—	—	—	—	—	8262	8273	8284	8285
8500	—	—	—	—	—	—	—	8208	8218	8228
9000	—	—	—	—	—	—	—	8149	8157	8165
9500	—	—	—	—	—	—	—	—	8099	8106
10000	—	—	—	—	—	—	—	—	8046	8050

found the coefficient of compressibility, β, of water, per atmosphere, at different temperatures :

Temperature	0°	2·4°	49·3°	66·2°	77·4°	99·2°
$\beta \times 10^7$	503	496	403	389	398	409

The inversion at about 60° is supposed to be the joint effect of (*a*) the diminution which attends the passage of ice into water molecules, and (*b*) that due to the squeezing of the molecules together. The higher the temperature the less the disturbance arising from the former ; at about 63°, it becomes negligibly small. Under very great compression, E. H. Amagat (1891) found that water behaves like a normal liquid, showing that under great pressures virtually all the ice molecules are probably transformed into molecules of one kind. Hence, as indicated above, the temperature of maximum density of water is lower the greater the pressure. Under great pressures, too, ice can be melted, because pressures prevent the formation of or depolymerizes the ice molecules. At still greater pressures further complications arise. The compressibility at different pressures, expressed in kilograms per sq. cm. at 0° and 22°, found by P. W. Bridgman, are :

Pressure . .	500	1000	2000	4000	6000	7000	11,000
Compressibility at 0° .	0·0224	0·0414	0·0735	0·1195	0·1520	0·1644	—
Compressibility at 22° .	—	0·0383	0·0679	0·1137	0·1465	0·1600	0·2042

The disturbances have been traced by G. Tammann and P. W. Bridgman to the transformation of ordinary ice into a number of different allotropic forms.

Table V, showing the volume water at different temperatures and pressures, was compiled by P. W. Bridgman in an important memoir : *Water, in the liquid and five solid forms, under pressure* (1912). Some results are plotted in Fig. 7. The pressure and volume at 0° are indicated on each curve. Each curve is drawn to scale, but, for the sake of compactness, the curves for the different pressures have been brought together, otherwise the curves would have been about ten times their present distance apart. Up to 3000 kilograms pressure, the expansion at 0° is increased with a rise of pressure ; but at higher pressures, the expansion decreases with rising pressure. There thus appears to be a maximum in the curve between 0° and 20°. The relation between the temperature and volume of a given mass of a normal liquid at a constant temperature is illustrated by the curve *A*, Fig. 8, where the expansion is greater the higher the temperature. With an abnormal liquid like water, after passing the minimum at the temperature of maximum density, it might be expected that there would be a limit to the increase in volume with decreasing temperatures when all the water molecules have been converted into ice molecules ; and the liquid might be expected to behave in a normal manner and decrease in volume with a fall of temperature. The volume temperature curve *B*, Fig. 8, would represent the behaviour of such a liquid. With water, the exploration is prevented by freezing, but such a curve has been actually realized by P. W. Bridgman with water under a constant pressure of 1500 kilograms per sq. cm.—Fig. 8.

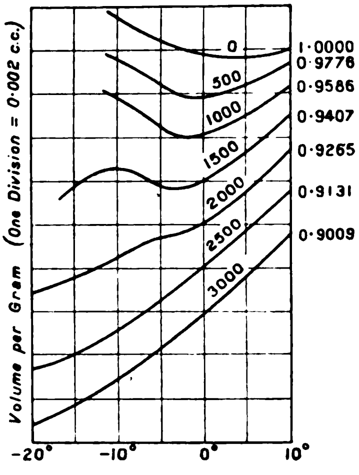

Fig. 7.—Relation between Temperature and Volume of Liquid Water at various constant Pressures.

According to O. Tumlirz (1909),[14] the data obtained by E. H. Amagat for the relation between the pressure p and volume v of liquids at the absolute temperature T, can be represented by the equation $(p+\mathrm{P})(v-b)=RT$, where R and b are constants for any given substance, and P, the internal pressure, is a function of temperature only, and is evaluated from the experimental data. The results apply very well for pressures up to 3000 kilograms per sq. cm., but not so well for P. W. Bridgman's results up to 10,000 kilograms per sq. cm. The values given by the formula for the compressibility become small too rapidly at high pressures, so that the observed compressibility remains larger than the values calculated by O. Tumlirz's formula valid at lower pressures. One possibility is that b is not constant, and that the molecules themselves are compressible, apart altogether from the closing up of the intermolecular spaces. D. Tyrer compared the coefficients of isothermal and of adiabatic compressibilities of water between 1 and 2 atm. pressure, and found at 0°, 70°, and 100°, the former to be respectively $502{\cdot}8\times10^{-7}$, $452{\cdot}9\times10^{-7}$, and $418{\cdot}8\times10^{-7}$, and the latter respectively $502{\cdot}5\times10^{-7}$, $424{\cdot}5\times10^{-7}$, $429{\cdot}0\times10^{-7}$. If β be the ordinary isothermal compressibility, *i.e.*—dv/vdp, and a the adiabatic compressibility, C_p the specific heat at constant pressure, v the specific volume, T the absolute temperature,

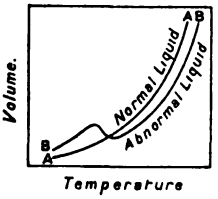

FIG. 8.—Volume Temperature Curves of Liquids.

$$a=\beta-\left(\frac{T}{vC_p}\frac{dv}{dT}\right)^2$$

T. W. Richards and C. L. Speyers find the compressibility of ice between 100 and 500 megabars, at —7·03°, to be 0·000012, that is, about one-fourth the compressibility of water at a neighbouring temperature. K. R. Koch found the elastic modulus of ice to be 626 kilograms per sq. cm.

According to W. C. Röntgen and J. Schneider, and M. Schumann (1887),[15] the coefficient of compressibility, β, of aqueous solutions of salts is less than that of water, and this the more the more concentrated the solution. Thus, with solutions of potassium chloride,

Per cent. potassium chloride . .	0	2·52	5·35	10·68	16·81
$\beta\times10^7$	500	481	424	400	354

The facts are explained by the assumption that the proportion of ice molecules is less in aqueous solutions than in pure water. W. C. Röntgen and J. Schneider could not confirm M. Schumann's observation that the compressibilities of aqueous solutions of potassium, calcium, ammonium, and strontium chlorides are greater than that of water, for they always found a lower compressibility with these solutions than with water. G. de Metz also found that cane sugar also diminishes the compressibility of aqueous solutions in a similar manner; and T. W. Richards and S. Palitzsch, that the compressibility of aqueous solutions of urethane at 20° rapidly decrease with increasing concentration from $42{\cdot}25\times10^{-5}$ for pure water to $38{\cdot}91\times10^{-6}$ with 39·4 per cent. solutions; the compressibility then increases at first slowly and then rapidly with increasing concentration. The results agree in showing that the first effect of dissolving anything in water is to dissociate the ice molecules; increasing the pressure or temperature acts in the same direction. With normal liquids there is an increase in the compressibility with increasing concentration. K. Drucker found that the compressibility of aqueous solutions of organic acids likewise show a minimum in the compressibility curve. The compressibility coefficient of solutions of salts in water usually increases as the temperature rises. According to J. Guinchant (1901), with pressures up to 4 atm. the volume of the dissolved substance does not change; the observed change is solely due to the medium.

The tensile strength of liquids.—About 1850, M. Berthelot[16] filled a glass tube nearly full of liquid, removed the air, sealed the tube, heated the tube until the liquid almost filled the interior, and allowed the whole to cool slowly to the ordinary temperature. The liquid continued to fill the tube so that the volume of water was $\frac{1}{420}$th larger than it should be for the given temperature; with alcohol the volume was $\frac{1}{93}$rd and ether $\frac{1}{50}$th larger. This represents the **tensile strength of water** to be 50 atm., and over 100 atm. in the case of alcohol and ether. R. H. Worthington found 17 atm. for the breaking strain of alcohol. J. Stefan and O. Tumlirz calculated a strength of about 2000 atm. for alcohol on the assumption that the internal pressure is a measure of the theoretical tensile strength. H. M. Budgett found a breaking strength for water of nearly 900 lbs. per sq. in., or about 60 atm. O. Reynolds recorded the fact that when a liquid is flowing through a pipe with a constriction, the velocity may be so high that the corresponding diminished pressure of the liquid is sufficient to break it. He regarded the effect as a boiling of the liquid under diminished pressure. S. Skinner and F. Entwistle regard the phenomenon in the constricted tube as a true tensile rupture produced in the moving liquid, and in their study of the effect of temperature on the rupture of water flowing through constricted tubes, they found indications that the tensile strength of water becomes zero at about 320°, a temperature approaching the critical point of water, and by forcing the liquid through a capillary constriction until the speed in the capillary is sufficient to produce rupture, they found that the tensile strength becomes zero in the neighbourhood of 245°. J. Larmor found that if J. D. van der Waals' equation holds in the liquid state, a negative pressure can subsist only at $\frac{27}{32}$nd of the absolute critical temperature, meaning that the tensile strength could subsist up to 538° K. or 265°.

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§ 4. The Vapour Pressure of Water—Fusion and Boiling

> So long as a body retains its normal state of aggregation and properties we can observe an increase of temperature corresponding with an increase in molecular energy, but as soon as the destruction of form begins to take place, the increase of temperature no longer becomes sensible and the energy is directed to breaking up the structure of the body and to keeping its molecules apart. When this has been accomplished, and not till then, the additional energy imparted again produces accelerated motion, and the substance gets hotter and hotter.—W. ANDERSON (1887).

When a liquid evaporates in an open space, there is apparently a continual flow of the molecules from the surface of the liquid into the space outside, and evaporation proceeds at a steady rate, as long as the significant conditions remain constant. The vapour pressure of water in the atmosphere varies because a state of equilibrium has not been attained between the water and the atmosphere. Water is therefore evaporating slowly, and K. Jablezynsky and S. Przemysky [1] have emphasized that the rate of evaporation is a slow process of diffusion from the layers in the immediate vicinity of the water which are saturated with vapour to the surrounding atmosphere; but, in consequence of secondary disturbances, the water never attains a state of equilibrium with the atmosphere.

The conditions which favour rapid evaporation are important to the chemical engineer because so many operations on a large and on a small scale are dependent on this process. John Dalton made a first approximation to the laws of evaporation in 1803; he said:

> Some liquids evaporate much more quickly than others. The quantity evaporated is in direct proportion to the surface exposed when all other circumstances are alike. An increase in the temperature of the liquid is attended with an increase of evaporation, not directly proportional. Evaporation is greater where there is a stream of air than where the air is stagnant. Evaporation from water is greater the less the humidity previously existing in the atmosphere when all other circumstances are the same.

The speed of evaporation depends on: (i) *The nature of the liquid.* B. G. Babington showed that the speed of evaporation of solutions of many salts is less than for water, and this the more the greater the concentration. Sea-water, for example, evaporates approximately 5 per cent. slower than fresh water under similar conditions. (ii) *The temperature of the liquid and that of the surrounding air;* the rate of evaporation of water increases roughly with temperature, and it is roughly proportional to the saturation pressure at that temperature when the general humidity of the air is low. If the water surface be colder than the dew-point temperature, evaporation is negative and condensation begins. (iii) *The pressure of the atmosphere.* The presence of one gas retards the diffusion of other gas molecules of like or different nature; consequently, when the vapour pressure is comparatively small, the rate of evaporation varies nearly inversely as the total barometric pressure. (iv) *The hygrometric state of the air.* As a first approximation, the rate of evaporation is directly proportional to the difference of the temperature of the wet and dry bulb hygrometers. (v) *The rate at which the vapour is removed from the surface of the liquid.* The speed of evaporation increases as the velocity of the wind, but the exact rate is not certain. D. J. Fitzgerald finds the rate of evaporation is approximately represented by $\frac{1}{60}(p_1-p_0)(1+\frac{1}{2}/w)$ inches per hour, where w represents the velocity of the wind in miles per hour. (vi) *The area of the evaporating surface.* The rate of evaporation increases as the area of the evaporating surface, but not necessarily at the same rate. John Dalton supposed the rates were proportional, but with a circular area in still air, the speed of evaporation increases approximately as the square root of the surface area.

The relation between the rate of evaporation of a liquid from a circular area of radius r and the pressure of the gas when P denotes the barometric pressure, that is, the total pressure of gas and vapour; and p_1, the vapour pressure of the liquid at the evaporating surface or the saturation pressure of the liquid, and p_0 is the vapour pressure in free air at a great distance from the evaporating surface, is, according to J. Stefan,

$$\text{Rate of evaporation} = 4rk \log \frac{P-p_0}{P-p_1}$$

where k is a constant. This expression represents the rate of evaporation into still air from a circular tank or pond filled flush with a relatively extensive plane which neither absorbs nor gives off any vapour. When p_0 and p_1 are small in comparison with P, this expression reduces to: Rate of evaporation$=4rk(p_1-p_0)/P$. The evaporation from an elliptical surface under similar conditions when the major and minor axes, a and b, do not differ greatly, is obtained by substituting $\sqrt{ab}$ in place of r. When the major axis is several times larger than the minor axis, the ratio of evaporation from elliptical surfaces is much greater than from circular ones. Curiously enough, the mass of vapour which evaporates from the surface of a liquid in a given time is not proportional to the surface area, as was once supposed, for the rate of evaporation is not the same on all parts of the surface, being fastest near the edges, and slowest near the centre. Rather is the rate of evaporation more nearly proportional to the linear dimensions—thus with a circular vessel, the rate of evaporation is more nearly proportional to the square root of the area, *i.e.* to the radius than it is to the area of the circle. If the evaporation takes place into still air from a vertical tube of fixed length and constant cross section, when h represents the distance of the surface of the liquid from the top of the tube ; a, the cross-sectional area of the tube : p_1 and p_2, the partial pressures of the vapour at the free end of the tube and at the evaporating surface respectively :

$$\text{Rate of evaporation} = \frac{ka}{h} \log \frac{P-p_2}{P-p_1}$$

where k is a constant whose value for any given liquid can be determined since all the remaining terms can be measured. Given k, therefore, the rate of evaporation of the given liquid from a circular tube or well can be computed from the total gas pressure and the vapour pressures at the surface of the liquid and at the top of the tube. P. Vaillant found the rate of evaporation of a liquid, *i.e.* the quantity of liquid evaporated per second, is proportional to its molecular weight, M, and the four-thirds power of the maximum vapour pressure p ; so that the speed of evaporation$=KMp^{\frac{4}{3}}$, where K is a constant$=0{\cdot}43$ for normal liquids. For water, $K=3\times0{\cdot}43$, which means that this liquid is polymerized.

Kinetic theory of evaporation.—The molecules of a liquid are probably much closer together than is the case with gases, and they are accordingly subjected to the action of comparatively powerful intermolecular forces. Diffusion also shows that the molecules of a liquid are in motion, but, in consequence of great overcrowding, the number of collisions must be comparatively great. The molecules in the body of the liquid are attracted by the other molecules, equally in all directions, but at the surface the molecules can be attracted inwards alone. What will happen to a molecule which, in the course of its wanderings, reaches the surface ? If its velocity be great enough, the molecule will rush upwards beyond the range of attraction of the other molecules in the liquid, and thus, passing into the space above, become an integral part of the surrounding gas or atmosphere. On the other hand, if the velocity of the escaping molecule be not great enough to carry the molecule so far, the upward velocity of the molecule will become less and less, and finally the molecule will fall back and plunge into the liquid again. The case is somewhat analogous with the behaviour of a stone thrown up into the air. If the stone were projected upwards with a sufficient velocity, say 50,000 feet per second, it would leave the earth never to return. Many of the molecules which leave the surface of the water fall back again ; those which leave and do not return reduce the volume of the liquid, and finally lead to complete evaporation. Just as the kinetic energy of some of the molecules of a liquid carries them into the space above, so does the kinetic energy of the molecules of the gas phase cause them to penetrate into and become an integral part of the liquid.

Evaporation from and condensation on the surface of a liquid are thus continuous processes whose ratio may be any value whatever. When both values appear to be zero, condensation and evaporation are really progressing at equal rates. As usually understood, the term evaporation refers to the net loss, and condensation the net gain in a given time. Raising the temperature of the liquid accelerates the motions of the molecules and so hastens the process of evaporation. A draught of air across the surface also favours the passage of the molecules away from the atmosphere above the evaporating liquid and reduces the chance of return.

Steam may be wet or dry. These qualities are of great importance in boiler and engine trials. Wet steam is water vapour which has minute globules of liquid water mechanically entrained with the vapour. This may arise (i) by ebullition ; water is projected into the steam space, part falls back, but part is carried along with the current of steam. (ii) The steam may be subject to variations of pressure, and some water is condensed as a mist during the adiabatic expansion of steam ; and (iii) some water may also be condensed to mist as the steam passes through pipes which are losing heat by radiation, etc.[2]

The cooling effect during evaporation.—In J. D. van der Waals' theory of liquids, the mutual attraction of the particles of the liquid is the restraining force which keeps them more or less together; this force has been estimated to be very great—some hundreds of atmospheres. During vaporization, the particles break away from the surface in spite of this attraction; this cannot be done without a supply of energy, and the curious fact is that the escaping molecules attract the required energy from the rest of the liquid so that a liquid becomes cooler during evaporation. In 1755, W. Cullen placed water under a bell jar from which the air was rapidly withdrawn,[3] evaporation was so rapid that the water was cooled until it froze; similarly, by placing some liquid sulphur dioxide and water in a red-hot platinum crucible the water therein has been frozen by the rapid evaporation of the sulphur dioxide. The kinetic theory shows how this can occur. During evaporation, the fleetest molecules can alone escape from the liquid; the more sluggish molecules cannot get beyond the range of attraction of the molecules remaining in the liquid. The surface of the liquid acts as a kind of grid separating the faster from the slower moving molecules. The fleetest molecules have the greatest kinetic energy, and the temperature of a mass of molecules is proportional to the average kinetic energy of the molecules. If, therefore, the fastest molecules escape, the more sluggish molecules will remain behind, and the average velocity of the molecules of the liquid must be reduced. Hence **a liquid which is evaporating is cooling rapidly.** Observations show that the temperature of a vapour is never very far from that of the liquid which produces it, and it is therefore assumed that the attraction of the liquid reduces the mean kinetic energy of the escaping particles down to near the mean kinetic energy of the liquid, so that the kinetic energy of the molecules of the vapour like that of the molecules of the liquid varies from zero upwards.

To illustrate the cooling effect of evaporation, a little ether is placed in a small beaker with a few drops of water on the underside, the water will freeze if the ether be evaporated quickly by blowing a jet of air across the surface. Advantage is taken of this fact to solidify carbon dioxide by the rapid evaporation of liquid carbon dioxide; and to solidify hydrogen by the rapid evaporation of liquid hydrogen. If a large test tube containing liquid air be fitted with a one-hole rubber stopper fitted with a tube connected with an air pump, the tube becomes so cold that the outside air, in contact with the test tube, is liquefied. The rapid evaporation of the liquid air inside the tube may even produce cold enough to freeze the contents solid. The principle is also utilized in cold storage, etc.

If water be placed in a flask dipping in boiling water, its temperature remains many degrees below the boiling point owing to the cooling effect of the evaporating water; but if the water in the flask be covered with a layer of oil, its temperature rises to that of the bath, and bubbles of vapour pass through the oil.[4]

The heat of vaporization and fusion.—A relatively large amount of energy is needed to transform a gram of water into steam. The thermal energy, or the work done in accelerating the motion of the individual molecules and at the same time imparting to the molecules sufficient momentum to tear them apart against the attraction of those molecules remaining in the liquid is measured by the so-called latent heat of vaporization. The amount of heat required to turn one gram of water at 100° into steam at 100° reported by different observers[5] ranges from the 532·0 to the 538·9 cals. per gram. T. W. Richards and J. H. Mathews found at 100°, 538·1 cals., and A. W. Smith, 540·7 cals. per gram. Few methods of measurement have been so unsatisfactory as those employed for the latent heat of vaporization, and the published data are very discordant, due partly to impure materials but mainly to faults in the method of measurement. The best representative value may be taken as 540 cals., or 9·73 Cals. per gram-molecule at 100°. This is the **latent heat of vaporization** of water at 100°. The number means that steam at 100° has the equivalent of 537 cals. of energy—internal or potential—more than liquid water at 100°, or that 537 cals. of thermal energy are needed to convert a gram of liquid water at 100° into steam at 100°. In symbols, for a gram-molecule (that is, 18 grams of water): $H_2O_{liq.} \rightarrow H_2O_{gas} - 9·7$ Cals., meaning that during the passage from the liquid to the gaseous state, energy equivalent to 9·7 Cals.

in becoming latent or potential, so to speak, is charged on to the molecules—probably as kinetic energy of translatory motion. This energy is degraded as heat when steam at 100° is cooled to liquid water at 100°. The values[6] for 0° range from 599·92 to 587·5 cals. per gram. The best representative value may be taken as 587·7 cals. per gram, or 10·69 Cals. per gram-molecule. The latent heat of vaporization of water is the highest known. and this also helps to moderate the earth's temperature, for it absorbs heat during its evaporation in torrid climates, and gives it up during condensation in cooler climes. These properties of water also help to regulate the temperature of living organisms.

During the change from liquid to vapour, a volume v_1 of liquid expands to a volume v_2 of vapour. The total change in volume is therefore v_2-v_1, and this expansion occurs in spite of the fact that the atmosphere continually acts as if it were a weighted piston which has to be pushed back as the liquid expands into vapour. If p denotes the pressure of the atmosphere, the work done during the expansion can be represented by the product $p(v_2-v_1)$. If the volumes be expressed in c.c., the thermal energy equivalent to the work $p(v_2-v_1)$ will be $0{\cdot}00003183\,p(v_2-v_1)$ cals. If then l represents the observed latent heat of expansion, and E that portion which is spent in overcoming external work, the so-called **external heat vaporization**, the residue, $l-E$, will represent the heat actually spent in doing internal work as the substance expands; this is the so-called **internal heat of vaporization** λ, where $l-E=\lambda$. According to R. Clausius, the relation between the three latent heats of vaporization of water and temperature, $\theta°$, is

$$l=607-0{\cdot}708\theta\,;\quad E=31{\cdot}6+0{\cdot}083\theta\,;\quad \lambda=575{\cdot}4-0{\cdot}791\theta.$$

Many other formulæ have been published. According to F. Henning,[7] the effect of temperature on the latent heat of water is given by the expression $l=93{\cdot}706(366{\cdot}25-\theta)^{0{\cdot}31312}$, which deviates from the observed values by 0·3 per cent. at 140°, and by 0·2 per cent. at 180°. At the critical temperature, 366·25°, the latent heat l is zero. Better agreement between the observed and calculated results at $\theta°$ between 100° and 140° is given by the formula: $l=538{\cdot}46-0{\cdot}6422(\theta-100)-0{\cdot}000833(\theta-100)^2$, which in many cases can be simplified to $l=539{\cdot}66-0{\cdot}718(\theta-100)$. W. Nernst represents the molecular heat of the vaporization of ice at $T°$ by $11938+3{\cdot}5T-0{\cdot}0096T^2$ cals. F. Henning's observations of the latent heat of vaporization of water l in Cals. (15°), at different temperatures θ, and L. Holborn and F. Henning's values for the saturation pressure p and the temperature coefficient $dp/d\theta$ in mm. of mercury per degree, are indicated in Table VI.

TABLE VI.—HEATS OF VAPORIZATION OF WATER AT DIFFERENT TEMPERATURES.

$\theta°$ C.	l cals.	$\frac{dl}{d\theta}$	p mm Hg.	$\frac{dp}{d\theta}$	v_2 c c.
30	579·3	—	31·71	1·819	33010
40	574·0	0·54	55·13	2·939	19600
50	568·5	0·56	92·30	4·588	12050
60	562·9	0·57	149·19	6·916	7677
70	557·1	0·59	233·53	10·11	5046
80	551·1	0·61	355·1	14·40	3406
90	545·0	0·62	525·8	19·99	2360
100	538·7	0·64	760·0	27·12	1673
110	532·1	0·67	1074·5	36·10	1210
120	525·3	0·70	1488·9	47·16	891·3
130	518·2	0·72	2025·6	60·60	667·5
140	510·9	0·72	2709·5	76 67	507·8
150	503·8	0·72	3568·7	95·66	392·1
160	496·6	0·72	4633	117·7	307·1
170	489·4	0·72	5937	143·4	243·0
180	482·2	—	7514	172·7	194·7

Similar remarks might be applied to energy changes during the melting of ice as to the vaporization of liquid water; and similarly with the freezing of liquid water into ice, and the condensation of steam to liquid water. In the case of melting ice, one gram of ice at 0° in melting to liquid water at 0° requires about 80 cals.—this is the so-called **latent heat of fusion**—in symbols, for one gram-molecule (that is, 18 grms.), $H_2O_{\text{solid}} \rightarrow H_2O_{\text{liquid}} - 1{\cdot}44$ Cals. When compared with other liquids, the freezing point of water is high; the latent heat of fusion also, if liquid ammonia be excluded, is the largest which has yet been discovered. All these properties of water play an important part in regulating the temperature of the earth, for a comparatively large amount of heat must be abstracted from a large body of water before it can freeze, and this helps to prevent an excessive fall of temperature in lakes and seas. The latent heat of fusion of ice was first investigated by J. Black [8] near the beginning of the nineteenth century, and culminated in the important work of H. V. Regnault (1847), in which 79·25 cals. was obtained for the latent of fusion of ice. Other determinations at 0° range from the 79·20 cals. per gram of E. Leduc (1906) to the 80·025 of R. Bunsen (1870). L. F. Guttmann (1907) introduced certain corrections in A. W. Smith's data, and then obtained 79·67, the identical result obtained by W. A. Roth (1907). The best representative value may be taken as 79·7 cals. per gram or 1·436 Cals. per gram-molecule—it is interesting to note that this result is identical with the 79·7 cals. obtained by J. Black in 1762. According to O. Petterson, the value drops to 77·71 at −2·8° and to 75·99 at −6·62°. According to P. W. Bridgman (1912), the latent heat of the transformation of ice into water at different temperatures is:

Temperature . . .	−20°	−15°	−10°	−50°	0°
Latent heat	57·7	62·5	68·0	73·7	79·8 cals.

O. Petterson has studied the application of Kirchhoff's equation $d\lambda/dT = C_2 - C_1$ to water when C_2 denotes the specific heat of the liquid, and C_1 the specific heat of the solid. The results were satisfactory When the fusion temperature T is lowered 1°, the latent heat of fusion λ diminishes $C_2 - C_1$ calories. Similar relations hold for other substances. The latent heats of fusion of some common metals are:

Iron.	Copper.	Silver.	Zinc.	Gold.	Tin.	Lead.
69·0	43·0	24·3	22·6	16·3	13·82	4·0 cals.

If secondary changes—*e.g.* decomposition during fusion—do not occur, all substances exhibit characteristic latent heats of fusion and vaporization. In virtue of these facts, it follows that weight for weight a liquid contains a greater amount of energy than a solid, and a gas contains a greater amount than a liquid. In order to change a solid to a liquid, or a liquid into a gas, energy must be *added* to the substance, and for the converse changes, gas to liquid, or liquid to solid, energy must be *withdrawn* from a substance. In general, when a substance passes from one physical state to another, a definite amount of energy is simultaneously added to or withdrawn from the substance. The energy needed for the evaporation of natural waters is mainly derived from the "heat paid out by the sun."

Most solids expand in passing from the solid to the liquid state; according to G. Vicentini and D. Omodei (1886),[9] one volume of the following elements changes δv volumes on melting:

	Cadmium.	Mercury.	Phosphorus.	Lead.	Tin.	Potassium.	Sodium.
δv . .	0·047	0·037	0·035	0·034	0·028	0·026	0·025

corresponding with a 3·3 per cent. average expansion, and the melting point of all these solids is raised by pressure. Water, on the contrary, contracts nearly 9·1 per cent. on melting. As P. W. Bridgman has shown, the freezing temperature of water is lowered approximately 1° for each 100 atmospheres in accord with the fact that the specific volume of ice is greater than that of liquid water; but when the pressure has reached 2115 atmospheres, the freezing temperature begins to rise again, because a form of ice denser than the liquid appears. Hence, the maximum pressure obtained by cooling water in a closed vessel is 2100 atmospheres, and pipes capable of withstanding this pressure would never burst by the freezing of water. *The molecular theory of the raising of the melting point by pressure* is somewhat as follows: The mean distance between the molecules of a solid vibrating about their centres of oscillation, is increased when the temperature is raised; this causes the solid to expand. When the mean distance increases to such an extent that the motion of one molecule does not retard those of the others, the molecules start migratory motions, and the solid is said to melt. If, at the melting point, pressure is applied, the molecules are forced nearer together, and a further rise of temperature is needed for the solid to melt. An increase of temperature is needed to counterbalance the increased pressure. The reason the melting point of ice is lowered by pressure depends on the fact that an increase of pressure facilitates the conversion of the complex ice molecules to simpler water molecules. A somewhat similar phenomenon probably occurs with sulphur trioxide which also expands on solidifying. Mutual attractions draw the molecules of water together during solidification; this requires an expenditure of energy, for there is an evolution of heat during the passage of water into ice. The latent heats of fusion and vaporization of water are abnormally high:

	Water.	Mercury.	Sulphuric acid.	Acetic acid.	Benzene.
Latent heat of fusion . .	79·89	2·8	22·82	46·4	30·39
Latent heat of vaporization .	536·4	62	122·1	79·8	94·4

The approximately 80 cals. required to fuse a gram of ice at 0° do not solely represent the purely physical change, but probably include the latent heat of dissociation corresponding with the change of some ice to water molecules, and the solution of the remaining ice molecules in the water molecules. Similarly with the heat of vaporization, there is here allowance to be made for the passage of some complex water molecules into the simpler steam molecules.

The effect of pressure on transition points.—Let unit mass of a liquid pass into vapour at each of the temperatures T and $T+dT$, and let the respective vapour pressures be p and $p+dp$; further, let the volume of the liquid be v_1 and the volume of the vapour v_2 when the pressure is p, the external work done during the vaporization of unit mass be $p(v_2-v_1)$, and if λ denotes the internal latent heat of vaporization per gram, we have $E-L=\lambda$, and for a small change of pressure dp, the work dE will be $(v_2-v_1)dp$. Substituting these values of $E-L$ and of dE, *i.e.* respectively $W-Q$ and dW, in H. von Helmholtz's equation (indicated later), there remains:

$$\lambda=T\frac{dp}{dT}(v_2-v_1)$$

a relation often called **E. Clapeyron's equation,**[10] because an equation similar in meaning was deduced by E. Clapeyron (1834). The same result follows another way. For equilibrium between heat energy, $(\lambda/T)/dT$, and volume energy, $(v_2-v_1)dp$, in any given change, $(\lambda/T)/dT$ must be equal to $(v_2-v_1)dp$, where v_2-v_1 represents the increase in molecular volume by the change under consideration. Obviously, if any five of the six terms are known, the sixth can be calculated.

The fraction dp/dT is sometimes called the **pressure coefficient** because it represents the change of pressure dp which occurs with unit change of temperature. In words, **the molecular heat of vaporization of a substance is equal to the product of the absolute temperature into the pressure coefficient and the change of volume which occurs when the substance changes its state.** It is easy to see that an analogous expression will be obtained if a similar argument be applied to any change of state—liquefaction, vaporization, sublimation, allotropic and other physical and chemical changes—and Q can be used in place of λ, where Q denotes the heat of transformation. Hence, said P. Duhem (1902): *Tous les changements d'état physique ou de constitution chimique dépendent des mêmes lois générales.*

If the latent heat of a change of state be positive, then the raising or lowering of the transition point with unit change of pressure (dT/dP) is dependent on whether the volume v_2 is greater or less than the volume v_1. If the volume of the material decreases during a change of state so that v_2 is less than v_1, the transition point will be lowered by pressure, and if the volume increases during the change of state so that v_2 is greater than v_1, the transition point will be raised by pressure. This furnishes a general rule for the effect of pressure on transition points: **an increase of pressure favours that state which has the smaller volume.** The latent heat of fusion of ice is always positive, and consequently, as a corollary from Clapeyron's equation, it follows that *an increase of pressure lowers the temperature of transformation of substances which contract on passing from one state to another*, for if v_2 be less than v_1, dp and dT must have opposite signs in order that λ and T may remain positive; but if the pressure be increased, dp must be positive, and dT will therefore be negative, and an increase of pressure will lower the temperature of the transformation—*e.g.* ice, bismuth, bismuth sulphide, cast iron, nitre, and sulphur trioxide contract on melting, hence, their melting points are lowered by increase of pressure. Another corollary: *an increase of pressure raises the transition temperature of substances which expand on passing* from one state to another; for if λ and T are positive, and v_1 be greater than v_2, dp and dT must have the same sign, and if dp be positive, dT will also be positive—*e.g.* the boiling points of liquids are raised by an increase of pressure; so are the melting points of solids like phosphorus, sulphur, lead, tin, and many other metals which expand on melting.

In 1850, M. Faraday[11] drew attention to the fact that when two moist pieces of ice are in contact, pressure is not essential for the solidification of two moistened surfaces of ice. J. Thomsòn (1860) tried to explain Faraday's experiment by capillary action, but M. Faraday showed that this could not be the case because the blocks froze together when under water as well as when in air. From a suggestion made by J. Hooker, J. Tyndall applied the term *regelation* to the phenomenon, and both he and J. D. Forbes explained regelation by assuming that the melting point of ice in the interior of a mass is lower than the normal freezing point at the surface. Hence, it was assumed that when the two surfaces come into contact, they become interior parts of the enlarged block and thus the water film is at once frozen. The explanation now generally accepted is that water at 0° is a saturated solution of ice molecules; and a film of water at 0° with ice on both sides would grow together by natural crystallization, without the need for introducing the effects of pressure. This phenomenon is not to be confused with the lowering of the freezing point of water by pressure. This latter is probably more truly a regelation because the ice can be squeezed into water by pressure, and the ice re-forms when the pressure is removed.

W. Spring has also shown that many metals liquefy under great pressures, and an increase in volume (decrease in specific gravity) has been observed after many metals have been subjected to external mechanical forces—pressure, twisting, rolling, etc.; thus the specific gravity of bismuth changed as follows:

Pressure in atmospheres	1	18,000	27,000	36,000
Specific gravity	9·783	9·779	9·655	9·586

The increase in volume which persists after the pressure has been withdrawn is supposed to be due to the dislocation of the molecules of the solid as it was passing to the liquid condition under the influence of a gradually increasing pressure, and that pressure was relieved too quickly to give the molecules sufficient time to take up the condition characteristic of the solid state.

EXAMPLES.—(1) If the melting point of ice under a pressure of one atmosphere is 0°, what will be the melting point of ice under a pressure of n atmospheres, and also in vacuo when the latent heat of ice is 80 cals. and one c.c. of liquid at 0° furnishes 1·09 c.c. of ice at 0°? One atmosphere pressure is equivalent to 1033·3 grms. of mercury per sq. cm., and since 1 cal. is equivalent to 47,600 dynes, or 80 cals. are equivalent to 80 × 47,600 dynes, $T=273$, $dp=1033{\cdot}3$, $dp=n-1$; $v_1-v_2=0{\cdot}09$; and dT, the melting point of ice under a pressure of n atmospheres, is $-0{\cdot}0074(n-1)$; the melting point of ice in vacuo when $n=0$ is 0·0074°. Lord Kelvin found a change of 0·0072° per atmosphere pressure. According to E. Riecke (1912), if the pressure be p atm., the melting point of ice is lowered $\theta=0{\cdot}00036p$.

(2) Water boils at 100° under normal atmospheric pressure and at 100·1° under a pressure of 1·00355 atm. The volume of one gram of steam at 100° is 1645·55 c.c., and of liquid water at the same temperature 1·04 c.c. Show that the latent heat of steam at 100° is nearly 532·6 cals. The deviation from the observed 537 cals. rests on the inaccuracy in the values assigned to dp and dT.

(3) L. T. Reicher (1883)[12] found that when sulphur changes from α- to β-sulphur at the transition temperature 95·6°, there is an expansion of 0·0000126 c.c., the latent heat involved in the transformation being 2·52 cals. Hence compare the computed change in the transition temperature with change of pressure with the value 0·05° per atmosphere observed by L. T. Reicher. $dT/dp = 368 \cdot 6 \times 0 \cdot 0000126 \div 2 \cdot 52 = 0 \cdot 045°$ per atmosphere.

In the special case of vaporization when the volume v_1 of the liquid is very small in comparison with v_2 the volume of the vapour, v_1 can be neglected without sensible error; and if the ordinary gas law, $pv=RT$, describes the behaviour of the gas, Clapeyron's equation becomes $p\lambda=RT^2(dp/dT)$, which can be written in the equivalent forms:

$$\frac{1}{p}\cdot\frac{dp}{dT}=\frac{\lambda}{RT^2};\quad\frac{d\log p}{dT}=\frac{\lambda}{RT^2}$$

This is called **Clapeyron and Clausius' equation**—after R. Clausius (1851)—and it is supposed to represent the observed data more accurately than Clapeyron's at low temperatures, when the vapour pressure is small.

EXAMPLE.—Water at 760 mm. pressure boils at 373° absolute, and dp/dT, the variation of the vapour pressure, is 27·12 mm. per degree. Hence, if $R=1 \cdot 985$ cals., the molecular heat of vaporization is $(1 \cdot 985 \times (373)^2 \times 27 \cdot 12) \div (760 \times 18) = 547 \cdot 5$ cals., a number about 2 per cent. too large.

Vapour pressure.—Suppose that a liquid is evaporating in a closed vacuous space. The fleetest molecules cannot escape into boundless space, and consequently they accumulate as a gas or vapour in the space above the liquid. The concentration of the vapour in the space above the liquid will go on increasing. The molecules of the vapour behave like the molecules of an ordinary gas, and consequently a certain percentage will plunge back into the liquid. The number of molecules which return to the liquid from the space above per second of course increases as the concentration of the vapour increases, although the rate at which the molecules leave the liquid probably decreases as the concentration of the vapour increases. **When the number of molecules which return to the liquid in a given time is equal to the number of molecules which leave the liquid in the same time, the vapour must be saturated, and the system in equilibrium.** With the notation previously used:

$$\text{Water}_{\text{liquid}} \overset{100°}{\rightleftharpoons} \text{Water}_{\text{steam}}$$

The equilibrium, it will be observed, is not a passive (static) condition—that is, a state of rest—for both processes are active (kinetic). There is a shower of molecules streaming into the liquid, and an efflux of molecules away from the liquid. The effect of one is neutralized by the other; neither can produce any visible result. Anything which disturbs this equality—*e.g.* a desiccating agent or a condenser in the space above (as in distillation), etc.—will alter the conditions. Experiments show that **at a given temperature the vapour pressure of a liquid in contact with its own liquid is a constant quantity, but it increases as the temperature rises, and is independent of the absolute amount of vapour and of liquid present in the system.** It is easy to see this. If the surface of the liquid be doubled, it is true that twice as many molecules will leave the surface in a given time, but twice as many molecules will return.

The higher the temperature of the liquid the swifter will be the movements of the molecules; the greater the relative number of molecules escaping from the liquid per second into the supernatant atmosphere; and the greater the resulting pressure. The vapour pressure of water at 0° is just equal to 4·60 mm. of mercury.

This means that if a little water be introduced into the Torricellian vacuum of a barometer, at 0°, the mercury will be depressed from 760 mm. to 755·4 mm. If the mercury barometer be 760 mm. high, and a drop of water be introduced so that there is a film of liquid water on the surface of the mercury, the height of the mercury column will be reduced one-half if the temperature be raised to 81°, because the vapour pressure of water at that temperature is nearly 380 mm. of mercury. The higher the temperature, the greater the vapour pressure, provided all the water is not vaporized; but for any assigned temperature, the vapour pressure of water has one fixed and definite value. The effect of temperature on the vapour pressure of liquid water is indicated in Tables VII and VIII, and on the corresponding vapour pressure of ice in Table VIII. These tables of physical constants are very useful. E. W. Morley (1912) has said:

> The importance of physical constants is that each one holds condensed in a small volume the essence of many observations. Some constants are like the words in a dictionary or the figures in a mathematical table. Such constants must be determined and tabulated in order that the call for them may be answered without delay or waste of time.

The equilibrium pressures of water vapour in contact with the liquid—*i.e.* the vapour pressure of water at different temperatures—have been measured by H. V. Regnault, G. Magnus, L. P. Cailletet and E. Colardeau, and others. The results in Table VII up to 70° are based on the measurements of K. Scheel and W. Heuse; from 70° to 100°, on the measurements of H. F. Wiebe; and from 100° to 370° on the measurements of L. Holborn, F. Henning, and A. Baumann. In illustration, the vapour pressure of water at 95° is 634·01 mm., and at 150°, 3568·7 mm.

TABLE VII.—THE VAPOUR PRESSURES OF WATER OVER THE LIQUID BETWEEN −16° AND 370°.

Temperature. °C.	Vapour pressures of liquid water in mm. of mercury.									
	0	1	2	3	4	5	6	7	8	9
−1	2·144	1·979	1·826	1·684	1·551	1·429	1·315	—	—	—
−0	4·579	4·255	3·952	3·669	3·404	3·158	2·928	2·712	2·509	2·321
+0	4·579	4·926	5·294	5·685	6·101	6·543	7·014	7·514	8·046	8·610
1	9·210	9·845	10·519	11·233	11·989	12·790	13·637	14·533	15·480	16·481
2	17·539	18·655	19·832	21·383	22·383	23·763	25·217	26·747	28·358	30·052
3	31·834	33·706	35·674	37·741	39·911	42·188	42·19	44·58	47·08	49·71
4	55·34	58·36	61·52	64·82	68·28	71·90	75·67	79·62	83·74	88·05
5	92·54	97·24	102·13	107·24	112·56	118·11	123·89	129·90	136·16	142·68
6	149·46	156·52	163·85	171·47	179·40	187·64	196·19	205·07	214·29	223·86
7	233·79	244·11	254·82	265·91	277·41	289·32	301·65	314·42	327·64	341·32
8	355·47	370·11	385·25	400·90	417·08	433·79	451·07	468·91	487·33	506·36
9	526·00	546·27	567·19	588·77	611·04	634·01	657·69	682·11	707·29	733·24
10×1	760·00	1074·5	1488·9	2025·6	2709·5	3568·7	4633·0	5937·0	7514·0	9404·0
10×2	11647	14291	17376	20950	25064	29771	35127	41186	48011	55680
10×3	64290	73860	84480	96270	109300	123660	139480	157200	—	—

The vapour pressure of ice is less than that of water, and is quite appreciable. Determinations have been made by H. V. Regnault,[13] L. Rolla, etc. The results in Table VIII are based on the measurements of K. Scheel and W. Heuse. The vapour pressure of ice explains how ice and snow can evaporate at temperatures below 0°, without melting to liquid water. The curve *ROO*, Fig. 9, represents the vapour pressure of liquid water, and the curve *PO*, the vapour pressure of ice. W. Nernst calculates that at —20° the vapour pressure of water is 0·940; at —73°, $2·5 \times 10^{-3}$; and at —173°, $6·6 \times 10^{-16}$.

The exact relation between the temperature and pressure of a vapour in contact with its own liquid is not known. Quite a number—between thirty and forty—of empirical formulæ has been proposed. J. Dalton's, the earliest,[14] represented the pressures increasing in geometrical progression while the temperatures increased in arithmetical progression. In symbols, if p_0 be the pressure at 0° and p the pressure at $\theta°$, $p=p_0a\theta$, or, what is the same thing, $\log p=a+b\theta$, where a, a, and b are constants; but H. V. Regnault's exact measurements on vapour pressures proved J. Dalton's rule to be inaccurate. A number of formula of this type but with more terms have been employed, *e.g.* J. B. Göbel (1905) represented the vapour pressure of water, p, at $\theta°$ in the vicinity of 0° by $p=0{\cdot}4600+0{\cdot}03293\theta+0{\cdot}00105\theta^2+0{\cdot}0000167\theta^3$; and for ice, $p=0{\cdot}45996+0{\cdot}03741\theta+0{\cdot}001895\theta^2+0{\cdot}0000716\theta^3$. *W. J. M. Rankine's vapour pressure formula* (1849) is one of the favourites; G. Kirchhoff, in 1858, and A. Dupré, in 1869, employed similar formulæ. W. J. M. Rankine represents the vapour pressure p, at the absolute temperature T, by the expression:

TABLE VIII.—THE VAPOUR PRESSURE OF WATER OVER ICE BETWEEN 0° AND −65°.

Temperature.	Vapour pressure of ice in mm. of mercury.									
	0	1	2	3	4	5	6	7	8	9
−0	4·579	4·215	3·879	3·566	3·277	3·009	2·762	2·533	2·322	2·127
−1	1·947	1·780	1·627	1·486	1·356	1·237	1·127	1·026	0·933	0·848
−2	0·770	0·699	0·633	0·574	0·519	0·469	0·424	0·383	0·345	0·105
−3	0·280	0·252	0·226	0·203	0·182	0·163	0·146	0·131	0·117	0·105
−4	0·094	0·083	0·074	0·066	0·059	0·052	0·047	0·042	0·037	0·033
−5	0·029	0·026	0·023	0·021	0·021	0·018	0·016	0·012	0·010	0·009
−6	0·008	0·007	0·005	0·004	0·003	0·003				

$$\log p=a+\frac{b}{T}+c\log T \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The constants, a, b, c of this formula have a physical meaning in that they are related to the other properties of matter—specific heat, vaporization, and molecular weight. For water, between −100° and 365°, P. Juliusburger gives $\log_{10}p=9{\cdot}30027-21113{\cdot}2T^{-1}-0{\cdot}28771\log_{10}T$ mm. of mercury. Rankine's formula has also been deduced by H. Hertz, J. W. Gibbs, M. Planck, and O. Stern from reasoning based on the assumption that Boyle's law is valid, meaning that the formula is strictly applicable only with very small pressures. *J. D. van der Waals' vapour pressure formula*

$$\log\frac{p_c}{p}=f\left(\frac{T_c}{T}-1\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

has also been largely used. Here $p_c=164940$ mm., and $T_c=374°$ or $647{\cdot}09°$ K. respectively denote the critical pressure and absolute critical temperature; f is a number which H. von Jüptner and H. Happel found to vary partly with the nature of the substance and partly on the temperature; and L. Schames found that there is a minimum value of f which is the same with all substances at the same reduced temperature. The value of f falls from 3·3261 at 0° to a minimum 3·1244 at 215°, and rises to 3·2283 at 360°. I. W. Cederberg found that $f=a\beta^{(T/T_c-\gamma)^2}$, where a denotes the minimum value of f; β is a constant; and γ the reduced minimum temperature. For water, $a=3{\cdot}1244$; $\beta=1{\cdot}7887$; and $\gamma=0{\cdot}7500$. The deviations calculated from the observed results, between −173° and the critical point, with $\log p_0/p=a\beta^{(T/T_c-\gamma)^2}(T/T_c-1)$, are less than 0·01 per cent. J. D. van der Waals' formula may be written $\log p=(\log p_c+f)-fT_c/T$, which resembles Rankine's formula with the $c \log T$ term missing. Introducing W. Nernst's values for the constants,

$$\log p = -\frac{13512}{4·571T} - \frac{10·089}{1·985} \log T + 23·86774$$

P. E. Brunelli (1917) claims that $\log p = 23·08647 - 4·5 \log T - 2980·46T^{-1} - 0·00278T + 0·000002825T^2$ represents the vapour pressure of water over a longer range of temperature than any hitherto proposed. T is taken to be $273·09+\theta$. C. E. Carbonelli represents the vapour pressure p at the absolute temperature T, below the critical temperature, T_c, by the expression

$$\log \frac{p_c}{p} = \frac{T_c - T}{T} \log \frac{aT_c}{T}$$

where a is a constant characteristic of the liquid. It is 2·21503 for carbon disulphide; 2·58124 for chloroform; 3·6765 for alcohol; 2·92714 for water; 2·80416 for ethyl ether; 2·64664 for benzene; 2·79064 for sulphur dioxide; 2·92481 for cyanogen; and 2·79 for ammonia. A. March deduces for the vapour pressure p at the absolute temperature T

$$p = p_c e^{-\beta(T_c/T - 1)}$$

from Maxwell and Boltzmann's theorem, J. D. van der Waals' theory and the quantum theory; p_c and T_c respectively denote the critical pressure and temperature; β is a constant whose value depends on the nature of the substance.

W. Nernst deduced a vapour pressure formula from Clausius and Clapeyron's equation $\lambda = T(v_2 - v_1)dp/dT$, where the unit of mass is the gram-molecule; λ is the molecular heat of evaporation or sublimation; v_2 and v_1 the specific volumes of gas and liquid or solid phase respectively; p is the pressure of the saturated vapour at the absolute temperature T. If the effect of temperature T and pressure p upon the specific volume v, and if the heat of evaporation be known, then the results substituted in the Clausius-Clapeyron equation will give a relation between p and T. W. Nernst adopts the empirical formulæ:

$$p(v_2 - v_1) = RT\left(1 - \frac{p}{p_c}\right); \text{ and } \lambda = (\lambda_0 + AT + BT^2)\left(1 - \frac{p}{p_c}\right) \quad . \quad (3)$$

where A and B are constants; R is the gas constant. The result of the substitution is $\lambda_0 + AT + BT^2 = T^2Rd \log p/dT$; or, after integration $\log p = -\lambda_0/RT + A \log T/R + BT/R + \mathbf{C}$, where $\mathbf{C}$ is the constant of integration. If the gas constant R be 1·985 and ordinary logarithms are used, *W. Nernst's vapour pressure formula* for water becomes

$$\log p = -\frac{\lambda_0}{4·571T} + \frac{A}{1·985} \log T + \frac{B}{4·571} T + \mathbf{C} \quad . \quad . \quad (4)$$

The constants λ_0, A, and B can be evaluated through the second of equations (3), and also indirectly by the relation $d\lambda/dT = C'_p - C_p$, where C'_p is the molecular heat of the liquid or solid, and C_p that of the vapour. The numerical values for any particular liquid can be also obtained by substituting the corresponding values of p and T for three different temperatures, and solving the resulting equations.

It has been found that the so-called constant $\mathbf{C}$ is, for normal substances, characteristic of the molecule to which it refers, and is independent of the physical state of the substance, so that $\mathbf{C}$ is the same for the vapour pressure formulæ of both liquid and solid carbon dioxide. This has been established for a number of substances by E. Falck and C. F. Mündel. Consequently $\mathbf{C}$ is called the **chemical constant** of the molecules of the substance in question, and it enables the chemical equilibrium of a reacting system to be computed when the thermal value of the reaction is known.

The second of equations (3) represents the observed relations between the heat of evaporation λ and temperature T fairly well, and W. Nernst found that in a great number of cases A is 3·5; hence, W. Nernst's vapour pressure formula becomes

$$\log p=-\frac{\lambda_0}{4{\cdot}571T}+1{\cdot}75\log T+\frac{B}{4{\cdot}571}T+\mathbf{C} \quad . \quad . \quad (5)$$

It will be observed that Nernst's vapour pressure formula is dependent on the validity of the first of equations (3), which for small pressures reduces to Boyle's law, and this law is more nearly in accord with observations the smaller the pressure. Hence, **C** is best evaluated at low pressures. The first of equations (3) is also dependent on J. D. van der Waals' law of corresponding states, and does not apply to those abnormal substances which deviate from that rule. Water is one of the abnormal substances, and its vapour pressure does not follow the rule. W. Nernst (1910) therefore assumed that doubled molecules are present in aqueous vapour corresponding with $(H_2O)_2 \rightleftharpoons 2H_2O$; and if D be the observed vapour density, and D_1 the theoretical value, the degree of dissociation γ is $\gamma=(D-D_1)/D_1$. Hence, W. Nernst represents the **vapour pressure of water** by the formula :

$$\log p=\log\frac{1+\gamma}{\gamma}-\frac{2936{\cdot}39}{T}-4{\cdot}94\log T+23{\cdot}44837 \quad . \quad . \quad (6)$$

H. Levy also deduced an expression for the vapour pressure of water on the assumption that the molecules of the liquid are partially associated into dihydrol molecules. For the **vapour pressure of ice,** p mm. of mercury, at $\theta°$, M. Thiesen gives $\log (p/p_0)=9{\cdot}632(1-0{\cdot}000036\theta)\theta/T$, where T is the absolute temperature, and p_0 the vapour pressure at 0°. He also gives $\log p=8{\cdot}891p_0\theta/(252+\theta)$. W. Nernst found

$$\log p=-\frac{2611{\cdot}7}{T}-1{\cdot}75\log T-0{\cdot}00210T+6{\cdot}5343$$

which he afterwards altered to $\log p=$

$$-\frac{5896}{T}+4\log T+3\log(e^{\frac{226}{T}}-1)+6\log(e^{\frac{1200}{T}}-1)-0{\cdot}020837\times10^{-15}T^6+0{\cdot}76876$$

to accommodate the results with the quantum formula for the specific heat of ice. The two formulæ give equally good results, and therefore, for calculations, the simpler type is preferred. S. Weber's measurements of the vapour pressure of ice accord well with the simpler form of W. Nernst's vapour pressure formula :

$T°$ K. . . .	203·96°	199·55°	190·36°	185·51°	177·01°	175·21°
°C. . . .	−69·13°	−73·54°	−82·73°	−87·58°	−96·08°	−97·38°
p obs. . .	2·92	1·50	0·338	0·141	0·029	0·020
p calc. . .	2·936	1·504	0·338	0·145	0·0293	0·0205

The calculated value for 79·79° K., or 193·30°, is $1{\cdot}3\times10^{-23}$ mm. ; and for 157·61° K., or 115·48°, 0·00040 mm. K. Scheel and W. Heuse, and M. Thiesen and K. Scheel found the vapour pressure of liquid water at 0° to be 4·5788 ± 0·0008 mm. of mercury ; and for ice, 4·5785 mm. The vapour pressure of ice and water are the same at the triple point, and therefore, practically speaking, the vapour pressure of water will be the same for ice and undercooled water at the triple point.

The pressure and volume relations of dry saturated vapours have not been represented by a satisfactory equation, and the law pv^n=constant, which is applicable for the permanent gases, does not give a constant index with the vapours. B. Leinweber[15] found that for steam the exponent n varies within wide limits for large pressures, but for low pressures up to 0·35 atm. n is fairly constant.

The distinction between a gas and a vapour.—The distinction between a gas and a vapour is somewhat vague. If the elastic fluid be very far from its temperature of liquefaction, or above its critical temperature, it is generally called a **gas** ;

and **vapour** if it is near its temperature of liquefaction, or below its critical temperature. Oxygen, nitrogen, etc., at ordinary temperatures are gases; whereas water or alcohol on evaporation furnish vapours. Otherwise expressed, **a gas is an elastic fluid at a temperature above its critical temperature, and a vapour is an elastic fluid below its critical temperature, but in a liquid state.** The term **permanent gases** was once applied to gases like oxygen, nitrogen, etc., because they could not be liquefied by any known process. The term has lost its significance since all known gases which have been tried have been liquefied, and all but helium solidified. However, the term permanent gas is sometimes even now applied to gases which approach nearest to the ideal gases, and which deviate least from the gas laws of Boyle and Charles.

Boiling or ebullition.—Steam or water vapour is an invisible colourless gas which condenses to a visible cloud of small particles when it comes in contact with the atmosphere. This is readily shown by boiling water in a flask; inside the flask, the vapour is invisible, and a cloud of minute water particles—condensed steam—appears where the steam comes in contact with the cold air. Raising the temperature of an evaporating liquid increases the average speed of the molecules, and favours rapid evaporation. When the temperature is high enough, the exposed surface of the liquid is not sufficient to allow the swift-moving molecules to escape fast enough, bubbles of vapour are accordingly formed *within* the liquid. Each bubble as it forms rises to the surface—increases in size as it rises—and finally escapes into the atmosphere. The process of vaporization by bubble formation is called **boiling**; and the temperature at which boiling commences, the **boiling point** of the liquid. When the vapour pressure of the liquid is the same as the external pressure to which the liquid is subjected, the temperature does not usually rise any higher. Increasing the supply of heat increases the rate at which evaporation proceeds, or at which bubbles are formed. Hence it is sometimes convenient to define: **The boiling point of a liquid is the temperature at which the vapour pressure of the liquid is equal to the external pressure exerted at any point on the liquid surface.** The external pressure may be exerted by the atmospheric air, by vapour and air, by other gases, etc. Hence, the vapour pressure curve not only represents the vapour pressures of a liquid at different temperatures, but it also shows the boiling points of that liquid under different pressures. Water boils at 100° and 760 mm. pressure. The greater the pressure, the higher the boiling point; and conversely, the less the pressure, the lower the boiling point—roughly, the boiling point changes about $\frac{1}{27}°$ C. per mm. change of pressure for a few degrees above and below 100°. These phenomena occur with liquids generally, and it is therefore necessary to state the pressure when giving the boiling point of a liquid—although if no pressure is stated, 760 mm. is understood. Thus at Quito (9350 feet above sea-level), with the barometer at its average height, 525·4 mm., water boils at 90·1°; and on the top of Mount Everest (29,002 feet), barometer at 255·3 mm., water would boil at 72°. Table IX represents the boiling points of liquid water at atmospheric pressures ranging from 680 to 799 mm. of mercury.

From Clapeyron's equation, and Trouton's rule for water, and remembering that $pv=2T$ cals. when v represents a gram-molecule of saturated vapour, $dt/dp=T/13p$, and if $p=760$ mm., $dT=Tdp/9880$. Consequently, the change dT produced in the absolute boiling temperature T of a liquid when the pressure changes by the small amount dp, will be $dT=0{\cdot}0001012T.dp$. Accordingly, a change of $dp=1$ mm. in the pressure of a liquid boiling at $T=373°$ K, will produce a change, $dT=0{\cdot}0377°$, in the boiling point. The observed result is 0·0370°—approximately $\frac{1}{27}°$ per mm. change of pressure. The formula similarly gives approximate values for liquids other than water. A comparison of the boiling points of some metals in vacuo and at ordinary pressures are indicated in the following scheme:

	Mercury.	Cadmium.	Zinc.	Potassium.	Sodium.	Silver.
In vacuo . .	155°	450°	550°	365°	418°	1360°
At 760 mm. . .	357°	749°	920°	667°	742°	2070°

As a rule, if the boiling point has been observed at a pressure p not far removed from the normal, it can be reduced to the standard by adding or subtracting $c(760-p)(273+b)$, where b denotes the observed boiling point at a pressure p, and c is a constant approximately 0·00010 for water and alcohols.

TABLE IX.—THE BOILING POINTS OF WATER AT DIFFERENT PRESSURES.

Height of barometer 0° mm	Boiling points °C.									
	0	1	2	3	4	5	6	7	8	9
68	96·915	955	996	*036	*076	*116	*156	*197	*237	*277
69	97·317	357	396	436	476	516	555	595	635	674
70	97·714	753	792	832	871	910	949	989	*028	*067
71	98·106	145	184	223	261	300	339	378	416	455
72	98·493	532	570	609	647	686	724	762	800	838
73	98·877	915	953	991	*029	*067	*104	*142	*180	*218
74	99·255	293	331	368	406	443	481	518	555	592
75	99·630	667	704	741	778	815	852	889	926	963
76	100·000	037	074	110	147	184	220	257	293	330
77	100·366	403	439	475	511	548	584	620	656	692
78	100·728	764	800	836	872	908	944	979	*015	*051
79	101·087	122	158	193	229	264	300	335	370	406

The asterisk means that the number in front of the decimal is to be raised one unit.

The boiling point of a liquid is raised either by increasing the external (atmospheric) pressure; or by the increase of pressure which occurs when a liquid is heated in a closed vessel. The rise in the boiling point which occurs when a liquid is heated in a closed vessel fitted with a safety valve was first utilized by Denis Papin in a digester or autoclave for softening bones, and described in his *La manière d'amollir les os* (Amsterdam, 1681). In *la marmite de Papin,* a temperature of 130° was obtained, and the corresponding pressure—Table VII—was 2025·6 mm. of mercury, on the assumption that water is alone confined in the boiler. The solvent action of water at this temperature and pressure is much greater than at 100°—the maximum temperature attainable under normal atmospheric pressure. Conversely, observations on the boiling points of a liquid at different pressures also show the vapour pressures of the liquid at different temperatures. Thus, the vapour pressure of water at 0° is 4·6 mm.; and water at a pressure of 4·6 mm. boils at 0°. Hence, liquids which decompose at their boiling point under ordinary atmospheric pressure can frequently be distilled without decomposition at the lower boiling temperature obtained by reducing the pressure. Hydrogen peroxide can be cited in illustration. Hence, the so-called process of **distillation under reduced pressure,** or, as it is sometimes less accurately styled, **distillation in vacuo.** S. T. Preston[16] and G. J. Stoney have estimated that there are not less than $2·7 \times 10^{19}$ molecules per cubic centimetre of gas at n.p.t.; when the gas is reduced to the lowest obtainable pressure, say, $\frac{1}{10000}$th atmosphere, there are still $2·7 \times 10^{9}$ molecules per c.c. Hence, in the best of so-called vacua, an enormous number of molecules is still present. E. Fischer and F. Penzoldt estimate that one part of musk in ten million parts of air and one part of mercaptan in fifty thousand million parts of air could be detected by the sense of smell.

The critical temperature of water.—There is a continuous diminution in the additional temperature required to overcome the effect of an increased pressure on the boiling point of water. This is shown by the following numbers:

Pressure	1		5		10		15		20		25		30 atm.
Boiling temperature .	100°		152°		180°		199°		213°		213°		235°
Rise per 5 atm. pressure		52°		28°		19°		14°		12°		10°	

Hence, it appears likely that a temperature will ultimately be reached at which an additional pressure will require no additional rise of temperature to convert the liquid into vapour. Above that temperature, the temperature of vaporization will be independent of the pressure. This deduction involves an extrapolation, and hence there may be a flaw in the reasoning—the curve, for example, may be asymptotic and approach but never reach the condition just indicated. Experiment shows, however, that **there is a critical temperature, nearly 366°, at and above which no known pressure can condense water vapour into the liquid condition.** At this temperature, the vaporous and liquid states merge into one. It is probable that all other volatile substances have their own particular critical temperatures; for instance, the critical temperature of hydrogen is nearly —271°, and of oxygen —119°. The **critical pressure** of water is 194·6 atm., the **critical volume,** 0·003864,[17] and the **critical density,** between 0·329 and 0·429.

Measuring the volume of moist gases.—In 1801, John Dalton showed that **the mass of vapour required to saturate a given space at a given temperature, and consequently also the vapour pressure of a given liquid, is the same whether the vapour be by itself, or associated with other gases upon which it has no chemical action.** In other words, the total pressure of a mixture of gas and vapour is the sum of the partial pressures of each constituent; hence, added J. Dalton (1801):

> If the aërial atmosphere was at once annihilated, leaving only its aqueous portion, this would be but little augmented, because it already exists in the air nearly at a maximum of that which the temperature can produce and support. The suppression of the obstacle will only accelerate the evaporation, without sensibly augmenting the absolute quantity.

When a gas is confined over water, the observed volume of the gas is determined by the mass of the gas as well as by the temperature and the barometric pressure. By Dalton's law the total pressure of the gas is the joint effect of two partial pressures: (1) the partial pressure of the water vapour at the observed temperature; and (2) the partial pressure of the gas under observation. Hence the barometer reading does not represent the pressure of the gas alone, but rather the pressure of the gas plus the pressure of the water vapour. To find the latter, note the temperature, and Table VII furnishes the desired vapour pressure of water expressed in millimetres of mercury. This must be subtracted from the observed pressure (barometer) in order to find the pressure of the gas at the temperature in question.

EXAMPLE.—What is the volume of 4½ litres of a gas at 0°, 760 mm., when it is measured in contact with water at 15°, and the barometer reads 767·8 mm.? From Table VII, the vapour pressure of water at 15° is 12·8 mm. Hence the gas is really under a partial pressure of 767·8 − 12·8 = 755 mm. of mercury. The problem is now to be solved like the example previously indicated. The answer is 4·24 litres.

The boiling points of liquids.—As a rule substances formed with a large evolution of heat, and highly associated substances have a high boiling point. In 1801, J. Dalton[18] suggested that different liquids, at temperatures equally distant from their boiling points, have the same vapour pressure; or, if θ be the boiling point of the substance under normal pressure, and t_1 the boiling point of the same substance at another pressure; and if θ_2 and t_2 be the corresponding boiling points of another substance, then, $\theta_1-\theta_2=t_1-t_2$. C. G. Schmidt found the rule to be valid for the series of fatty acids—formic, acetic, propionic, butyric, . . ., acids—but not the corresponding alcohols, and numerous workers[19] have found the rule to be invalid when applied to liquids generally. U. Dührung,[20] in 1878, maintained that if θ_1 and θ_2 respectively denote the boiling points of two liquids under the same pressure; $\theta_1=a+b\theta_2$ when a and b are constants, and W. Ramsay and S. Young found a similar rule applicable to some organic liquids; for, if T_1 and T_2 represent the absolute boiling temperatures of two liquids under a pressure p, and T_1' and T_2' the boiling temperatures under another pressure p', the ratios $T_1/T_2=T_1'/T_2'$ =constant. As a rule, however, the relation is not so simple, and W. Ramsay and

S. Young find that $T_1'/T_2'=T_1/T_2+a(T_1'-T_1)$ better expresses the result, or, when a is very small, $T_1'/T_2'=T_1/T_2+a(T_2'-T_2)$.

According to P. Walden,[21] for a great number of non-associated organic liquids, the boiling temperature T_b is related with the specific cohesion a^2 in sq. mm. by the empirical expression $Ma^2/T_b=1\cdot16$, where M denotes the molecular weight of the substance; since σ, the surface tension in dynes per cm., is equal to $4\cdot9a^2D$, where D is the density of the liquid, $\sigma v/T_b=5\cdot67$, where v denotes the molecular volume.

Many attempts have been made to establish a relationship between the boiling points and the composition of members of the same homologous series of carbon compounds. H. Kopp,[22] for instance, noticed that every addition of CH_2 raised the boiling point of some series by about 19°, and he laid down the rule: the same differences in the chemical composition or organic compounds correspond with the same differences in the boiling points; but C. Schorlemmer [23] showed that with the monohalogens of the normal paraffins, the differences were not constant, but decreased 2° at each step. It was soon found that Kopp's rule was not at all general, and many empirical formulæ have been proposed, but these are usually applicable only to a limited number of homologous series,[24] and usually over but a limited range of a particular series. Many of these formulæ are described in W. Nernst and A. Hesse's *Siede und Schmelzpunkt* (Braunschweig, 1893), and in W. Marckwald's *Ueber die Beziehungen zwischen den Siedepunkten und der Zuzammensetzung der chemischen Verbindungen* (Braunscheweig, 1898). J. Walker had some success with the formula $T_b=aM^b$, where a and b are constants for particular series, but vary from series to series; M represents the molecular weight; and G. G. Longinescu,[25] with the formula $T_1/T_2=M_1n_1^{\frac{1}{2}}/M_2n_2^{\frac{1}{2}}$, where M_1 and M_2 respectively denote the molecular weights of liquids with n_1 and n_2 atoms per molecule, and boiling points T_1 and T_2. G. G. Longinescu's formula can also be represented in the form $(T_b/100D)^2=n$; where T_b represents the boiling point; D the density of the liquid at 0°; and n the number of atoms per molecule. For water, $n=12$, while for the normal molecular weight 18, n should be 3. Hence, says G. G. Longinescu the molecule of water must be more complex than $(H_2O)_4$. P. Pawlewsky found about seventeen organic liquids in which the difference between the boiling points under normal pressure and the critical temperature was the same; but further investigations have shown that the rule is not even roughly applicable to liquids generally. This is illustrated by the penultimate column of Table X, from S. Young's *Stoichiometry* (London, 1908). The last column, however, shows that the ratio of the absolute critical temperature, T_c, and the absolute boiling temperature, T_b, is more nearly constant, as pointed out by C. M. Guldberg in 1890,

$$\frac{T_c}{T_b}=1\cdot7$$

This rule, however, is but a rough approximation, though it may be employed to get an idea of the critical temperature of a substance.

TABLE X.—RELATION BETWEEN THE BOILING POINT AND THE CRITICAL TEMPERATURE.

Substance	Critical temperature T_c.	Boiling point T_b.	Difference T_c-T_b.	Ratio $\frac{T_c}{T_b}$
Hydrogen . .	35°	20°	15°	1·75
Oxygen . . .	154	90·5	63·5	1·70
Methane . . .	191	108·3	82·7	1·76
Octane . . .	569·2	398·8	170·4	1·43
Benzene . . .	561·5	353·2	208·3	1·63
Water . . .	633	373	260	1·59

According to T. E. Thorpe and A. W. Rücker, if D_1 and D_2 denote the densities of a liquid respectively at the absolute temperatures T_1 and T_2, the critical temperature T_c is $0·50125(T_2D_1-T_1D_2)/(D_1-D_2)$; or, if V_b denote the specific volume at the boiling point,

$$T_c=\frac{T_bV-273}{2(V_b-1)}$$

According to S. Young, the quotient p_cv_c/T_c, where p_c, v_c, and T_c respectively denote the critical pressure, volume, and temperature, is approximately 22 for normal liquids; water gives the value 26·4. W. Herz showed that the ratio increases in homologous series with an increase in the number of carbon atoms.

Relation between heat of vaporization or fusion and the boiling or freezing point.—In 1823, C. M. Despretz[26] showed that the heat of vaporization L of a liquid divided by the increase in the specific volume which is experienced by the liquid in passing into the state of vapour, is equal to the result obtained with any other liquid at a temperature where the vapour pressures are equal; that is, if v_l and v_g be the specific volumes of a substance in the liquid and gaseous states at its boiling point, $L=k(v_g-v_l)$, where k is a constant, the same for all liquids. J. D. van der Waals has given a theoretical foundation for C. M. Despretz's rule, and shown that if the absolute temperatures of any two liquids be the same fraction of their respective critical temperatures, then the volumes of the liquids and of their saturated vapours is the same fraction of their critical volumes. C. M. Despretz's rule agrees well with many liquids. Assume that Q, the latent heat of vaporization in R. Clausius' equation, $d(\log p)/dT=Q/RT^2$, does not vary with temperature, and that the molecular weight of the substance in the two states of aggregation is the same, it follows, on integration, that $\log p=-Q/RT+$a constant; otherwise expressed, $Q=T\{R(\text{constant}-\log p)\}$, where the bracketed term is constant at the standard pressure p. Hence, the heat Q required to vaporize one gram-molecule of a substance is equal to the absolute boiling temperature, at atmospheric pressure, multiplied by a number which is always the same. A rule analogous to this was proposed by F. Trouton (1884): **The molecular heat of vaporization of a liquid is proportional to the absolute boiling temperature**; or, the quotient of the molecular heat of vaporization and the absolute temperature of the boiling point at one atmospheric pressure is a constant. This is known as **Trouton's rule,** in symbols $M\lambda/T=$a constant which approximates to 20, when L represents the molecular heat of vaporization, which is the product of the latent heat of vaporization (per gram of liquid) into the molecular weight M of the substance; and T represents the boiling point of the liquid on the absolute scale. R. Schiff (1886) found the rule valid for organic liquids, particularly those in related groups. The following examples illustrate Trouton's rule:

	Carbon disulphide, CS_2.	Phosphorus trichloride, PCl_3.	Stannic chloride, $SnCl_4$.	Hydrogen sulphide, H_2S.	Water, H_2O.
Latent heat of vaporization (λ) .	86·7	51·4	30·5	124·4	537
Molecular heat of vaporization .	6384		7962	4230	9666
Boiling point	46°	76°	113·9	−61·6°	100°
Absolute boiling point (T) . .	319°	349°	386·9°	211·4°	373°
Trouton's constant ($\lambda M/T$ or L/T)	20·32	20·07	20·49	20·01	25·9

R. de Forcrand has made a simple extension of Trouton's rule: **The molecular heat of solidification of a gas is proportional to its absolute boiling point (760 mm.)**; so that if L and S respectively denote the molecular heats of vaporization and fusion, $(L+S)/T=$a constant which for a number of substances falls between 28 and 32. If λ and s respectively denote the molecular latent heats of vaporization and solidification at constant pressure, and M the molecular weight of a substance, Trouton's and Forcrand's rules can be respectively symbolized:

$$\frac{\lambda M}{T}=20 \qquad \frac{(\lambda+s)M}{T}=30$$

It is generally considered that Trouton's rule is near the mark for substances in the normal condition, or rather, when the molecules of the substance are the same in the liquid and in the gaseous condition. There are two cases :

(i) *Trouton's constant is greater than* 20. Illustrating by example, ethyl alcohol, C_2H_5OH, furnishes an abnormally high value, *viz.* 26·9 (=9443÷351·4). This is attributed to the association of the molecules $(C_2H_5OH)_n$ in the liquid state, while the molecules of the vapour are normal, C_2H_5OH. Consequently, the observed latent heat of vaporization is the sum of two factors : (*a*) The heat absorbed during the conversion of the molecules of liquid C_2H_5OH into vapour C_2H_5OH ; and (*b*) the heat absorbed during the depolymerization, $(C_2H_5OH)_n = nC_2H_5OH$, in the liquid at its boiling point. Water is another example with Trouton's constant 25·9 ; nitric oxide, 27·7 ; etc.

(ii) *Trouton's constant is less than* 20. Acetic acid, CH_3COOH, furnishes an abnormally low value for Trouton's constant, *viz.* 12·7 (=5094÷391). If the molecules of a vapour are associated and the molecules of the liquid are non-associated, the observed molecular heat of vaporization will be less than would be the case if the molecules were not associated in passing into the state of vapour because heat is evolved during the polymerization of the molecules. In the case of acetic acid, it happens that liquid and vapour molecules are associated to approximately the same extent, and if the molecular latent heat be taken for $(CH_3COOH)_2$ the quotient is normal.

Trouton's rule thus enables an estimate to be made of the molecular complexity or the molecular weights of substances at their boiling points. Thus, iodine approximates I_3 ; sulphur, $S_{8\cdot3}$; mercury, $Hg_{1\cdot18}$; nitric acid, $(HNO_3)_{1\cdot37}$; etc. Even among non-associated substances, however, Trouton's constant may increase considerably with temperature if the substances chosen have widely different boiling points. Thus :

	Hydrogen.	Oxygen.	Carbon disulphide.	Aniline.
Absolute boiling point . . .	20·4	90·6	319	457
Trouton's constant	10·4	18·13	20·4	23·1

W. Nernst (1906) employed the empirical formula $\lambda/T = 8{\cdot}5 \log T$; or $\lambda/T = 9{\cdot}5 \log T - 0{\cdot}007T$; E. C. Bingham (1906), $\lambda/T = 17 + 0{\cdot}011T$; and R. de Forcrand, $\lambda/T = 10{\cdot}1 \log T - 1{\cdot}5 - 0{\cdot}009T + 0{\cdot}0000026T^2$ to represent the increase in the value of Trouton's constant with temperature. W. Hess found that Trouton's rule gave irregular results with homologous carbon compounds.

H. Crompton[27] introduced the idea of valency in Trouton's formula ; P. W. Robertson, the cube root of the atomic or molecular volume ; W. Nernst, specific cohesion ; E. Baud, the change of volume at the melting point ; J. de Guzman, the coefficient of viscosity ; H. Tsutsumi, the specific resistance ; H. S. Allen and K. Honda, electronic frequency ; and H. G. Wayling, Moseley's atomic number. If N be the sum of the atomic numbers of the atoms of the elements forming a compound, and T the absolute temperature of the melting point, H. G. Wayling writes N/T=a number ranging from 2 to 5. The salts with water of crystallization have higher values ; G. N. Lewis represents the relation between the heat of vaporization, the absolute temperature T, the coefficient of expansion of the liquid a, the density D, and the coefficient of compressibility β, by $\lambda = -Ta/D\beta$, when the liquid is normal, and not polymerized or associated.

J. H. Hildebrand argues that the quotient of the heat of vaporization by the absolute boiling point represents the increase in the entropy of a substance during vaporization, per atmosphere pressure, and hence the term *entropy of vaporization* can be employed for this ratio at temperatures other than the boiling point. Trouton's rule fails for normal substances at extreme temperatures, because the constant is greater the higher the boiling point. J. H. Hildebrand further showed that by plotting log p against log T in Clapeyron and Clausius' formula

$$\frac{d \log p}{d \log T} = \frac{\lambda}{RT}$$

the tangent to the resulting curve at any point represents the entropy of vaporization at that temperature divided by R. If Trouton's rule be valid, the tangents to the curves for different substances should have the same slope at a value of log p, corresponding to one atm.; in reality, the slopes of the curves for equal values of log p, increase regularly with log T. Consequently, the entropy of vaporization of different substances cannot be the same at equal pressures, but rather at pressures which increase in some way with the temperature. J. H. Hildebrand found that the tangents to the curves at points cut by a line whose equation is $\log p = \log T + K$, where K is a constant, have the same slope "with a remarkable degree of precision."

For vapours at a low enough concentration to obey the gas law $p=RTC$, where C denotes the molecular concentration, $\log p = \log T + \log RC$, and hence $\log RC = K$, and therefore along such a line C is constant. Hence, *the entropy of evaporation is the same for all normal liquids, not as in Trouton's rule when the vaporization takes place at the same pressure (one atmosphere), but when it takes place at the same concentration of vapour; i.e.* when the mean distance between the molecules is the same. J. H. Hildebrand extrapolated the experimental data for λ and T for values of C arbitrarily selected to correspond with 0·00507 gram-molecules per litre. The values of L/RT_c, where T_c refers to equal concentrations of vapour, are between 13·1 and 13·9 for normal liquids and above 16 for associated liquids. There is no systematic deviation with temperature, and the deviations are much less than with Trouton's rule.

It will be observed that when a molecule escapes from a liquid to a vapour, it is relieved of the high internal pressure which exists in the liquid, and it may conceivably expand with an absorption of an amount of energy e so that the entropy of vaporization becomes $(\lambda+e)/RT$. The value of e is probably greater than for molecules containing the larger numbers of atoms, but in general the value of e is probably small in comparison with λ, for most of the energy of vaporization is expanded in overcoming intermolecular attraction, and but little in the expansion of the molecule itself. With associated liquids, energy is further expanded in the dissociation of complex molecules into simpler ones, and the total entropy of vaporization is greater than the normal value. For liquids at low temperatures where the specific heats change rapidly with changes of temperature, deviations from the rule at low temperatures might be anticipated.

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§ 5. Gibbs' Phase Rule

> The phase rule is one of the most comprehensive generalizations known to man. It is of unlimited application, and offers an accurate and ready means of classifying all states of physical and chemical equilibria.—W. MAYERHOFER (1893).

On plotting the vapour pressures of water at different temperatures, a curve *OQ*, Fig. 9, is obtained. This gives the vapour pressure of water corresponding with any given temperature when the liquid and vapour are in contact, and in equilibrium. Call this the **steam line,** or **vaporization curve.** The ordinate of *O* represents the vapour pressure of water at 0°; at lower temperatures the water freezes. Plot in a similar manner the vapour pressures of ice at different temperatures, and the curve *OP*, called the **hoar-frost line,** or the **sublimation curve,** is obtained. Under these conditions, there is no intermediate liquid state, vapour condenses at once to a solid, and the solid passes directly into vapour. Solid iodine, below its melting point 114°, also vaporizes without liquefaction; arsenic can be liquefied only be melting the element under pressure; since under ordinary conditions, arsenic sublimes without fusion. It is found that the effect of pressure on the melting point of ice can be represented by a curve *ON*, Fig. 9. The left-to-right downward slope of the curve shows that the melting point of ice is lowered by increasing the pressure. Thus the melting point of ice at different pressures, according to G. Tammann (1900), is approximately:

Pressure	260	490	1100	1790	2020 atm.
Melting point . . .	−2°	−4°	−10·11°	−17·6°	−20·59°

and *in vacuo*, ice melts at +0·0075°. To emphasize these relations the curves in the diagram are slightly exaggerated. The curve *ON* is called the **ice line** or **fusion curve ;** it represents the melting point curve of ice under uniform pressures. Before progressing further, it will be convenient to fix special meanings to three terms : component, phase, and degree of freedom or variance.

Components.—The components of a system are the individual substances which are not decomposed in the process. The number of components chosen to represent a system is the smallest possible. The components may be elements, or compounds which behave in a system, for the time being, *as if* they were elements. There is only one component in the system just considered, namely, water—H_2O ; and the components in an aqueous solution of sodium chloride are water (H_2O) and sodium chloride (NaCl). A solution of sodium sulphate in water in a closed vessel contains four elements—sodium, sulphur, oxygen, and hydrogen—but neither the sodium sulphate nor the water is liable to decomposition under the conditions of the experiment. Hydrogen cannot be removed without simultaneously removing oxygen, nor can sulphur be abstracted without taking away sodium and oxygen at the same time. Accordingly, while the composition of the system can be expressed in terms of four components, two are necessary and two are superfluous, for, if the quantities of any pair of these four elements are stated, the other two can be computed. Hence, only two components are involved, namely, water (H_2O) and sodium sulphate (Na_2SO_4).

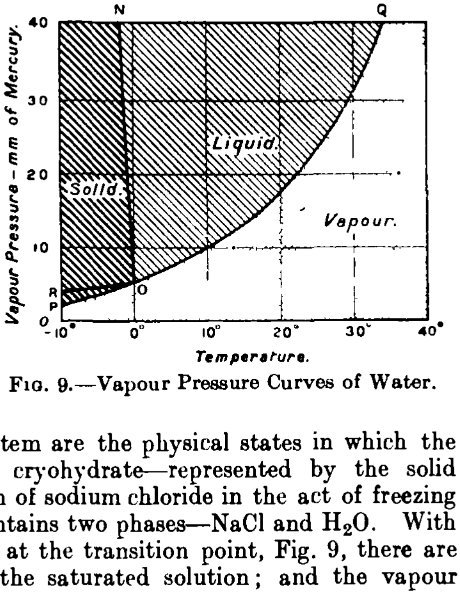

FIG. 9.—Vapour Pressure Curves of Water.

Phases. — The components may group themselves in various ways. They may pass from one physical state to another, as when water boils or freezes ; they may form simple solutions, as when salt dissolves in water ; they may combine with one another in various ways, as when sodium sulphate (Na_2SO_4) forms the decahydrate ($Na_2SO_4.10H_2O$), etc. **Every homogeneous state—solid, liquid, or gaseous —which the components can produce is called a phase.** The phases of a system are the physical states in which the components can exist. A eutectic or cryohydrate—represented by the solid which separates from an aqueous solution of sodium chloride in the act of freezing —is not a phase because the eutectic contains two phases—NaCl and H_2O. With an aqueous solution of sodium sulphate at the transition point, Fig. 9, there are four phases—Na_2SO_4 ; $Na_2SO_4.10H_2O$; the saturated solution ; and the vapour arising from the solution. With freezing water, there are three phases—ice, water, and vapour. In homogeneous systems there can be only one phase, *e.g.* aqueous solutions, solid solutions, gaseous systems ; and in heterogeneous systems there are always two or more phases.

Variance or degrees of freedom of a system.—It will be remembered that the **condition of equilibrium** of a gas with respect to temperature, pressure, and volume is defined by the equation, $pv=RT$, for R is a numerical constant whose value depends upon the units of measurement. If only one of these variables be fixed, say the volume, the state of the system will remain undefined, because the gas can retain one fixed volume, and yet have very different values for temperature and pressure. Two of the three variables must be known before the state of the system can be defined unequivocally, without ambiguity. If any two of the three variables be fixed, the third variable can assume only one definite value. The two fixed variables are said to be arbitrary or **independent variables ;** the third variable, which can be calculated from the condition of equilibrium ($pv=RT$) when the two independent variables are known, is called the **dependent variable.** Another term sometimes used for the independent variable is **degree of freedom ;** the number of degrees of freedom is also called the **variance** of the system (that is, the variableness of the system, from the Latin *variabilis*, variable). The gaseous system under consideration has two degrees of freedom because two physical conditions can be varied independently. **The degree of freedom or variance of a system is the number of independent variables which must be fixed before the state of the system can be defined without ambiguity.** The gaseous system defined by the equation, $pv=RT$, is **bivariant,** because it has two independent variables, or two degrees of freedom. The system consisting of liquid water and vapour has two variables : vapour pressure and temperature. So long as liquid water is present, the pressure is determined solely by its temperature; given either the pressure or the temperature, the other can be determined from the relation symbolized in the vapour pressure curve—Fig. 8. Hence the state of the system is defined by two variables—the one is dependent, the other independent. In other words, the system has one degree of freedom, that is, the system is **univariant.**

Triple point.—The three curves PO, OQ, and ON—Fig. 9—represent the conditions of equilibrium of three two-phase systems : solid-vapour, vapour-liquid, and solid-liquid respectively. These three curves meet at the point O. Here three phases can coexist in equilibrium. Hence the point O is called a **triple point.** The co-ordinates of the triple point are: pressure, 4·57 mm.; temperature, 0·0076° C. If the pressure or temperature be altered ever so little one of the phases—ice or liquid water—will disappear and a two-phase univariant system represented by a point on one of the curves OP, OQ, ON will appear. At the triple point the system is **invariant.** Confining our attention, for the moment, to the liquid and solid, and neglecting the vapour, we can define: **The freezing or melting point is the temperature at which both solid and liquid can exist side by side in contact with one another without changing.**

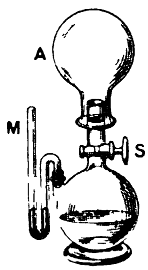

Fig. 10.—Experiment on the Phase Rule

Gibbs' phase rule.—J. W. Gibbs (1876-78) discovered an important relation between the number of components, the phases, and the degrees of freedom of a system. According to one setting of **Gibbs' phase rule, a system will be in equilibrium when its variance is equal to the number of components in the system less the number of phases increased by 2.** In symbols :

$$F=C-P+2$$

where C denotes the number of components, P the number of phases, and F the variance or degrees of freedom of the system. Otherwise expressed, P must be equal to or less than $C+2$, that is, a system of C components in a state of equilibrium cannot have more than $C+2$ phases. **The number of possible variations in the physical conditions of temperature, pressure, and concentration, without changing the number of phases, is two more than the difference between the number of components and the number of phases.** Conversely, the number of phases in a system can be determined from the maximum number of possible variations in the physical conditions. The phase rule thus serves as a test for stable states of equilibrium. Suppose the system water and steam, Fig. 10, be in equilibrium ; the vapour pressure indicated by the manometer M is not altered if the cock S be closed, and the globe A removed. This experiment emphasizes the fact that unlike chemical equilibria in homogeneous systems, **the equilibrium between different phases—heterogeneous equilibrium—is independent of the amount of substance in each phase,** a milligram of a solid in a saturated solution will be as truly in equilibrium as a kilogram. Accordingly, **the phase rule is a qualitative, not a quantitative**

criterion of equilibrium, it says nothing definite about the amount of each phase.

Derivation of the phase rule.—The following argument is based on that of H. W. B. Roozeboom.[1] A system is in stable equilibrium when its free energy has a minimum value. If a system has several phases in contact with one another, each phase can be regarded separately. Consider solid barium peroxide, BaO_2, in contact with gaseous oxygen and solid barium oxide, BaO. If some oxygen can pass from the gaseous to the solid phase, some of the monoxide will pass into the dioxide. If E_1 denotes the change in the free energy per unit mass of oxygen added to the one phase, and E_2 the corresponding change in the free energy for the same component removed from the other phase, the total change in the free energy per unit mass of oxygen will be E_2-E_1; if this magnitude be negative, oxygen will pass from phase 1 to phase 2, and conversely; if the system is in stable equilibrium, E_2-E_1 must be zero, and $E_1=E_2$. More generally, **for stable equilibrium, the free energy of each component in every phase must have the same value,** and no other condition is necessary.

If a heterogeneous system in equilibrium contains P phases and C components, and if each phase be supposed to contain a certain amount of each one of the C components, it follows that the *composition* of unit mass of each phase will be fixed when the amounts of C—1 of the components which the phase contains are known, for the amount of the remaining component is determined by difference. Since the composition of each phase is quantitatively defined by C—1 variables, the composition of P phases, otherwise expressed, the composition of the whole system, will be fixed by $P(C-1)$ variables. Besides composition, however, r other variables—temperature, pressure, etc.—can change independently, and consequently, *the state of the system will be defined by* $r+P(C-1)$ *variables.* These variables can be determined by remembering that the free energy of each component in each phase can be represented by an equation which is a function of the pressure, temperature, composition (concentration), etc.; but since any change in one phase implies a corresponding change in each of the remaining $P-1$ phases, the changes in each component will be described by $P-1$ separate equations. When the system is in equilibrium, the free energy of each component in every phase must be equal, and therefore, *the free energy of the* C *components in the system will be described by* $C(P-1)$ *equations.* Consequently, for equilibrium, the number of undetermined variables F in excess of the number of equations will be $F=r+P(C-1)-C(P-1)$, an expression which reduces to the phase rule for r independent variables, and one dependent variable: $F=C-P+r$. When in addition to composition, the state of the system is defined by pressure or temperature, $r=2$, and the rule reduces to $F=C-P+2$.

Invariant systems.—An invariant system has no degrees of freedom, and the state of such a system cannot therefore survive a change of temperature or pressure. In that case $F=0$, or $P=C+2$. This means that the system will have $C+2$ phases, if it is in equilibrium. If there be one component in the system, as in the case of water at the triple point, three phases can coexist in equilibrium—ice, liquid water, and steam. Otherwise expressed, if a system has three phases and one component, the phase rule tells us that it will be invariant, and therefore the slightest alteration of pressure or temperature will cause one of the phases to disappear. Again, in a system with three components—bismuth oxide, nitric anhydride, and water—and five phases—solution, vapour, and three solids—the system is invariant, and the three solid phases can exist at one temperature, one pressure, one concentration of the solution. Three phases of one substance cannot exist in equilibrium in one system—say, sulphur with two liquid and one vapour phase; or water with one solid, one liquid, and one vapour phase—and have an extended range of coexistence for the two non-vapour forms, because such a system must be invariant, and therefore cannot exist except at a single temperature and pressure.

Univariant systems.—These systems have one degree of freedom, and when the system is in equilibrium, $F=1$, or $P=C+1$. If one of the variables be known, the state of the system can be determined as indicated above. If the system bismuth oxide, nitric anhydride, and water has two solid phases, it will be univariant, and the system can exist at different temperatures or with different concentrations of the solution, but at any assigned temperature, the liquid in equilibrium with the two given solid phases cannot vary in concentration.

Bivariant systems.—These systems have two degrees of freedom, and hence $F=2$, or $P=C$. Two variables must be known before the state of the system can be determined. A saturated solution in the presence of an excess of the solute is univariant, but bivariant if not saturated. In the former case there are two components and three phases—solid, solution, and vapour; in the latter case there are two components and two phases. Hence in the one case, $F=2+2-3$; and in the other, $F=2+2-2$. Again, in the region *PON*, Fig. 9, the system will be bivariant, because there is only one phase and one component. Pressure and temperature may be altered without interfering with the state of the aggregation of the ice so long as the variations keep within the boundary lines *PO* and *ON*. The same remarks may be applied to the condition of the water represented by points in the regions *NOQ* and *POQ*. In the system bismuth oxide, nitric anhydride, and water previously considered, if only one solid phase is present the system will be bivariant, and the solid can be in equilibrium at a constant temperature with a solution of varying concentration, or with a liquid of a fixed concentration at different temperatures.

Modification in the phase rule with restricted systems.—One of the chief difficulties in the application of the phase rule turns on the proper selection of the components. For example, if the four substances concerned in the system, $HgSO_4+H_2O\rightleftharpoons HgO+H_2SO_4$, be considered as components of the system, the variance will be one more than would be the case if mercuric oxide, water, and sulphur trioxide be regarded as the components. It will be observed that in the first case there is a limiting condition, for the concentration of the sulphuric acid is determined by that of the mercuric sulphate. **Each independent relation or fixed condition among the components of a system reduces the variance of the system by one.** Limitations and restrictions may be introduced from chemical necessity or by arbitrary choice. For example, in the reaction $2H_2+O_2\rightleftharpoons 2H_2O$ at a high temperature, the number of components may be taken as one since the free hydrogen and oxygen are always in the fixed proportions characteristic of water vapour; there is also one gaseous phase, and the system is accordingly bivariant. On the other hand, if the number of components be taken as two—hydrogen and oxygen—there is one restriction on the ratio of their concentrations, and the system has accordingly two degrees of freedom.

There are several different but equivalent methods of selecting the components. For example, what is here called component has also been called an *individual* (T. W. Richards, 1916), *constituent* (W. D. Bancroft, 1906), or *system-component* (F. Wald, 1906), and the true number of components C in a system is then regarded as equal to the number n of individuals less the number of restrictions r, so that $C=n-r$. In the equilibrium $CaCO_3\rightleftharpoons CaO+CO_2$, the system has one degree of freedom if no restriction be placed on the temperature or pressure, but if the temperature or pressure be fixed, there is one restriction, and the system is invariant. There is not a chemical limitation in the quantities of lime or carbon dioxide because adding more of either constituent without altering the pressure has no effect on the equilibrium. In a dilute solution containing potassium nitrate, potassium chloride, and potassium bromide in equilibrium with its vapour, in addition to the water there are the four components, K, NO_3, Cl, Br, subject to the limitation that the gram-molecular concentration of the potassium must be equal to the sum of the concentrations of the three radicles, NO_3, Cl, and Br. In a similar solution of potassium nitrate and sodium chloride, the components may be regarded as water plus the two salts; this makes the system tervariant; but if the five components, water, potassium, and sodium, and the two radicles, NO_3 and Cl, be considered as components, it is necessary to reduce the corresponding variance of the system by two owing to the two limitations imposed by the necessity for the concentration of the potassium and nitrate radicle to be equivalent and likewise for that of the sodium and chlorine radicle. This makes the variance of the system three the same as before.

Object of the phase rule.—The phase rule is (1) a method of grouping into one class, systems which behave in a similar manner. It is essentially a method for the classification of states of equilibrium. Systems having the same variance behave in an analogous manner under the influence of variations in temperature, pressure, and volume or concentration. It makes no difference whether the changes be chemical or physical. As indicated above, the phase rule also tells us (2) whether the phases of a heterogeneous system are those necessary for equilibrium ; (3) it is of assistance in identifying chemical individuals among a series of basic salts or solid solutions. This it does by indicating the variance of the system which, in turn, indicates whether or not the existing constituents have such a degree of stability that they can survive a change of temperature or concentration. A knowledge of the conditions of equilibrium of a system containing solution and solid may therefore show whether one or a mixture of two solid phases is present. The phase rule is therefore a help and guide in the interpretation of complex phenomena ; a set of facts may be under investigation and a number of explanatory hypotheses may be devised. The phase rule will select which hypotheses are worthy of being tested by direct experiment, and which can be rejected as fundamentally unsound. There are some differences of opinion as to the utility and value of the phase rule. Those who have done successful work with its aid are usually enthusiasts, but some say that it is an " over-ridden hobby " and dub it the " phrase rule."

Modification for systems affected by other than mechanical and thermal energy.—Other variables (electricity, gravitation, capillary tensions, etc.) besides concentration, pressure, and temperature may modify the state of equilibrium of some systems. Thus, light modifies the state of certain chemical equilibria. This introduces another degree of freedom, and the phase rule must be modified to allow for the action of light on systems sensitive to this agent. Accordingly, the phase rule would then read $F=C-P+3$. W. D. Bancroft (1906)[2] adds : Experience shows that there are many kinds of active light, and the phase rule would have to be altered accordingly ; usually, however, a beam of light can be treated as though it were homogeneous if the intensities of the constituent rays are varied uniformly. Similar remarks apply *mutatis mutandis* to other agents, *e.g.* variations in volume, the silent electric discharge, etc. Usually only mechanical energy (pressure) and thermal

TABLE XI.—CLASSIFICATION OF SYSTEMS BY THE PHASE RULE ($F=C-P+2$).

System.	Components. *C.*	Phases. *P.*	Degrees of freedom or variance. *F.*
Freezing water . . .	Water	Liquid ; solid ; vapour	Invariant
Water above 0°. . .	Water	Liquid ; vapour	Univariant
Unsaturated solution of sodium chloride	Water ; salt	Solution ; vapour	Bivariant
Saturated solution of sodium sulphate at transition point	Na_2SO_4 ; H_2O	Na_2SO_4 ; $Na_2SO_4 10H_2O$; solution ; vapour	Invariant
Freezing eutectic—sodium chloride and water	Water ; salt	Two solids ; one liquid ; vapour	Invariant
Solution of oxygen in water	Oxygen ; water	Gas ; liquid	Bivariant
Steam and metallic iron in a closed vessel	Iron ; oxygen (hydrogen)	One gas ; two solids	Univariant
$2NO_2 \rightleftharpoons N_2O_4$ . . .	NO_2	One gas	Bivariant
$2H_2+O_2 \rightleftharpoons 2H_2O$ . .	Hydrogen ; (oxygen)	One gas	Bivariant
Heated mercuric oxide (over 400°)	Mercury ; (oxygen)	Gas and solid	Univariant
Heated barium peroxide .	Barium oxide ; (oxygen)	Two solids ; one gas	Univariant
$n\mathrm{CNOH}_{\mathrm{gas}} \rightleftharpoons \mathrm{C}_n\mathrm{N}_n\mathrm{O}_n\mathrm{H}_{n\,\mathrm{solid}}$	CNOH	One gas ; one solid	Univariant
Heated $CaCO_3 \rightleftharpoons CaO+CO_2$	CaO ; (CO_2)	One gas ; two solids	Univariant

energy (temperature) come into play, and the rule then reads, $F=C-P+2$. In the application of the phase rule to alloys, minerals, and solutions when the vapour pressure is negligibly small, only two variables need be considered—concentration or volume, and temperature. For such condensed systems, the phase rule reads :

$$F=C-P+1$$

Granite, composed of quartz, SiO_2 ; felspar, $K_2O.Al_2O_3.6SiO_2$; and mica, say, $K_2O.3Al_2O_3.6SiO_2$, has three components : SiO_2, Al_2O_3, and K_2O ; and three solid phases : mica, quartz, and felspar. The system is univariant. It is also in equilibrium, because not being at a transition point, it is able to survive a small variation of temperature without changing the state of the system.

Examples.—Table XI shows the phase rule classification of some typical systems. A component in brackets is regarded as being restricted by stoichiometrical relations.

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[2] W. D. Bancroft, *Journ. Phys. Chem.*, 10. 721, 1906.

§ 6. Undercooling, Supersaturation, and Metastability

A metastable system, though stable, is constantly menaced by a spontaneous transformation.—G. URBAIN (1912).

Undercooling.—Heat a solution of sodium thiosulphate to, say, 70° in a glass flask ; stir the molten mass with a thermometer as it cools ; read the thermometer every two minutes ; and finally plot the results on squared paper. A curve—called a **cooling curve**—resembling that illustrated in Fig. 11, *A*, will be obtained. The terrace in the cooling curve at 56° shows that a change of some kind takes place in the nature of the cooling substance at 56°. The terrace corresponds with the temperature at which solidification or freezing was in active progress. The sudden slackening in the rate of cooling corresponds with the evolution of the latent heat of fusion as the liquid solidifies. Repeat the experiment, but do not agitate the liquid ; take care that the cooling liquid is quite still and protected from dust by, say, a loose plug of cotton wool in the neck of the flask. A cooling curve like that shown in Fig. 11, *B*, will be obtained. The liquid does not freeze, and no abnormal behaviour can be detected in the cooling curve. The liquid " ought to " crystallize at 56°, but it does not. Drop a crystal of sodium thiosulphate into the liquid mass. The contents of the flask seem to solidify with almost explosive rapidity, and the thermometer immediately indicates a rise of temperature. The phenomenon is illustrated by Fig. 11, *C*. The liquid sodium thiosulphate at a temperature below 56°

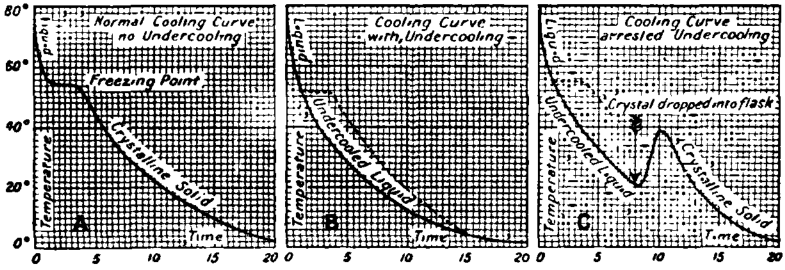

FIG. 11.—Cooling Curves of Molten Sodium Thiosulphate.

is said to be **surfused,** or, better, **undercooled.** The liquid may be kept in the surfused or undercooled condition an indefinite time, and the process of solidification can be started, in general, only by the introduction of a crystal of the same type as that which is formed during the solidification of the given substance. Often a fleck of the right kind of dust floating in the air suffices to upset the state of apparent equilibrium. Clear glasses and pottery glazes are solutions of silicates which have congealed to hard masses without crystallizing.

Supersaturation.—Similar phenomena occur if water be saturated with Glauber's salt—$Na_2SO_4.10H_2O$—at 30°. Make sure that no excess of solid is in contact with the liquid, and let the solution cool as before—without agitation and without dust. Probably no salt will separate from the solution. The solubility curve of this salt tells us that the solid " ought to " separate from the system as the temperature is reduced. Here is another case of apparent, false, or metastable equilibrium. If a solution holds more salt than corresponds with the normal solubility curve of the salt, the solution is said to be **supersaturated.** Although the solution can be kept an indefinite time in this condition, **the seeding or inoculation of a supersaturated solution** by the introduction of a very minute quantity of a crystal of the dissolved salt will upset the state of apparent equilibrium. According to W. Ostwald,[1] as little as 10^{-8} gram of salol suffices to start the crystallization of undercooled salol, and with sodium chlorate, 10^{-10} gram is needed. The crystal fragment becomes the centre or nucleus from which crystals radiate into the solution on all sides. Similar results can be obtained with aqueous solutions of sodium acetate, sodium chlorate, etc. The following illustrative experiment is due to G. R. Robertson:

> A solution of 5 grms. of benzil in hot alcohol is filtered while hot into a 250 c.c. flask, heated to boiling, and set aside in a warm place to cool. The flask is fanned so as to cool the glass walls, condense alcohol on the sides, and wash down any benzil into the body of the liquid and so prevent marginal crystallization. The liquid can thus be cooled to 15° without crystallization. A minute fragment of benzil is then dropped into the centre of the flask, and a complex of lemon yellow crystals spreads radially through the mass of liquid. The experiment can be adapted to lantern.

According to A. L. Potilitzin (1893), salts forming hydrates which have a considerable dissociation pressure in dry air at ordinary temperatures usually form supersaturated solutions readily ; while salts forming hydrates which do not readily dissociate in dry air or in vacuo do not usually form supersaturated solutions so readily. Calcium sulphate, $CaSO_4.2H_2O$, is an exception, for it does not lose water at ordinary temperatures, and it forms supersaturated solutions.

In 1795, J. T. Löwitz [2] found that any crystal will not do for the inoculation. Thus, if a crystal of nitre be introduced into a mixed solution of nitre and Glauber's salt, prepared hot, and subsequently cooled, the nitre alone crystallizes out, while if the solution be seeded with Glauber's salt, the latter alone crystallizes from the solution ; and D. Gernez tried the action of 220 different substances on supersaturated solutions of Glauber's salts, and found 39 to be active stimulants ; 18 of the 39 substances were insoluble, and lost their activity after washing with water, and drying while protected from dust, and the remaining 11 substances lost their property when purified by recrystallization. Hence, D. Gernez assumed that the 39 substances which had inaugurated the crystallization of sodium sulphate all contained this salt as an impurity. In H. A. Miers' experiments on the crystallization of the organic compounds, salol and betol, it was found that the substances did not crystallize at first when allowed to cool in open vessels in the laboratory ; but after a time, when the air of the laboratory had become impregnated with dust, presumably containing minute grains of both substances, crystallization readily occurred in open vessels exposed in the laboratory. **The fragment of crystal used for seeding must be either a fragment of the same salt as that in solution or of an isomorphous salt.**

The particular salt which separates is to some extent determined by the nature of the inoculating salt. For example, J. T. Löwitz found that a crystal of potassium nitrate introduced into a supersaturated solution of both potassium nitrate and sodium sulphate was followed by the separation of nitre alone, while a crystal of sodium sulphate in a similar solution gave a crop of crystals of sodium sulphate alone. If fragments of both salts were added to a similar solution, crystals of both salts were simultaneously deposited. L. de Boisbaudran[3] found the addition of copper sulphate to solutions of nickel sulphate gave short thick prisms of nickel sulphate, while magnesium sulphate or ordinary nickel sulphate gave fine needle-like crystals. The crystallization of a supersaturated solution is not always induced by the addition of isomorphous substances, as L. de Boisbaudran, C. Tomlinson, and others have assumed from the fact that a supersaturated solution of nickel sulphate commenced to crystallize by contact with zinc sulphate.

It is possible that in some cases of seeding by isomorphous salts, the effect is due to the presence, as impurity, of the salt to be crystallized. Thus, N. Dhar (1916) showed that no change is induced in solutions of copper sulphate by the addition of crystalline sulphate of magnesium, manganese, iron, cobalt, zinc, or cadmium; sodium selenate has no effect on supersaturated solutions of sodium sulphate, strontium chloride on solutions of calcium chloride, or sodium nitrate on solutions of silver nitrate. This shows that the induced crystallization of supersaturated solutions is not a sufficient test for isomorphous substances. Similarly, a solution may be supersaturated with respect to the hydrate of one salt and not another. Thus, C. E. Linebarger (1893) showed that at 10° it is possible to prepare four different solutions of manganous sulphate saturated respectively with the hexa-, penta-, tetra-, and trihydrates. For example, at 10°, the solubility is

	$MnSO_4.6H_2O$	$MnSO_4.5H_2O$	$MnSO_4.4H_2O$	$MnSO_4.3H_2O$
Parts $MnSO_4$ per 100 of water	71	68	64	61

If a crystal of one of the three lower hydrates be added to a saturated solution of the hexahydrate a separation of the crystals of the lower hydrate will occur. Thus, by adding a pentahydrate crystal, the corresponding crystals will be deposited, more hexahydrate would pass into solution, and be deposited in turn as pentahydrate. This will continue until all the hexahydrate has been transformed into the pentahydrate. A supersaturated solution of ammonia alum, $Al_2(SO_4)_3.(NH_4)_2SO_4.24H_2O$, will deposit the same salt if sown with crystal fragments, but according to A. Piccini and V. Fortini (1902), if sown with fragments of octahydrated ammonium thallic alum, $Tl_2(SO_4)_3.(NH_4)_2SO_4.8H_2O$, crystals of $Al_2(SO_4)_2.(NH_4)_2SO_4.8H_2O$, not $Al_2(SO_4).(NH_4)_2SO_4.24H_2O$, separate.

It is possible to distinguish between a *saturated* and a *supersaturated* solution by bringing each in contact with more of the solid. If the solution is unsaturated, more solid will dissolve; if saturated, none will dissolve; and if supersaturated, solid will separate until the solution is saturated. The concentration of an unsaturated solution is less, while the concentration of a supersaturated solution is greater than that of a saturated solution.

Related phenomena.—Many other examples of related phenomena are known. In analytical work the slow appearance of precipitates in dilute solutions is very common. Pure water may be easily cooled to —3° or —4° without the appearance of ice if kept quite still while the temperature is reduced; and the water can be easily cooled to —6° or —7° if a layer of oil be placed over the surface of the cooling water. The undercooling of water was observed by D. G. Fahrenheit[4] in 1724, and the undercooling of freezing mercury by T. Hutchins in 1783. The vapour pressure of *liquid* water from about 30° to —10° is represented by the curve *QOR*, Fig. 9; if the water freezes at 0°, the vapour pressure curve of the solid from 0° to —10° is given by the curve *OP*. In the former case the curve *QO* does not show a break or abrupt change of direction at *O*, and in the latter case it does. Phosphorus, sulphur, etc., behave in a similar manner. W. C. Roberts-Austen[5] measured the undercooling of gold, copper, and some other metals, and A. D. van Riemsdyk showed that the sudden flashing of gold beads during cupellation is due to the crystallization of an undercooled liquid. The melting points of solids usually appear somewhat higher than their freezing point. Thus, sodium hydroxide is said to melt at 310°, and to solidify at 290°. The phenomenon is attributed to supercooling carrying the observed freezing point below its true value, or to a slight lagging in the speed of the change.

Ice has not been heated above 0° without melting, but liquid water can be heated to 105° or 106° without boiling. When the boiling does start, it proceeds with almost explosive violence. The phenomenon is called **bumping.** In 1772, J. A. de Luc noted that the bubbles of air which develop in a liquid while it is being heated serve as nuclei for the generation of the bubbles of vapour formed when the liquid boils, and he found a liquid free from dissolved air could be heated to 130° without boiling. F. Donny heated water to 137° without boiling, and observations in the same direction were made by D. Gernez, G. Krebs, W. R. Grove, etc. By suspending drops of water in a mixture of olive and linseed oils—which has the same specific gravity as water, and a high boiling point—L. Dufour (1863) raised water to 178° without boiling. P. J. Coulier (1875) found that dust-free air saturated with moisture may be cooled below the normal temperature of condensation : and John Aitken [6] (1880) showed that dust is necessary for the formation of fogs and raindrops, so that in perfectly clean dust-free air, aqueous vapour does not condense, and mist does not form. Without solid nuclei cooling vapours may become supersaturated.

The vapour pressure of small drops of liquid.—There is an exception to the general observation that at any given temperature the vapour pressure of a given liquid is always the same whatever be the *mass* of the liquid. In 1870, Lord Kelvin (W. Thomson) [7] showed that the vapour pressure of a liquid with a concave surface must be less than that of the same liquid with a plane surface. If a capillary tube, *A*. Fig. 13, dips in water confined in a closed vessel, it follows that the vapour pressure of the liquid at *a* must be less than that of the liquid at *b* ; and that the vapour pressure p_0 at *b* must be equal to the vapour pressure *p* at *a* plus a pressure *h* equivalent to the weight of a column of the vapour of height *ab* and the same sectional area as the bore of the capillary tube. For equilibrium, $p_0=p+h$, otherwise there would be a perpetual circulation of the liquid owing to distillation from *a* to *b* or conversely, while the height of the liquid in the capillary remained constant. The converse of the above can be extended to convex surfaces. The vapour pressure of a minute spherical drop of liquid (convex surface) must be greater than that of larger masses of liquid with approximately plane surface.

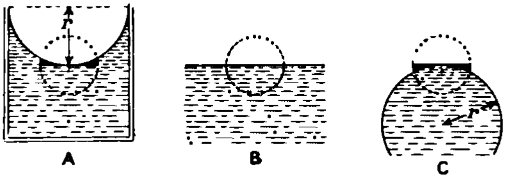

FIG 12

If p_0 denotes the vapour pressure of a liquid with a plane surface, and p its vapour pressure for a convex surface with a radius of curvature r, then, if S denotes the specific gravity of the liquid, and s that of the vapour, and σ the surface tension (or pressure) of the liquid, Lord Kelvin showed that with common logarithms, $\log (p_0/p)=2\sigma s/2{\cdot}3rp_0S$. For example, with water, $\sigma=80$; s, 0·00081 at 0° and 760 mm. ; p_0, 1014000 ; S is unity, $\log(p_0/p)=0{\cdot}56\times10^{-7}/r$. When r is large, say 10^{-1} to 10^{-4} cm., the ratio p_0/p is nearly unity, and only when r approximates to the millionth of a centimetre will the vapour pressure of a liquid be sensibly greater than that of a plane surface. The formula was deduced from thermodynamics by E. Warburg and R. von Helmholtz ; and from the molecular theory by G. F. Fitzgerald, J. Stefan, and B. Galitzine. The vapour pressure of an electrically charged surface was studied by R. Blondlot, N. Schiller, A. Gouy, and W. Kistjakowsky ; and the effect of a magnetic field has been studied by P. Duhem and J. Königsberger.

The kinetic theory interprets the phenomenon by showing that the inter-attraction of the molecules of a liquid on a molecule partially immersed, as illustrated by the dotted circle, *B*, Fig. 12, will be *less* than on a molecule similarly situated with respect to a concave surface, *A*, Fig. 12; and *greater* than a molecule similarly situated in a convex surface, *C*, Fig. 12. The differences in these magnitudes is illustrated by the blackened portions of *A* and *C*, Fig. 12, and it will be obvious without a mathematical demonstration. The greater the molecular attraction on the partially immersed molecules the less the vapour pressure of the liquid, and the less the tendency to evaporation; the smaller the drop of liquid the more convex the surface, and the greater the tendency to evaporation. Accordingly, in a given space the larger drops of liquid will grow at the expense of the small ones. Hence, a space saturated for a liquid with a plane surface is not saturated for minute drops, and this explains the observation that it is difficult for small drops of vapour to form in a space supersaturated for a plane but not for a convex surface. If small drops were momentarily formed they would at once evaporate. If dust particles be present the water will first condense upon them, and the liquid spread out on them will have a large radius of curvature so that re-evaporation will be comparatively slow, and the liquid has time to evaporate—assuming the nearer the ratio p_0/p approaches unity, the slower the evaporation.

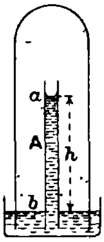

Fig. 13. — (Diagrammatic).

Metastable and labile states of supersaturation.—Inoculation or seeding is usually necessary to start the process of crystallization of a supersaturated solution; and yet the supersaturation may be carried so far that the crystals will grow spontaneously in the solution without seeding. Indeed, it is possible to draw a **supersaturated solubility curve** representing the concentration of a solution at different temperatures where the supersaturation is so great that crystallization will begin spontaneously without inoculation. The idea is illustrated in Fig. 14, where the region between the normal solubility curve and the supersolubility curve represents what W. Ostwald[8] called the **metastable state,** where inoculation is necessary to inaugurate the process of crystallization; and the region beyond this, below the freezing point, represents the so-called **labile or unstable state** where crystallization may start spontaneously without inoculation. *E.g.* a solution of sodium nitrate at 20° is saturated when it contains 45·8 per cent. of the salt, and it is *labile* when it contains over 48·8 per cent.; between these two concentrations the solution is metastable. Similarly, solutions of sodium bromide saturated with the hydrate, NaBr.2H$_2$O, at 30°, are in a labile condition, and crystallize spontaneously at temperatures between 5° and 16°; they are in a metastable condition above 19°.

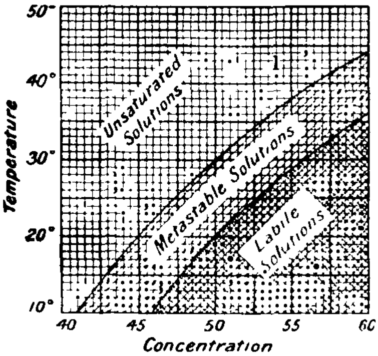

Fig. 14.—Labile and Metastable Equilibria of Saturated Solutions (after H. A. Miers).

The existence of the metastable and labile states was predicted by W. Ostwald in 1897, and demonstrated experimentally by H. A. Miers[9] and his co-workers in 1906. Can a metastable liquid be made to crystallize in any other way than by introducing a solid crystal? Ordinary shaking, scratching, and the like fail to provide the necessary stimuli. According to H. A. Miers,

> If the growth of a crystal is really the coming together of vibrating particles which cohere with one another . . . is it not possible that we may be able to communicate these vibrations to a supersaturated solution, which is so densely crowded that it is ready to crystallize, by some other means than by inoculating it with an appropriate crystal? . . . Some knowledge of those movements may be obtained by studying the sort of shock or movement, if there be any such, which starts crystallization in supersaturated solutions.

S. W. Young did succeed in making water and metastable salt solutions crystallize by applying mechanical shocks of sufficient intensity-mechanical hammers striking on metallic anvils. For instance, water was made to freeze at —0·02° without the addition of ice, with repeated blows of sufficient intensity. H. A. Miers and F. Isaac crystallized water at —1·9° without seeding, and H. Hartley and N. G. Thomas observed the formation of ice at —0·5° without seeding.

Supersaturation and the phase rule.—The phase rule, it will be observed, applies to systems in real equilibrium, not to systems in a state of apparent, false, or metastable equilibrium. We are repeatedly confronted with those little-understood phenomena which, for convenience, have been grouped under the general term passive resistance.

The kinetic theory of supersaturation.—The kinetic theory throws a little light on the phenomenon of supersaturation. A saturated solution in contact with the solid is supposed to be closely analogous with a closed vessel containing a liquid in contact with its vapour. When in equilibrium, the same number of molecules pass from the surface of the solid into the solution and return from the liquid to the surface of the solid. If the state of equilibrium be disturbed by evaporation or by lowering the temperature, the equality of the two opposing actions is disturbed and a new condition of equilibrium is established. In the case of a metastable supersaturated solution, the exchange of molecules cannot take place because no free solid is present. Directly a particle of the same substance as the dissolved solid is added, the dissolved substance is rapidly deposited about the submerged particle as a nucleus until the concentration of the solution has reached its normal value. In the case of a labile supersaturated solution, the crowding of the molecules is so great that they are able to form aggregates large enough to serve as nuclei about which the crystals can grow.[10]

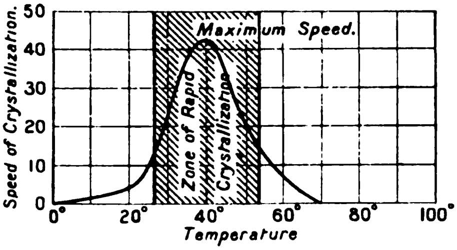

FIG. 15.—The Effect of Temperature on the Speed of Crystallization of Piperine.

The speed of crystallization. — Within certain limits of temperature, the speed of crystallization is greater the lower the temperature.[11] This might be expected if it be assumed that the lower the temperature, the smaller the speed of molecular motion, and the less the probability of a molecule escaping from the sphere of action of a growing crystal; but there is an influence retarding crystallization, for the slower the molecular motion, the greater the viscosity, and the smaller the number of molecules which travel into the sphere of action of a growing crystal. Instead of the speed of crystallization increasing continuously as the temperature is lowered, it reaches a maximum value and then progressively diminishes as the temperature falls, presumably because the viscosity of the groundmass is so great that it is superior to the vectorial forces which arrange the structural units into crystal forms, and completely inhibits their action.

Observations on the influence of temperature on the speed of crystallization can be illustrated by fusing hippuric acid (melting point 188°) in a dish; and making a number of capillary tubes—about 15 cm. long and 1 mm. bore—by drawing out a test-tube in the usual manner of making melting-point tubes. The molten acid is sucked into a warm tube, and immediately cooled under the water-tap. The surfused acid congeals to a glass-like mass as is demonstrated by breaking one of the tubes. If the tubes are warmed, say, in the hot air over a Bunsen's flame, crystallization immediately sets in, although the tubes may be preserved at atmospheric temperatures for some days. The speed of crystallization can be determined by exposing the surfused compound for, say, four minutes to the temperature in question, and then counting the number of centres of crystallization—the greater the number of crystal nuclei, the faster the crystallization. The maximum speed with hippuric acid is attained at about 100°.

G. Tammann's observations (1898) on the rate of crystallization of surfused piperine, melting at about 129°, show that the speed increases with decreasing temperatures down to about 40°; after that, the rate decreases as the temperature falls. The maximum speed is at about 40°. The speed of crystallization of undercooled water has been measured [12] by undercooling water and starting crystallization by introducing a fragment of the solid. The time necessary for the crystals to fill a certain length of the tube gives the linear velocity of crystallization. J. H. Walton and R. C. Judd's values for the linear velocity of crystallization of water in cm. per minute, for water in a tube (12 mm. outside diameter, and 7 mm. internal diameter), were

	−2·0°	−3·61°	−4·67°	−5·86°	−6·18°	−7·10°	−8·19°	−9·07°
Velocity .	31·6	48·4	71·4	107·1	114·7	266·7	415·2	684·0 cm. min.

The internal diameter, and the thickness of the walls of the tube have a marked influence on the results since they determine the rate of cooling of the crystallizing liquid. Spontaneous crystallization of the undercooled liquid prevented measurements being conducted at lower temperatures, and the temperature of maximum velocity of crystallization has not been determined. J. H. Walton and A. Brann measured the effect of forty-five substances on the velocity of crystallization of water supercooled to −9°, and found that all retarded the speed. The retardation is a colligative property. For substances with over eight atoms per molecule, the greater the number of atoms the slower the rate of crystallization; for substances with less than eight atoms per molecule, the power of retardation is a specific property. In dilute solutions, substances which undergo the greatest hydration in solution have the greatest effect in reducing the speed of crystallization; and this is explained by assuming that if the formation of ice crystals is due to a change of the type, $3(H_2O)_2 \rightleftharpoons 2(H_2O)_3$, any part of the solvent would have to be decomposed before crystals could be produced. H. T. Barnes has measured the rate of growth of the ice mantle in R. Bunsen's ice calorimeter. Similar phenomena are shown by glasses and pottery glazes, which are really congealed surfused liquids. There is a special range of temperature peculiar to each surfused compound which is particularly favourable to rapid crystallization—**zone of rapid crystallization.** This is illustrated in Fig. 15.

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§ 7. The Allotropic Forms of Water

> Water is water, not a single substance in the proper acceptation of the term, but a mush or mixture; an entirely peculiar material, not to be represented by any one formula, nor spoken of by any single name.—H. E. ARMSTRONG (1913).

The vapour pressure curve of a substance comes to an abrupt end at the critical point, for the liquid ceases to exist. In Clapeyron's equation

$$\lambda = T\frac{dp}{dT}dv$$

at the critical temperature, dv is zero, and consequently also the latent heat of vaporization becomes zero.

Just as a liquid, at a constant pressure, when subjected to a constantly decreasing temperature, solidifies at a definite temperature called the **freezing temperature,** so will a liquid, at a constant temperature, when subjected to a constantly increasing pressure, solidify at a definite pressure—**the freezing pressure.**[1] For example, the freezing temperature of water is 0° under a pressure of one atmosphere, and at +1° the freezing pressure is 7600 atm. The curve of freezing pressure, dT/dp, is convex towards the pressure axis corresponding with the fact that each successive increment of pressure produces a smaller and smaller effect. Every substance has its own peculiar dT/dp-curve, but usually the slopes of the curves for different substances vary within comparatively narrow limits—less than 50° per 1000 atm.

The question has been discussed: What is likely to be the result of extrapolating the observed results for the effect of very high pressures on the course of the melting-point curve? J. H. Poynting and W. Ostwald[2] argue that, when the pressure is great enough, the melting-point curve of a solid will have a critical end-point, analogous to the critical temperature of a liquid. W. Ostwald further suggests that liquid crystals are solids near their critical points at ordinary pressures; and that the effect of pressure is to diminish the vectorial properties of crystals and reduce all matter to an isotropic or amorphous condition. If there be such a critical end-point, dv and λ of Clapeyron's equation should vanish simultaneously, but there is no sign of this in any substance which has been investigated at high pressures—in some cases λ increases rather than diminishes with increasing pressures. G. Tammann, M. Planck, and H. W. B. Roozeboom[3] have also raised objections to this hypothesis. G. Tammann assumes that if the pressure be great enough, all solids can be melted no matter what the temperature. G. Tammann assumes that the pressure-volume curves of liquid and solid will probably cross when $dv=0$ as indicated in Fig. 16; and under that condition, the latent heat will change its sign and be no longer positive, but negative. Under these assumed conditions, the melting point with an increase of pressure will first rise, and then fall; and at the turning point, the melting-point curve will be a maximum. G. Tammann, therefore, represents the melting-point curve as shown in Fig. 17. Inside the curve the crystalline solid is stable; outside, the liquid is the stable form. It is, however, not necessary to develop the idea further because P. W. Bridgman's work would probably have shown some signs in favour of Tammann's assumptions if they were valid at the enormous pressures under which he worked. Although the value of dv becomes smaller and smaller as the pressure increases, there is no sign of dv approaching zero.

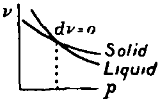

FIG 16.

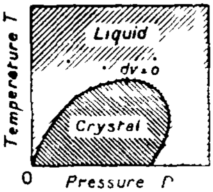

FIG. 17.

There is, therefore, no satisfactory evidence that the melting temperature of a solid will pass through a maximum (G. Tammann) or terminate at a critical end-point (J. H. Poynting) as the pressure increases, but the evidence rather indicates that the melting temperature will rise indefinitely with increasing pressure, or else the solid will change abruptly into another allotropic form. For example, liquid water under very great pressures, at a constant temperature, exhibits some peculiarities which show that the water then freezes, even though the temperature is above the normal freezing point, 0°. The melting point of ice is reduced by pressure, and ice can be melted by increasing the pressure. At temperatures below —22°, however, ice cannot be melted by an augmented pressure, for the ice passes into another variety more dense than water. The denser ice changes back into ordinary ice, specifically lighter than water, when the pressure is removed. G. Tammann (1910) and P. W. Bridgman (1912)[4] have studied the effects of great pressures on the properties of ice, and although the two investigators do not agree in certain details, they are agreed on the main points.

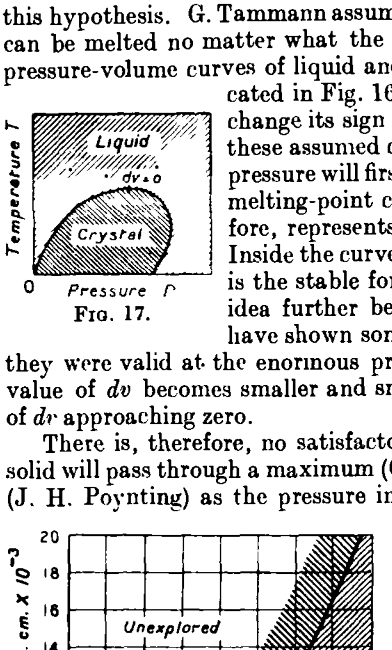

FIG. 18.—P. W. Bridgman's Exploration of the Equilibrium Conditions for the Varieties of Ice.

There are at least four kinds of ice more dense than water. Suppose that ordinary ice—called **ice I**—be maintained at —10° and gradually compressed to about 1000 kilograms per sq. cm., the ice melts to water. The relation between the freezing point and pressure is given by the curve ON, Fig. 18. When the pressure rises to about 4400 kgrm. the liquid freezes to a form of ice denser than water—called **ice V**—and at about 6300 kgrm. pressure, ice V changes to another still denser variety—

called **ice VI.** Again, if the temperature be maintained at —30°, and the experiment repeated, ordinary ice, ice I, changes into another variety—called **ice III**—at a pressure of 2200 kgrm. At —25°, this change is sudden and abrupt, sometimes it takes place with a kind of click. At about 3000 kgrm. ice III changes into another variety—called **ice II**—and with a further application of pressure, ice II passes into ice V, and finally into ice VI. The relations between the temperature and pressure of the five different forms of ice are illustrated in Fig. 18.

In practice, the water is compressed in a suitable cylinder by means of a piston worked by a hydraulic press. At any given temperature, the pressure, measured by a manometer, increases regularly with the displacement of the piston representing the volume of the substance, as shown by *AB*, Fig. 19; when the pressure has attained a certain critical value, *P*, the volume suddenly decreases, *BC*, without the pressure rising at all. Afterwards the pressure resumes its regular rise, *CD*, with the displacement. The pressure at which the piston drops abruptly into the cylinder without producing a rise of pressure is the pressure at which the water freezes at the temperature of the experiment. The pressure at which water freezes is different at every different temperature. A series of pressure-temperature curves, like Fig. 18, is taken to represent the melting curves of ice to water, or transition curves of one form to another. Given the displacement of the cylinder, and the density of the water, the density of the ice can be calculated; and if the temperature and pressure at which the ice melts, and the change in volume which simultaneously occurs are known, the latent heat of fusion of the ice can be computed. All the experiments show is that at certain temperatures and pressures there is an abrupt change in volume. It is inferred that the abrupt change of pressure must be due to a change in the molecular structure of the liquid, either a change of liquid to solid, or from one liquid to another. The latter possibility is rejected because no substance is known with two liquid modifications, and in some cases the solid is stable enough to allow a momentary glimpse to be obtained when the pressure is suddenly released. The estimated densities of the different varieties of ice (water unity) are:

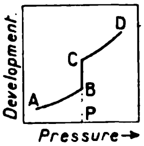

Fig. 19.

	Ice I.	Ice II.	Ice III.	Ice IV.	Ice V.	Ice VI.
Density . .	0·92	1·03	1·04	—	1·06	1·09

The latent heats of fusion of the different modifications of ice to water are not very different from that of ordinary ice; and there is therefore very little heat involved in the transformation of one variety of ice into another. The latent heats of transformation of the different forms of ice into one another and to liquid water at the triple points are indicated in Table XII, along with the volume changes which occur, and the co-ordinates of the triple points.

Table XII.—Properties of the Different Forms of Ice at the Triple Points.
(L denotes liquid water; Roman numbers a particular form of ice.)

Triple point.	Co-ordinates of triple point.		The upper line within the brackets represents the change in volume *dv* in c.c. per gram, and the lower line, the latent heat of transformation in gram calories.					
	Temp. °C.	Press. kgrm. per sq. cm.						
III, L, I	−22·0	2115	III→L	0·0466 +50·9	L→I	0·1352 −56·1	III→I	0·1818 −5·2
II, III, I	−34·7	2170	II→III	0·0215 +12·3	III→I	0·0215 +2·2	II→I	0·2178 +10·1
V, III, L	−17·0	3530	V→III	0·0547 +0·9	III→L	0·0241 +61·4	V→L	0·0788 +62·3
V, II, III	−24·3	3510	V→II	0·0401 −16·0	II→III	0·0145 +16·9	V→III	0·0546 +0·9
VI, V, L	+0·16	6380	VI→V	0·0389 +0·2	V→L	0·0527 +70·1	VI→L	0·0916 +70·3

It will be observed that ice VI is stable above 0°, and with the application of 20,000 kgrm. pressure, *water can be frozen under great pressure even though it be nearly at the boiling point of water under ordinary pressures!* If the pressure upon ordinary ice rises much above 2000 kgrm. the ice changes into ice III which has a less volume, hence, 2000 kgrm. per sq. cm. "is the highest pressure which can be obtained by freezing water in a closed space." As soon as the pressure is removed, the different varieties of ice revert to ordinary ice. If ice II or ice III be at the temperature of liquid air when the pressure is relieved, the change from the unstable to the stable form is slow enough to demonstrate that the ice is really a solid denser than ordinary ice. A variety of ice—called **ice IV**—was announced by G. Tammann, but has not been confirmed by P. W. Bridgman.

The molecular formula of water.—The vapour density of steam is slightly greater than is required for the molecular formula H_2O, and much too small for H_4O_2. It is therefore assumed that steam is a mixture of H_2O molecules with a few H_4O_2 molecules, and it is found that the equilibrium condition for water vapour in the vicinity of 100°, namely, $H_4O_2 \rightleftharpoons 2H_2O$, corresponds with about 91 per cent. of H_2O molecules. According to E. Bose (1908),[5] measurements of the vapour density of saturated water vapour under the pressure of its own vapour at the corresponding temperatures, show that:

Temperature	0°	50°	100°	150°	200°
Pressure	4·6	92·2	760	3581	11688 mm.
Per cent. H_2O molecules	93·4	91·8	91·1	91·0	91·3

An increase in the proportion of the H_2O molecules with a rise of temperature is counterbalanced by the converse effect of the increased pressure. According to G. Oddo (1915), under normal pressure below 32°, some water vapour is dissociated into ions, $H_2O \rightleftharpoons H^{\cdot} + OH'$, and the vapour pressure is almost that required for H_2O.

The estimated **diameter of a molecule** of water vapour is $4·54 \times 10^{-8}$ cm.; the **mean free path**, $4·0 \times 10^{-6}$ cm. at 0° and 760 mm.; the **collision frequency** is $79·80 \times 10^{8}$ per c.c. per sec.; the **molecular velocity** at 0° is 566 cm. per sec.; and the values of J. D. van der Waals' $a=0·01173$, and $b=0·00151$. Lord Kelvin[6] estimated the mean distance between the centres of contiguous water molecules probably lies between 10^{-8} and 5×10^{-10} cm. If the lower limit be used H. J. S. Sand has shown that there are 10^{24} **molecules per c.c.**, or 18×10^{24} molecules of water per gram-molecule of the liquid; this number is regarded as obsolete, and H. J. S. Sand obtained $8·5 \times 10^{23}$ as a better approximation for what is analogous to Avogadro's constant for liquid water.

Liquid water.—The formula of water is so frequently represented by H_2O, that it is easy to acquire the belief that this symbol correctly represents the molecule of the liquid. The molecule of liquid water is much more complex. A comparison of the boiling points of the hydrides of chlorine, HCl, sulphur, H_2S, nitrogen, NH_3, and carbon, CH_4,

	Hydrogen chloride, HCl	Water, H_2O	Hydrogen sulphide, H_2S	Ammonia, NH_3	Methane, CH_4
Boiling point	−83°	+100°	−62°	−33·5°	−164°
Critical temperature	+52°	+360°	+100°	+130°	−90°

has led to the argument that if water were represented by the formula H_2O, and remained in that condition during its condensation from the gaseous (steam) to the liquid state, it would probably fall in line with the hydrides just indicated, and be a gas at ordinary temperatures; that is, instead of boiling at 100°, it would boil at a much lower temperature. The boiling points of liquids are raised by association, and a comparison of the boiling points of water with those of the corresponding hydrides of sulphur, H_2S, selenium, H_2Se, and tellurium, H_2Te,

	Water, H_2O	Hydrogen sulphide, H_2S	Hydrogen selenide, H_2Se	Hydrogen telluride, H_2Te
Boiling point	+100°	−62°	−42°	0°

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led H. M. Vernon (1891)[7] to infer that the molecule of liquid water is very complex. J. H. van't Hoff (1900) calculated that if water were not associated it would boil at −207°. P. Walden (1900) also argued that the substitution of oxygen by sulphur raises the boiling point of the methyl and ethyl compounds by about 60°, and if a similar difference prevailed with the hydrogen compounds, water should boil at −120°. Thus,

Methyl sulphide, $(CH_3)_2S$	37°	Ethyl sulphide, $(C_2H_5)_2S$	91°	Hydrogen sulphide, H_2S	−61°
Methyl oxide, $(CH_3)_2O$	−23°	Ethyl oxide, $(C_2H_5)_2O$.	35°	Water, (H_2O) .	−120°
Difference .	60°	Difference .	56°	Difference .	59°

H. M. Vernon's deduction is confirmed by the lowering of the freezing points of solutions of water in several other solvents[8] which point to a higher molecular weight for the liquid than is required by the simple formula H_2O ; thus, in *p*-toluidine the molecular weight varies from 28·7 to 33·3, although in phenol and related solvents, acetic acid, liquid hydrogen cyanide, etc., the result corresponds with a molecule H_2O. It is, however, remarkable that so many lines of evidence all converge about Röntgen's assumption that water contains polymerized molecules, *e.g.* the thermal expansion, compressibility, surface tension, viscosity, specific heat, index of refraction, dielectric constant, magnetization, Trouton's rule, J. D. van der Waals' deductions, boiling points, molecular volumes, etc. J. Thomsen[9] also assumed that water has a molecular weight corresponding with $(H_2O)_2$, because the heat developed during the hydration of some salts agrees with the assumption that the water frequently enters into combination in pairs, $(H_2O)_2$.

W. Sutherland's hypothesis of the constitution of liquid water.—W. Sutherland (1900)[10] calls W. C. Röntgen's ice molecules **trihydrol** on the assumption that molecular weight corresponds with $(H_2O)_3$ or H_6O_3 and the water molecules **dihydrol,** $(H_2O)_2$ or H_4O_2 ; the steam molecules are called **hydrol** H_2O. Alternative terms have been suggested : *trioxylene* for trihydrol, and *dioxylene* for dihydrol. Instead of the curve for the variation of the volume of water with temperature—Fig. 5—sweeping round a minimum at about 4°, W. Sutherland makes the line continuous and thus extrapolates a value 1·089 for the density of dihydrol at 0°. This agrees with values deduced in a similar manner from other physical properties of water. Similarly he gets the value 0·88 for the density of trihydrol at 0°. Hence, it follows from the observed density of water at 0°, that 37·5 per cent. of trihydrol and 62·5 per cent. of dihydrol are present. The percentage amounts of hydrol in water at different temperatures, estimated from the observed densities at pressures of one and 50 atmospheres, are indicated in Fig. 20. It is further estimated that at 2300 atmospheres pressure there will be no trihydrol in water at 0°. W. Sutherland also estimates that dihydrol and trihydrol have the following physical properties at 0° :

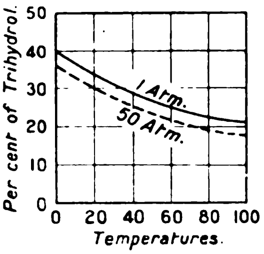


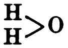
FIG. 20.—Estimated Proportion of Trihydrol in Water at Different Temperatures.

TABLE XIII.—COMPARISON OF THE SUPPOSED PHYSICAL PROPERTIES OF DIHYDROL AND TRIHYDROL.

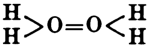
	Density at 0°.	Compressibility per atmosphere.	Surface tension.	Critical temp.	Specific heat 0°.	Viscosity.	Latent heat calories.	
							Fusion.	Vaporization.
Dihydrol .	1·089	0·000016	78·3	368°	0·8	0·0030	—	257
Trihydrol .	0·88	0·000010	73·3	538°	0·6	0·0381	16	250

A. Piccard estimated that in liquid water at 0° there is 29·1 per cent. of ice ; and in water at 100°, one per cent. of ice. With this assumption, and his observations on the refractory power of water, C. Chéneveau estimates that hydrol at 0° has a specific refraction by J. H. Gladstone and Dale's formula, of 0·3228; and by Lorenz and Lorentz's formula, of 0·2049; the corresponding numbers for hydrol at 100° are 0·3319 and 0·2058. From his experiments on the evaporation and condensation of small drops, C. Barus concludes that water contains different constituents, and that one is more volatile than the other. G. Gillet ascribes all the reactions of water to the hydrol molecules, and he says that a substance is soluble in water because it forms a soluble compound with the hydrol, and this disturbs the equilibrium $(H_2O)_2 \rightleftharpoons 2H_2O$, and that the evolution or absorption of heat in the process of solution is dependent on this reaction. H. Schade believes that the equilibrium constant $nH_2O \rightleftharpoons (H_2O)_n$ varies with temperature, and that the polymerized molecules are present in water in a colloidal form.

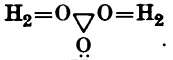
J. W. Brühl considered that water is an unsaturated compound with quadrivalent oxygen $H-\dot{O}-H$. W. Sutherland suggests that, on J. W. Brühl's assumption that oxygen is quadrivalent, the dihydrol and trihydrol molecules are constituted as indicated by the graphic formulæ:


$\begin{matrix}H\\H\end{matrix}\!>O$

Hydrol.

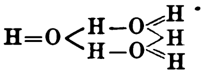

$\begin{matrix}H\\H\end{matrix}\!>O=O<\!\begin{matrix}H\\H\end{matrix}$

Dihydrol.

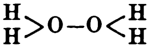

$\begin{matrix}H_2=O\nabla O=H_2\\ O\\ H_2\end{matrix}$

Trihydrol.

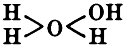
R. de Forcrand believes that the ice molecules are either $(H_2O)_2$ or $(H_2O)_{2\cdot 5}$, and he assumed that oxygen is quadrivalent, and the hydrogen bivalent. As a result, he obtained the graphic formula:


$$H=O<\!\begin{matrix}H-O\lessgtr H\\ \qquad\quad\ H\\ H-O\lessgtr H\end{matrix}$$

In an attempt to account for the properties of dilute solutions, H. E. Armstrong (1908) further assumed that some of these molecules have the same composition but a different structure: thus, the dihydrol molecules, H_4O_2, are assumed to exist in the two different forms:


$\begin{matrix}H\\H\end{matrix}\!>O-O<\!\begin{matrix}H\\H\end{matrix}$

Dihydrone.


$\begin{matrix}H\\H\end{matrix}\!>O<\!\begin{matrix}OH\\H\end{matrix}$

Hydronol.

The former kind are said to be inactive molecules because they are formed by direct association unaccompanied by rearrangement; and the latter are said to be active molecules. When non-electrolytes of the type RX are dissolved in water, active complexes of the hydronol type $HO-RX-H$ and inactive hydrone complexes of the type $RX=OH_2$, as well as polymerides, are supposed to be formed; while with electrolytes, the compound becomes hydrolated by the formation of (*a*) hydronol complexes $HO-RX-H$, and (*b*) complexes of the type $X-H_2O-R$, which are distributed in the solvent. Such solutions, says Armstrong, will be electrolyzed when the composite molecules *a* and *b* act reciprocally on one another under the influence of an electric strain.

If these views about the constitution of water be well-founded, and if these different varieties of ice really exist, it is hardly correct, without some reservation, to say that the passage of ice to liquid water and to steam, and the converse changes, are purely physical changes. P. W. Bridgman appears to think that the different forms of ice arise from a difference in the alignment or arrangement of the molecules whereby each molecule preserves its individuality so that the changes undergone by the different forms of ice are purely physical. In physical processes, the molecules of the substance are supposed to remain intact and unaltered; in chemical processes, on the contrary, the molecules are altered. Is the magnetization of iron a physical or a chemical process? A chemical process if the molecules are changed; and physical, if the molecules are not changed. Selecting one of the many definitions of chemical action, say H. E. Armstrong's (1885),

> Chemical action may be defined as being any action of which the consequence is an alteration in molecular constitution or composition; the action may concern molecules which are only of one kind—cases of mere decomposition, or isomeric change, and of polymerization; or it may take place between dissimilar molecules—changes of combination and interchange.

With this definition, the vaporization of ethyl alcohol would be a chemical process because it is probable that there is a simultaneous depolymerization $(C_2H_5OH)_n \rightleftharpoons nC_2H_5OH$, while the vaporization of carbon disulphide would be a physical process, because, so far as is known, the molecules are not altered in constitution or composition. In this sense, vaporization would be sometimes a chemical and sometimes a physical process. Indeed, the mere raising of the temperature of water involves a change in the composition of the molecules, and is accordingly a chemical change (depolymerization).

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§ 8. The Physical Properties of Water

Liquid water freezes at 0° into crystalline ice while water vapour freezes directly into hoar frost, and snow. If water be carefully cooled in a dust-free space it can be reduced to $-12°$ without freezing,[1] and H. C. Sorby cooled water to $-13°$ in a capillary tube 2·5 mm. diameter, and to $-15°$ in a tube of 0·0127 mm. diameter. According to J. Thomson, the freezing point of water is lowered $0·0075n°$ by a pressure of n atmospheres.

Ice appears to be colourless and transparent when pure, but in reality it is pale blue when seen in large masses. Artificially formed ice is often white and more or less opaque. According to R. Pictet, if artificial ice be slowly formed between 0°

and —1·5°, it is as transparent as natural ice ; but if the temperature at which the freezing occurs be below — 3°, the ice appears to be more or less opaque and white, and of low specific gravity, and this the more the lower the freezing temperature. The whiteness and opacity is due to the presence of small air bubbles, 0·01 to 0·5 mm. diameter, mechanically entangled among the elementary crystals during freezing. If precautions be taken to use air-free water, water freezes at very low temperatures to transparent ice. The bubbles of air are developed owing to the reduction in the solubility of the air dissolved in the water as the water freezes into ice.

The formation of *sheet ice* on the surface of an expanse of quiet water as cold weather approaches is interesting. So long as the temperature of water is above 4°, convection currents help to keep a uniform distribution of the temperature, for the cold and denser water slowly sinks, and the warmer layers rise to the surface. As the temperature of the surface falls below 4°, the colder layer remains on the surface and finally reaches the freezing point. Long needles of ice then shoot out from the borders over the top of the water and the crystals ramify outwards until the whole surface is covered with a thin sheet of ice. The sheet of ice then gradually thickens by the conduction of heat through the ice. According to G. Quincke's hypothesis, a freezing liquid is regarded as a liquid jelly which forms invisible foam cells containing water. The lower the temperature, the greater the viscosity of the liquid in the walls and interior of the foam cells. In streams which run too swiftly for the border ice to meet, the so-called *frazil-ice* or *slush-ice* is produced on the surface, but it cannot remain attached and freezes to a continuous sheet. In special circumstances where the bottom of a river can be cooled by the radiation of heat, the so-called *anchor ice,* or *ground ice, bottom ice*—*glâce-du-fond,* or *Grundeis*—may form on the bottom of a river or stream.

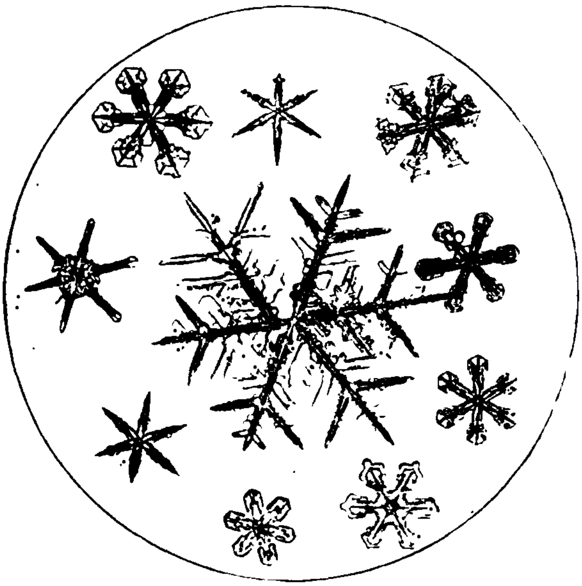
FIG. 21.—Snow Crystals.—G. Hellmann.

Well-defined **crystals** of ice are extremely rare and difficult to measure. According to A. E. von Nordenskiöld, F. Rinne, and A. B. Dobrovolsky, the bipyramidal crystals of ice belong to the hexagonal system and appear as ditrigonal prisms or plates; and P. Groth gives the axial ratio $a : c = 1 : 1·617$; but this, however, is somewhat doubtful. With hail, combinations of the rhombohedron have been reported. Sea-ice is usually a complex of crystal particles with the chief axes at right angles to the surface. The crystals can be often seen when a piece of ice is examined with a lens while a beam of bright light is passing through it. Snow crystals are common; this is readily demonstrated when snow-flakes are examined under a low-power microscope. Over a thousand different patterns have been noted, but all appear in the form of hexagonal (six-sided) nuclei, or six-rayed stars with the rays developed in bewildering complexity—some are rounded, others serrated, others reticulated—but all are of inimitable delicacy and beauty. A rough idea of the form of snow crystals can be obtained from Fig. 21, by G. Hellmann.[2] No two crystals seem to be alike, yet there is no deviation from the hexagonal style of architecture.

Albertus Magnus, of the thirteenth century, is said to have been the first writer to mention the *figura stellæ*, the hexagonal form of snow crystals, and in 1611, J. Kepler, the celebrated astronomer, wrote a pamphlet on six-rayed snow. J. Kepler was greatly impressed by the beauty and regularity of the shapes of the snow stars; but he perforce left unanswered the obvious question: Why are the crystals six-rayed? Why does nature unsparingly fashion such strange contrasts, all built according to one definite type—the six-rayed star—each

> Frail, but a work divine, made so fairily well,
> So exquisite, minute, a miracle of design?
> TENNYSON

Few indeed would deny what an anonymous writer has said: "The chemist is assured that if he could wholly understand a drop of water, he would know the origin and destiny of all things, and hold the key to every happening;" the same remark would apply to a drop of any other liquid. According to M. Trautz, Pontus knew in 1833 that if water be rapidly frozen, it sends out bright flashes of light—**crystallo-luminescence.** The **X-ray structure** of ice has been investigated by A. St. John.

The **viscosity** of water at 0°—that is, the resistance which water offers to flow—is here given along with a few other liquids for comparison:

Water.	Mercury.	Sulphuric acid.	Alcohol.	Ether.	Benzene.	Carbon disulphide.
0·0178	0·0169	0·3195	0·0184	0·0029	0·0089	0·0044

The viscosity of water diminishes with rise of temperature. Thus, G. Zémplen and B. Pogány found 0·010562 at 18°, and, according to R. Hosking and E. C. Bingham and G. F. White,

	0°	20°	40°	60°	80°	100°	124°	153°
Viscosity	0·017928	0·01002	0·006563	0·004730	0·003570	0·00284	0·00223	0·00181

R. Hosking recommends the interpolation formula, $\eta=\eta_0(1+a\theta+b\theta^2)$, for the viscosity η at θ° when the viscosity at 0° is η_0, and when a and b are constants. E. C. Bingham defines the fluidity of a liquid as the reciprocal of the viscosity, and he represents the fluidity ψ as a function of the absolute temperature T such that $T=0·23275\psi-8676·8/(\psi+120)+309·17$. G. F. White and R. H. Twing find the viscosity of undercooled water at −4·7°, −7·23°, and −9·30° to be respectively 0·02121, 0·02341, and 0·02549.

Water at high pressures is less viscous than at normal pressures provided the temperature does not exceed 36°, and this the more the lower the temperature and the lower the pressure. According to L. Hauser (1900),[3] the percentage changes in the viscosity coefficient of water at 400 atmospheres pressure are:

Temperature	90°	70°	51°	40°	35°	29°	18°
Percentage change of viscosity	+3·4	+2·5	+1·6	+0·7	0	−0·3	−1·6

Most other liquids which have been tried become more viscous under an increasing pressure. This also is in harmony with the assumption that with water the smaller the pressure, or the higher the temperature, the less the proportion of ice molecules transformed into less complex molecules, highly viscous ice molecules are replaced by less viscous water molecules. These facts were predicted by W. C. Röntgen (1891) from the hypothesis just outlined, and confirmed by R. Cohen (1891). The viscosity of some aqueous solutions is less than that of water itself owing to the fact that the solute converts enough viscous ice molecules into less viscous water molecules to more than compensate for the increase of viscosity which its own presence imparts. With aqueous solutions of urethane, there is a steady increase in the viscosity with rising concentration, probably because the increase in the viscosity produced by the solute more than compensates the decrease due to the diminishing concentration of the ice molecules. The coefficient of viscosity of water vapour[4] at about 20° is 0·0000975. F. Houdaille found the coefficient of the viscosity of water vapour to be smaller at low pressures, possibly as a consequence of dissociation.

The viscosity of ice is enormously greater than that of water, and it depends on the direction of the crystal axes. The viscosity of ice has been studied by B. Weinberg, J. F. Main, etc. R. M. Deeley[5] found that the viscosity at 0° is 2×10^{10} in a direction perpendicular to the optic axes; while both he and P. H. Parr calculated the viscosity of glacier ice moving in winter to be between 125×10^{12} and $147{\cdot}7\times10^{12}$. The difference is taken to mean that in glaciers, the optic axes of the ice crystals are inclined in different directions. B. Weinberg gives for the relation between the viscosity η and the absolute temperature, $\eta\times10^{-13}=1{\cdot}244-0{\cdot}502T+0{\cdot}0355T^2$. H. Hess (1902) found that a bar cut from glacier ice is slowly deflected when loaded in the middle and supported at both ends. The rate of change varies with the load. When the bar is relieved from the load it slowly recovers, due to what H. Hess regards as a kind of residual elasticity. J. C. McConnel (1891) also showed that a bar of ordinary ice yields continuously to pressure or tension, but if cut from a single crystal, with its length at right angles to the optic axis, it shows no sign of stretching under tension, or yielding to pressure. The crystal is brittle. Consequently, the bending of a bar of ice does not represent a gradual shearing of the ice crystals, but the slipping of a number of layers of finite thickness. This is the probable cause of the so-called plasticity of ice. The recovery of bent ice after the stress is relieved is out of all proportion to known effects in other substances, and is attributed to the slipping back of the forcibly displaced sliding layers. H. Moseley (1871) found **Young's modulus** for ice to be 92,700 kgrms. per sq. cm., and B. Weinberg (1905), 5×10^6 kgrms. per cm. at 1°. H. Hess cut bars of ice with the crystal axis parallel to the width, length, and thickness—1·2 cm. × 2·5 cm. and 4 to 16 cm. long—and measured the **modulus of elasticity** E; the **bending moment**, B grm. cms.; and the viscosity η with different loads as indicated in Table XIV. H. Reusch, R. Koch, and R. Trowbridge have published values for the elasticity constant. H. Hess concludes that for moderate loads the coefficient of viscosity η increases with the duration of the experiment from 15 to 60 to 120 to 300 seconds, and even after only 300 secs. the increase is nearly proportional to the time. For large loads near the point of rupture, the coefficient of viscosity decreases with the duration of the experiment.

TABLE XIV.—ELASTICITY AND VISCOSITY OF ICE.

	Axis parallel to length.			Axis parallel to width.				Axis parallel to thickness.		
Load in grms.→	2000	5000	6000	1000	1500	2000	3000	1000	1500	2000
B . .	1350	3400	4000	1500	2250	3000	4450	1600	2350	3100
$E\times10^{-10}$.	0·54	0·70	0·75	3·5	3·0	2·9	4·0	1·6	2·0	2·0
$\eta15\times10^{-10}$.	6·5	10·5	0·55	3·7	3·7	2·4	11·0	7·5	10·0	8·0
$\eta60\times10^{-10}$.	17·5	11·5	3·6	8·0	11·0	6·0	9·0	7·5	11·0	7·0
$\eta120\times10^{-10}$	10·0	13·5	3·65	12·0	10·0	10·0	—	7·5	9·0	11·0
$\eta300\times10^{-10}$.	11·0	16·6	3·5	21·0	19·0	17·6	—	8·0	12·0	12·0

H. Hess also measured the relation of pressure to the speed of **the flow of ice,** and found that with ice confined in cylinders, the flow increased rapidly with increasing pressure, and when the flow was once started, comparatively small pressures were required to maintain the flow. G. Tammann (1902) and N. Slatowratsky (1905) also studied the velocity of flow of ice, and showed that the **plasticity of ice** is relatively small, but increases rapidly near the melting point. The results with the pressures expressed in kgrm. per sq. cm. are shown in Table XV. J. Dewar (1905) pressed ice into wire-like threads at —80° and 50 tons per sq. in. pressure, but at lower temperatures he did not succeed in doing so.

T. Andrews (1886) measured the **hardness** of ice in terms of the depth of penetration of a steel rod into a cylinder of ice at different temperatures. The results showed that ice remains "almost impenetrable" from about —37° to about —12°; its power of resistance then decreases rapidly to about —7°, and still more rapidly at higher temperatures, until, at the melting point, the ice gives way "almost entirely," when it becomes very soft indeed. Ice on Mohs' scale (resistance to scratching) is said to have a hardness of 1·5. H. Morphy says the **coefficient of friction** of ice for small pressures—up to 14·3 grms.—between −5° and −6° is nearly constant, being 0·36 ± 0·01 ; and for large pressures—above 15 grms.—0·17 ± 0·01.

TABLE XV.—PLASTICITY OF ICE.

Temperature.	Highest pressure of steady flow.	Pressure when rapid increase occurs.	Melting pressure.
− 5·7°	642	665	678
−10·7°	1116	1130	1225
−15·7°	1611	1729	1681
−21·7°	2000	2100	2070
−27·6°	2220	2240	—

The **surface tension** of water is higher than that of all the common liquids, excepting mercury. For example:

Mercury.	Water.	Ammonia.	Benzene.	Acetone.	Alcohol.	Ether.
547	75·0	64·7	29·2	23·3	22·0	16·5 dynes per cm.

Surface tension and specific gravity determine the height to which a liquid will rise in a capillary tube. The high surface tension of water plays an important *rôle* in determining the ascent of this fluid in the capillary pores of the soil. Under ordinary conditions it is estimated that water can rise four or five feet under the influence of its high surface tension; if the surface tension of water were like that of most liquids the liquid would rise but two or three feet.[6] The high surface tension of water thus becomes an important factor in bringing water within reach of plants.

The reported values [7] for the surface tension, σ, of water in moist air at ordinary temperatures range from 7·13 to 7·945 mgrm. per mm. N. Bohr found the surface tension of water at 12° to be $\sigma=73·23$ dynes per cm. or $\sigma=7·465$ mgrm. per mm., and the specific cohesion to be 14·96 sq. mm. Many other determinations of these constants have been made by W. Ramsay and J. Shields. The following values below 40° are by P. Volkmann, and above 40° by C. Brunner:

	0°	10°	20°	30°	40°	50°	60°	70°	80°
σ .	7·692	7·541	7·389	7·237	7·086	6·91	6·73	6·54	6·35 mgrm. per mm.
σ .	75·49	74·01	72·53	71·03	69·54	67·8	66·0	64·2	62·5 dynes per cm.
a^2 .	15·406	15·105	14·821	14·556	14·295	13·99	13·70	13·39	13·08 sq. mm.

According to H. Sentis, the surface tension of water at $\theta°$ is $\sigma=76·09(1-0·002026\theta)$; and according to C. Forch $\sigma=\sigma_0(1-0·00190179\theta-0·0000024991\theta^2)$. The surface tension of water is extremely sensitive towards traces of impurities, and it is very difficult to get quite clean surfaces. G. Quincke (1870), F. von Lerch (1902), and F. Pockels (1899) have measured the surface tension in dynes per cm. at 20° at the interface of water in contact with different immiscible or partially miscible liquids, and their results include

Mercury.	Chloroform.	Carbon disulphide.	Alcohol.	Ethyl ether.	Benzene.	Petroleum.	Turpentine.	Olive oil.
$\sigma=37·47$	2·68	4·122	0·206	1·23	3·365	3·81	1·254	1·81

G. Hagen noted in 1845 that the surface tension of water is gradually reduced by exposure to air; G. Quincke, P. Volkmann, E. Bönicke, A. Kundt, and C. Forch found that from 17° to 18°, for solutions with m gram-molecules of gas per litre, the corresponding change in the surface tension of water per gram-molecule of dissolved gas is $\Delta\sigma/\sigma m$:

	CO_2	N_2O	H_2S	O_2	N_2	Air
m	0·041	0·029	0·127	0·00146	0·00073	0·00087
$\Delta\sigma/\sigma m$	−0·310	−0·307	−0·214	−2·225	−0·88	−1·30

At 17°, in vacuo, that is in saturated vapour, the surface tension of water is about 0·11 per cent. or 0·008 mgrm. per mm. greater than in air at atmospheric pressure.

T. W. Richards and J. H. Mathews found that the compressibility β and the surface tension σ of pure liquids are related approximately as $\beta\sigma^{\frac{4}{3}}=$a constant, while A. Ritzel could detect no simple relation with mixtures of water with other liquids. W. C. Röntgen and J. Schneider found that aqueous solutions of inorganic salts had a higher surface tension and a lower compressibility than pure water; while G. de Metz showed that cane sugar as solute always reduces the compressibility of water, the surface tension of these solutions is sometimes greater and sometimes less than water. K. Drucker found aqueous solutions of some organic acids have smaller surface tensions than water, and that the compressibility at first decreases and then increases with rising concentration. The surface tension of aqueous solutions shows that there is a possible action of the solute in dissociating some of the complex ice molecules in the surface film. T. W. Richards and S. Palitzsch observed that with aqueous solutions of urethane, there is a rapid decrease in surface tension with concentrations up to 40 per cent. of urethane, presumably owing to a decrease in the proportion of ice molecules with greater concentrations, the surface tension decreases in accord with the rule $\beta\sigma^{\frac{4}{3}}=$a constant.

G. Tammann denied the existence of any relation between the internal pressure of a solution—calculated from the thermal expansion—and the surface tension, but W. C. McC. Lewis found the internal pressure and surface tension of all but volatile and colloidal solutions change in the same direction. I. Traube based an explanation of some properties of solutions on the relationship between internal pressure and surface tension; T. W. Richards also interprets the compressibility of a pure substance as being in part contingent on the internal pressure, for the external pressure required to compress a substance to given extent is greater the more the molecules are previously compressed by molecular pressure.

The **specific cohesion** a^2 sq. mm. of water at different temperatures in moist air, is

	0°	10°	20°	30°	40°	50°	60°	70°	80°
a^2 .	15·406	15·105	14·821	14·556	14·295	13·99	13·70	13·39	13·08

It will be remembered that the specific cohesion a^2, is related with the surface tension so that $\sigma=\frac{1}{2}a^2(D-D')$, where D and D' respectively denote the specific gravities of water and moist air. According to L. Weinstein, the value a^2 at a temperature θ between 0° and 95° is $a^2=14{\cdot}987(1-0{\cdot}0014580\theta)$.

R. Eötvös (1886) found that the variations of the molecular surface tension $\sigma=a(Mv)^{\frac{2}{3}}$, with changes of temperature θ, namely, $d\sigma/d\theta$, are nearly the same, 2·12, for all normal liquids, but not so with liquids whose molecular complexity changes with temperature. W. Ramsay and J. Shields (1893) obtained the following values for water when the molecular weight is assumed to be 18:

θ .	0° to 20°	20° to 40°	40° to 60°	60° to 80°	80° to 100°	100° to 120°	120° to 140°
$\delta\sigma/\delta\theta$	0·88	0·95	1·00	1·05	1·09	1·14	1·18

If the molecular weight of water at 0° be taken to be 3×18, and the density of ice be assumed to represent the density of ice molecules, the constant becomes 2·08, very close to that for a normal liquid. Hence, the surface tension of water at 0° is sufficient to change practically the whole of the water in the surface film to ice molecules with a molecular weight 3×18, corresponding with $(H_2O)_3$. It also follows that the surface film of water is not changed very much with temperature up to about 40°, but, at higher temperatures, the surface tension is sufficiently reduced to form appreciable amounts of water molecules less complex than ice molecules. By applying the law for the surface tension of mixtures, and assuming that the surface film contains a mixture of the molecules with a molecular weight 3×18, and water molecules with a molecular weight 2×18, W. Sutherland calculated values for the variation of the surface tension of water in dynes per cm. with temperature which were in close agreement with the observed results, and with R. Eötvös' theory :

	0°	20°	40°	60°	80°	100°	120°	140°
Surface tension .	73·32	70·56	67·55	64·27	60·77	57·11	53·30	49·38

The **coefficients of diffusion** of water vapour into hydrogen, air, and oxygen, at 0°, are respectively 0·687, 0·193, and 0·131 per second.[8] The **velocity of sound** in water vapour is, according to A. Masson, 401 metres per second at 0° ; according to W. Jäger, 402·4 and 410·0 metres per second respectively at 93° and 96° ; and according to W. Treitz, 413 metres per second at 110° ; 417·5 at 120° ; and 424·4 at 130°.

Specific heat.—The specific heat or the amount of heat required to raise the temperature of one gram of liquid water per degree under certain assigned conditions, is taken unity as a standard—*e.g.* the *zero calorie* is the quantity of heat referred to water between 0° and 1° ; the *mean calorie*, to water between 0° and 100° divided by 100 ; and the *15°-calorie*, to water between 14·5° and 15·5°. The specific heat of water, as unity, is here given along with the specific heats of a few other liquids for comparison :

Water.	Mercury.	Sulphuric acid.	Alcohol.	Ether.	Benzene.	Carbon disulphide.
1	0·0334	0·317	0·547	0·529	0·397	0·235

The specific heat of water is abnormally high ; and it is remarkably nearly constant over a comparatively large range of temperature. From the time of H. V. Regnault (1847)[9] up to the present the specific heat of water, at constant pressure, has been the subject of investigation with more and more refined attempts to increase the degree of accuracy. Some of the later determinations almost agree up to the third significant figure. C. Dieterici's results (with the specific heat at 15° unity) are :

0°	10°	20°	30°	40°	50°	60°	80°	100°
1·0088	1·0021	0·9987	0·9984	0·9987	0·9996	1·0008	1·0045	1·0099

rising to 1·1543 at 300°. There is a minimum near 25° of 0·9983. The results of other observers give minima ranging from 12° to 35°. C. Dieterici's formula, referred to water unity at 0° for the specific heat C_p of liquid water at $\theta°$, between 35° and 300° is $C_p=0·99827-0·00016368\theta+0·00000207 36\theta^2$. H. L. Callendar gives for the specific heat C of water between 0° and 20°, $C=0·9982+0·0000045(\theta-40)^2+0·0000005(20-\theta)^3$. and between 20° and 60° the last term is omitted. Accurate measurements have also been made by C. E. Guillaume, A. Cotty, W. R. and W. E. Bousfield, and W. Jäger and H. von Steinwehr. J. Narbutt claims that for $\theta°$ between 0° and 100° the best observations are represented by the formula $C=1·00733-0·0007416\theta+0·000016845\theta^2-0·0000000955 2\theta^3$, when C for 15° is unity ; this gives a minimum between 20° and 30°. According to H. T. Barnes, the specific heat of undercooled water rises to 1·0155 at −5° (water at 15° unity). This is illustrated in Fig. 22. The specific heat of water at constant volume is obtained by computation from the expression $C_v=C_p-9a^2Tv_0/\beta$, where β represents the coefficient of compressibility, and a the coefficient of thermal expansion ; T the absolute temperature ; and v_0 the volume at 0°. When C_p at 0° is 1·0000, C_v is 0·9995. The specific heat of water at 0° is altered −0·0001025 per atmosphere increase of pressure. The specific heat of a solid is usually less, but

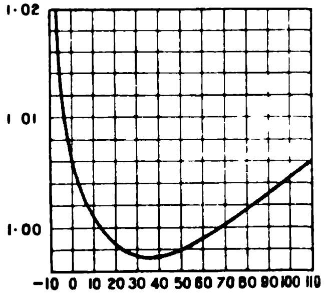

FIG. 22.—The Specific Heat of Liquid Water.

sometimes greater, than that of a liquid, with water the difference is abnormally great. For instance,

	Water.	Lead.	Mercury.	Sulphur.
Specific heat, solid .	0·502 (0°)	0·314 (0°)	0·0319 (−40°)	0·2026 (100°)
Specific heat, liquid .	1·000 (0°)	0·0402 (356°)	0·0333 (0°)	0·234 (120°)

J. Dewar found that the specific heat of ice falls from 0·502 at 0° to 0·463 at −78°, and to 0·146 at −252·5°. W. A. Smith found the specific heat of highly purified ice to be almost constant up to a temperature close to zero, but there is a sensible increase in the specific heat of ordinary ice, owing, it is supposed, to incipient fusion caused by the lowering of the melting point by dissolved impurities. H. C. Dickinson and N. S. Osborne found the specific heat of ice for a temperature θ between −40° and −0·05° to be $C=0{\cdot}5057+0{\cdot}001863\theta-79{\cdot}75\theta^{-2}$ cals. (20°), when the constant was found to diminish from −0·00125 to −0·00005 with increasing purity. Hence it was inferred that the departure of the specific heat of ice from a linear function of the temperature is less the purer the ice, consequently, the specific heat of pure ice is assumed to be $C=0{\cdot}5057+0{\cdot}001863\theta$. F. G. Jackson obtained between 0° and −78·4°, 0·424 ± 0·002; and between 0° and −188°, 0·337 ± 0·001; P. Nordmeyer and A. Bernoulli obtained analogous results; and A. Bogojawlensky worked with 5° intervals between −15° (0·500) and −50° (0·395). According to W. Nernst and F. Koref, the relation between the molecular heat of ice and temperature is represented by the relations $8{\cdot}47+0{\cdot}0276\theta-14{\cdot}0\theta^{-1}$.

The sudden rise in the specific heat of a substance just below its fusion temperature has given rise to some discussion. In some cases this is due to the presence of an impurity. For example, if a salt be present as impurity in water then, above the eutectic point for that salt, the apparent specific heat is increased by the fact that some of the ice melts to produce a larger specific heat than that of solid ice. The rise in the specific heat cannot be explained in this way; silver iodide shows a similar phenomenon, although it may be that different allotropic forms are present, and that with crystals of a one-phase substance, the phenomenon would not occur. G. N. Lewis and G. E. Gibson[10] found that with the exception of a small variation of ice below the melting point, the specific heat of ice can be represented by $\log C_v=0{\cdot}43(\log T-2{\cdot}51)$; accordingly the **entropy** of ice at 0°, calculated from absolute zero, $\phi=\int C_p d\log T$, is 9·96 per gram-molecule; the entropy for the liquefaction of ice is 1·58, at 0°; and the increase of entropy of liquid water from 0° to 25° is 1·58. Hence, the entropy of water at 25° is 16·8 per gram-molecule.

The mean specific heat of water vapour between 100° and 800° and at a constant pressure was found by L. Holborn and F. Henning[11] to be $C_p=0{\cdot}4460(1+0{\cdot}000096\theta)$ cals., and by A. Langen, for temperatures above 1100°, $C_p=0{\cdot}44(1+0{\cdot}00027\theta)$. The specific heat of water vapour at constant volume C_v, and at the absolute temperature T, according to W. Nernst and H. von Wartenberg, is $C_v=5{\cdot}61+0{\cdot}000717T+0{\cdot}0_6312T^2$ cals., or according to M. Pier, between 0° and θ°, $6{\cdot}065+0{\cdot}0005\theta+0{\cdot}0_882\theta^2$, from 1300° to 2500°.

The minimum in the specific heat curve of water is near 30°. W. Jäger and H. von Steinwehr give 33·5°. This, and other abnormal phenomena, are in agreement with the assumption that the observed specific heat of water is a complicated phenomenon involving both a true specific heat and an endothermal change of ice into water molecules on a rising temperature. If the presence of a substance in solution reduces the proportion of ice molecules in the liquid, it follows that the specific heat of an aqueous solution will be smaller than that of the pure solvent under the same conditions. This agrees with the observed facts, even when due allowance is made for the specific heat of the solute—that is, the dissolved substance; thus, A. Jaquerod (1901) found for solutions of potassium chloride, KCl, at about 16°,

Per cent. KCl . . .	0	2·4	4·8	9·6	19·2	28·8
Specific heat . . .	1·000	0·968	0·938	0·882	0·790	0·720

K. Puschl (1901) has also shown that the specific heats of many aqueous solutions are less than that which would be the case if solvent and solute were in the free state.

According to E. Mallard and H. le Chatelier (1881),[12] the molecular specific heat of water vapour at a constant volume, C_v, at a temperature θ, is $C_v=5{\cdot}91+0{\cdot}00376\theta-0{\cdot}0_6155\theta^2$; and according to J. M. Gray, the specific heat at a constant pressure is 0·3787. L. Holborn and L. W. Austin found the specific heat at constant pressure, between 110° and 270°, to be 0·4639; between 110° and 440°, 0·4713; and between 110° and 820°, 0·4881. The ratio of the two specific heats at 103° or 104° lies between 1·25 and 1·35—say 1·3. W. Freitz found 1·3301 at 110°, 1·3129 at 120°, and 1·3119 at 130°.

The specific heat of water is higher than that of any other liquid, excepting that of liquid ammonia. The general effect of the high specific heat of water is to make the ocean, lakes, and streams absorb on heating or give up on cooling comparatively large amounts of heat which help to maintain the temperature more nearly constant; and to moderate the heat of summer, and the cold in winter. This is shown by W. Zenker's comparison of the normal temperatures of continental and marine climates at different latitudes.

Latitude . .	0°	10°	30°	50°	70°	90°
Continental . .	34·6°	33·5°	24·1°	5·0°	−19·0°	−26·1°
Marine . . .	26·1°	22·7°	18·8°	7·1°	−5·2°	−8·7°

The large capacity of water for heat also helps in the regulation of the temperature by the transport of heat, so to speak, as ocean currents. Water being the chief constituent of the living organism, also favours the regulation of the body temperature. Thus, L. J. Henderson in his *The Fitness of the Environment* (New York, 1913) says:

> Man is an excellent case in point. An adult weighing 75 kgrms. when at rest produces daily about 2400 great calories, which is an amount of heat actually sufficient to raise the temperature of his body more than 32°; but if the heat capacity of his body corresponded to that of most substances, the same quantity of heat would be sufficient to raise his temperature between 100° and 150°.

The **heat conductivity** of liquid water, like that of other non-metallic liquids, is low. Water is a bad conductor of heat.[13] The conductivity may be represented by the number of calories transmitted per second per square centimetre through a centimetre layer with a difference of temperature of 1° between the two faces. The conductivities of a few liquids contrasted with silver is as follows:

Silver.	Mercury.	Water.	Alcohol.	Ether.	Benzene.	Carbon disulphide.
1·530	0·0163	0·00152	0·00055	0·00038	0·00033	0·00027

Consequently, water is one of the best of liquids for conducting heat, but even then, the thermal conductivity is small.

The thermal conductivity of water was determined by C. G. Lundquist in 1869, and he obtained 0·00156 in C.G.S. units at 40·8°; A. Winkelmann (1874), 0·00154 at 40°; H. F. Weber (1880), 0·00124 at 4°, and 0·00143 at 23·6°; R. Weber (1903), 0·00131 (23°); S. R. Milner and A. P. Chattock, 0·001433 (20°); R. Wachsmuth, 0·00129 (4·1°); C. Chree, 0·00124 (18°); L. Graetz, 0·00158 (30°); R. Goldschmidt, 0·00150 (0°); and C. H. Lees, 0·00147 (11°), 0·00136 (25°) with an increase of −0·0055 per cent. per degree up to 45°. The heat conductivity of ice and snow is relatively small, so that they protect the ground against the severe temperatures of a northern winter. The ordinary nocturnal cooling of the soil by radiation under normal conditions of soil exposure is of no significance when the ground is covered with snow. The loss of heat from a river is retarded by the rigidity of the surface sheet of ice which prevents direct contact of air and water. Although the conductivity of ice is rather higher than that of water, the loss of heat by conduction is relatively small in comparison with the heat losses by convection and wind currents which are immediately stopped when a surface sheet of ice is formed. The protective action of snow on the ground is of the greatest importance, for, when dry, as is the case in the severest weather, a covering of snow is one of the best non-conductors of heat. J. D. Forbes first determined the thermal conductivity of ice in 1874, and he found that the conductivity is greater in the direction of the principal axis than it is when perpendicular thereto. In the former case it is 0·0022 and in the latter 0·0021. These numbers represent the number of calories of heat which flow per sq. cm. per second in the direction of the fall of temperature when the temperature gradient is 1° per cm. A. C. Mitchell (1885) found the conductivity of ice to be 0·005; F. Neumann, 0·00573; M. Straneo (1897), 0·30 to 0·0052 in the direction of the principal axis, and 0·005 when perpendicular to that direction. C. H. Lees found the conductivity of ice to be 0·0052 at 3°; 0·0058 at −57°; and 0·0052 at −117°.

The heat conductivity of snow is much less than that of pure solid ice, and in 1885, T. Andrews found ice to conduct heat 122 per cent. better than snow. S. A. Hjelström (1889) found the conductivity of snow to be 0·00051; and H. Abels (1891) found the conductivity of snow to be proportional to the square of its density, or $K=0{\cdot}0068D^2$, and P. Jansson (1901) represented his results by the formula $K=0{\cdot}00005+0{\cdot}0019D+0{\cdot}006D^2$. T. Okada found that the density of snow varied with its depth, for a depth of 10–20 cm., $K=0{\cdot}00028$; and for a depth 20–30 cm., $K=0{\cdot}00045$; his results agreed better with H. Abels' than with P. Jansson's formula.

Optical properties.—Ice is optically positive. Its mean **refractive index** is high; and some have tried to show that Isaac Newton (1749)[14] anticipated the presence of combustible hydrogen in water, or at any rate the relation of water to combustible substances, because he worked with the hypothesis that substances with a high refractive index contained fatty, unctuous inflammable parts. According to C. Pulfrich[15] the refractive index of ice is $\omega=1{\cdot}30645$, and $\epsilon=1{\cdot}30775$ for the B-line; $\omega=1{\cdot}30911$, and $\epsilon=1{\cdot}31041$ for the D-line; and $\omega=1{\cdot}31140$, and $\epsilon=1{\cdot}31276$ for the E-line. According to A. Bertin, ice which is formed from water at rest has its optical axes vertical to the cold surface, and F. T. Trouton explains the greater heat conductivity of ice in the direction of the chief axis as the cause of the orientation of ice crystals vertical to the cold surface. The index of refraction of liquid water[16] at 16° is 1·3349 for the B-ray; 1·3322 for the D-ray; 1·3358 for the E-ray; and 1·3449 for the H-ray.

The refractive index of most transparent substances for light waves of wave-length within the limits of the visible spectrum, increases as the wave-length decreases—*e.g.* with water, alcohol, or carbon disulphide. The wave-length of violet-light is shorter than red-light, and the index of refraction accordingly is greater for violet than for red-light. With an alcoholic solution of fuchsine the reverse obtains, for the violet rays are less refracted than the red rays. According to A. Kundt, this anomalous phenomenon always accompanies great local absorption in the spectrum; and wherever there is a strong absorption band in passing up the spectrum from red to violet, the refractive index is abnormally increased below the band, and abnormally diminished above the band. The refractive index of water decreases from about 1·4 to 1·3 in passing from the violet to the red end of the visible spectrum. If the wave-length of the incident rays be increased upwards of 5 mm., the index of refraction increases to nearly 8·9; and generally with wave-lengths between 6 metres and 6 millimetres, the refractive index is nearly 8·9. There is therefore a big drop in the value of the index of refraction in passing from waves 5 mm. in length—and frequency 6×10^{x}—to the waves of red-light about $\frac{1}{1300}$th mm. in length—and frequency 400×10^{12}. This anomalous behaviour is supposed to be connected with the strong absorption band in the ultra-red spectrum of water. Similar results are obtained with alcohol, the index of refraction of which drops from about five to about half this value in passing from a wave-length 9 metres to about 8 mm.

According to J. H. Gladstone and T. P. Dale's data (1858) for the index of refraction μ, the dispersion equivalent $\mu_H-\mu_A$ and the **dispersive power**

$(\mu_H - \mu_A)/(\mu_D - 1)$ of water are indicated in Table XVI. J. Jamin represents the variation of the index of refraction of water with temperature by the formula $\mu_0 - 0{\cdot}0_4 12573 - 0{\cdot}0_5 1929\theta^2$—there is no maximum at 4°. The index of refraction for the extreme ultra-violet ($214\mu\mu$) is 1·40387; and for the ultra-red ($1256\mu\mu$), 1·3210. E. van Aubel gives 1·102 for the index of refraction of water at the critical temperature. According to J. W. Brühl, the molecular refraction for water by L. Lorenz and H. A. Lorentz's formula is 3·282 for sodium light; and the value calculated from the atomic refractions of hydrogen and oxygen is 4·14.

TABLE XVI.—OPTICAL CONSTANTS OF WATER.

Temperature.	Index of refraction.			Dispersion equivalent.	Dispersive power.
	μ_A	μ_D	μ_H		
0°	1·3291	1·3330	1·3438	0·0147	0·0429
10°	1·3288	1·3327	1·3434	0·0146	0·0439
20°	1·3279	1·3320	1·3427	0·0148	0·0445
30°	1·3270	1·3309	1·3415	0·0145	0·0438
40°	1·3257	1·3297	1·3405	0·0148	0·0449
50°	1·3241	1·3280	1·3388	0·0147	0·0448
60°	1·3223	1·3259	1·3367	0·0144	0·0441
70°	1·3203	1·3237	1·3344	0·0141	0·0435
80°	1·3178	—	1·3321	0·0143	—

Assuming that water is a mixture of two substances, a comparison of the index of refraction for water and ice shows that the specific refraction drops from 0·209680 for ice at 0° to 0·206342 for water at 0°, and subsequently, at 20°, 0·206208; at 60°, 0·206051; and at 100°, 0·206015. The increase in the value of this constant for 100 parts of the following liquids heated from 10° to 20°, is

Ether.	Chloroform.	Ethyl iodide.	Ethyl acetate.	Carbon disulphide.
0·08	0·04	0·05	0·11	0·12

C. Chéneveau found the refractive index of ice and liquid water at 0° to be 1·3095 and 1·3341 respectively, and the specific gravities 0·9176 and 0·99987. The specific refractions by J. H. Gladstone and T. P. Dale's formula are respectively 0·3373 and 0·3341; and by L. Lorenz and H. A. Lorentz's formula 0·2097 and 0·2063 respectively. Similarly, for water at 100° the specific gravity is 0·95838, the refractive index 1·3182, and the specific refractions 0·3320 and 0·2019 respectively. The decrease with water is supposed to show that the normal increase with temperature has superposed upon it a decrease due to a change in the molecular constitution of the molecules of the water so that water is a mixture of two substances in proportions varying with the temperature. The results calculated by C. Chéneveau (1913) on this hypothesis are in agreement with observation. J. Jamin found that difference between the refractive index of dry air and air saturated with aqueous vapour to be $0{\cdot}0_6 726$, an extremely small quantity.

The colour of water.—In 1828, H. Davy[17] described the water from snow and glaciers in different parts of the Alps, as "pure water," and added that "its colour, when it has any depth, or when a mass of it is seen through, is bright blue; and, according to its greater or less depth of substance, it has more or less of this colour." In 1851 R. Bunsen's attention was also directed to the greenish-blue tint of the Icelandic geysers, and he found that purified water in a glass tube blackened on the inside, and two metres long, appeared distinctly blue, and he accordingly denied that water is colourless, but is actually blue. Hence, it is generally considered that the purest water is colourless in moderately thin layers but that it appears faintly blue when viewed in thick layers—say in a tube 2 metres long. According to W. Spring, the blue tint can be closely imitated by a solution of cupric chloride of the proper concentration. Lord Rayleigh believes that the blueness of water at a depth of 4 metres is largely exaggerated by W. Spring, although possibly a fully developed blue may be obtained at much greater thicknesses. Lord Rayleigh says the colour of the transmitted light is a greenish-blue; and he believes that the pronounced blue colour reported by many observers is due to insufficient care being taken to start with white light.

According to W. Spring, the faint blue tint of purified water seems to be dependent upon the presence of oxygen. Liquid oxygen, O_2, is distinctly blue; liquid ozone, O_3, is intensely blue; and hydrogen peroxide, H_2O_2, has rather a deeper blue colour than water, H_2O, so that in hydrogen peroxide the oxygen loses less of its characteristic tint than it does in water. Many organic compounds containing the hydroxyl OH-group are also blue—*e.g.* methyl and ethyl alcohols (CH_3OH and C_2H_5OH) are bluish-green when viewed in a long tube. As the number of carbon atoms increase, making a longer chain, the colour changes into the golden-yellow which is found in liquid hydrocarbon compounds free from hydroxyl. As the carbon chain of the hydroxyl compound increases in length—C_3H_7OH, C_4H_9OH, $C_5H_{11}OH$, etc.—the yellow colour becomes more and more pronounced—with amyl alcohol, $C_5H_{11}OH$, the colour is yellowish-green—until finally the yellow overpowers the blue altogether.

According to J. Aitken (1880), the blue colour of large bodies of water—*e.g.* in china-clay settling pits; in tanks in which water is being softened by the addition of milk of lime; etc.—is an optical effect due to the action of the fine particles suspended in the liquid on the light. J. L. Soret (1869), E. Hagenbach (1870), and J. Tyndall (1871) stated that the water from Lake Geneva is not optically empty, but that the blue colour is possibly due to the scattering of light from numberless colourless particles. H St. C. Deville (1848) and G. C. Wittstein (1861) analyzed a great number of natural waters, and concluded that the brown or yellow waters contain more organic matter and less calcium salt than green waters, this organic matter is brown, and the blue colour of natural waters changes to green, yellow, brown, or black as the proportion of organic matter increases. W. Spring, however, has pointed out that G. C. Wittstein's data really show that the colour of natural water stands in no direct relation with the organic matter or alkali concentration. He showed that with water containing ferric oxide in solution or suspension, the colour is dark mahogany-brown with a concentration of 1 : 10000; golden-yellow with 1 : 1000000; grass-green with 1 : 8000000; and blue like pure water with 1 : 24000000. Similarly with humic matter, the colour is yellowish-brown with a concentration 1 : 500000; green with 1 : 20000000; and blue with 1 : 50000000. Consequently, W. Spring (1905) argues that the green colour of certain natural waters is not due to dissolved calcium salts, but rather to an invisible suspension—probably organic matter and silica. The brown or yellow colour of certain natural waters is due to humus or salts of iron. According to Lord Rayleigh, the apparent colour of the sea is largely determined by the colour of the sky seen by reflection.

A. Secchi found that the red and yellow rays are lacking in the absorption spectrum of sea-water. O. von Aufsess measured the transmission of light in various parts of the spectrum, and found the principal absorption is in the red and yellow; and with the purest water he found practically no absorption above the *F*-line, and a high transparency in this region was attained by many natural waters. Hence, if in sufficiently thick layers such waters must appear blue. The **absorption spectrum** of water is indicated in the diagram, Fig. 23. The infra-red heat rays are strongly absorbed. The maximum absorption is towards the red and orange, the maximum transmitted is towards the blue and green. There are large absorption bands in the spectrum of water [18] at the approximate wave-lengths 1·5, 2·3, 4·75, and 6μ. Water is very opaque to the deep infra-red radiation and the spectrum of numerous narrow absorption bands can be resolved only when the substance is reduced to a highly attenuated vapour; in the liquid state, these groups of small bands coalesce into larger bands. In the visible spectrum, and as far as 0·933μ in the infra-red, a thick layer of water is needed to produce absorption bands. A layer 1 cm. thick absorbs all frequencies beyond 1·4μ; a layer 0·5 mm. thick is quite opaque beyond 2μ; and a layer 0·1 mm. thick is quite opaque beyond 5μ. Beyond 8μ, water is transparent. According to W. W. Coblentz, if infra-red absorption spectrum bands of a hydrated compound be present at wave-lengths 1·5μ, 2·0μ, 3·0μ, 4·75μ, and 6·0μ, and the absorption bands at 1·5μ, 2·0μ, and 4·75μ, are weak while the others are strong, the product is a hydrate because these absorption bands are characteristic of water itself. The presence of a hydroxyl group may cause an absorption band near 3μ, but if water molecules be absent, the other characteristic bands are absent. G. Bode studied the infra-red spectrum of ice.

Water vapour is more transparent than the liquid. About the middle of last century there was an interesting controversy between J. Tyndall[19] and G. Magnus on the absorption spectrum of water vapour. The former obtained a strong absorption, the latter a negligibly small absorption. Other physicists investigated the subject, and it has now been established not only that water vapour absorbs heat rays but also what particular rays are absorbed, and how much of each. Atmospheric water vapour transmits the sun's radiation as far as 11μ, while a layer of liquid 2 cm. thick, and equivalent to the water in the earth's atmosphere, absorbs everything beyond 1·2μ.

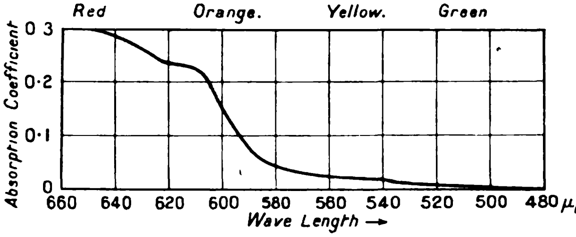

FIG. 23.—The Absorption of Light by Purified Water.

According to M. Faraday, ice is positively electrified by friction with water, and on this fact, L. Sohncke[20] has founded a theory of atmospheric electricity. The **electrical conductivities** of ice and water are very low, and this the more, the greater the degree of purity. With an alternating current of 1000 cycles per sec., the resistance of ice per centimetre cube is given as $7·22 \times 10^7$ ohms; the corresponding conductivity, as 1400×10^{-11}, where with a direct current the conductivity is $1·63 \times 10^{-9}$. With an alternating current of 1000 cycles, the breakdown voltage per cm. is $0·011 \times 10^6$;[21] the specific inductive capacity is 86·4, and with an alternating current of 15 cycles, 429·0. The electrical conductivity of ice, said G. Foussereau (1884),[22] is 15·000 times smaller than that of water, which is represented to have an absolute resistance of 9400 ohms. Ice, at 0°, has an electrical resistance of 4865 megohms, and at —17°, a resistance of 33,540 megohms. Dry ice indeed is considered to be one of the most perfect of insulators. Telephone câbles which are defective in insulating properties through moisture may become all right when the temperature falls below the freezing point.

The specific resistance of water at 15° was found to vary between 118,900 and 712,500 ohms, according to the degree of purity. The higher number was obtained with water distilled three times in a platinum vessel. The resistance of water kept for 24 hours in glass vessels at 15° was found to diminish about one-thirtieth owing to the solvent action of water on the glass; if kept in platinum vessels, the diminution is slower, and it is due to the slow absorption of salts and acid vapours from the atmosphere. F. Kohlrausch and A. Heydweiller[23] purified some water by distillation in vacuo which had a conductivity of $0·043 \times 10^{-6}$ reciprocal ohm per cm. cube at 18°, or $0·015 \times 10^{-6}$ reciprocal ohm at 0°. Twice-distilled water has a conductivity of from 1 to 2×10^{-6} reciprocal ohms. This, said F. Kohlrausch and A. Heydweiller, means that:

> One millimetre of this water has at 0° a resistance equal to that of a copper wire of the same cross-section 40,000,000 kilometres long, a wire that could therefore be wound a thousand times round the earth. This water is probably the purest that has ever existed, whether artificially prepared, or occurring ready formed in nature, not even excepting the water precipitated in the form of clouds in the highest strata of the atmosphere. Simple contact with the air for a short time raised its conductivity tenfold. The impurities still present in the water might be estimated at a few thousandths of a milligram per litre.

F. Kohlrausch further estimates that the specific conductivity of absolutely pure water at 18° is $0{\cdot}038\times10^{-6}$ reciprocal ohm. J. Negreanu found the conductivity of ordinary tap-water to be between 200 and 760 reciprocal ohms at 18°. J. J. Thomson found the conductivity of electrolytes under very rapidly alternating frequencies to be fairly constant up to 10^6 cycles. J. A. Fleming and G. B. Dyke found the conductivities of many solids increased rapidly with the frequency—*e.g.* ebonite at 4600 cycles had a conductivity 6·4 times greater than with 800 cycles. B. van der Pol found that the normal conductivity of sea-water with steady currents is 5×10^{-11}, and for currents of frequency 275, 1070, and 3400, the conductivities are respectively 1·005, 1·002, and 1·001 times the normal value, thus showing that the conductivity of sea-water for all frequencies used in wireless telegraphy is nearly equal to the value for steady currents to within less than a half per cent. K. T. Compton calculated the **ionizing potential** for water vapour from the formula $V=0{\cdot}194(K-1)^{-\frac{1}{2}}$ volts to be 8·64 volts, where K is the dielectric constant, and V the ionizing potential.

The velocity of migration of the H·-ion is $v^{\cdot}=318$ at 18°, and for the OH′-ion, $v'=174$. The concentration C of the ions in gram-ions per litre $C_{H}=C_{OH}$ is $\lambda/\lambda_{\infty}=\lambda/(v^{\cdot}+v')=0{\cdot}0384\times10^{-6}/(318+174)=0{\cdot}78\times10^{-7}$. The conductivity λ increases with temperature:

	0°	2°	10°	18°	26°	34°	42°	50°
$\lambda\times10^{3}$ . .	0·0115	0·0133	0·0233	0·0361	0·0567	0·0833	0·1210	0·1690

The change in the concentration of the H·-ions is about 0·04 per degree. If water be ionized $H_2O \rightleftharpoons H^{\cdot}+OH'$, the equilibrium condition is $[H^{\cdot}][OH']=K'[H_2O]$, where K is the ionization constant, and since the un-ionized water is in very great excess, the term $K'[H_2O]$ is also constant, and hence $[H^{\cdot}][OH']=K$, where K is the so-called *water constant*. The **ionization constant** for water has been worked out by several different methods. S. P. L. Sorenson reduced the more important of these to their values at 18°. S. Arrhenius and J. Shields obtained $K=0{\cdot}73\times10^{-14}$ from measurements on the hydrolysis of sodium acetate; J. J. A. van Wijs, $0{\cdot}83\times10^{-14}$ (hydrolysis of methyl acetate); H. Lunden $0{\cdot}61\times10^{-14}$ (hydrolysis of trimethyl pyridine *p*-nitrophenol); F. Kohlrausch and A. Heydweiller, $0{\cdot}63\times10^{-14}$ (conductivity of water); W. Ostwald and W. Nernst, $0{\cdot}64\times10^{-14}$ (e.m.f. of hydrogen electrode in acid alkali cell); R. Lowenheiz used an analogous process and obtained $0{\cdot}74\times10^{-4}$, and S. P. L. Sorenson obtained $0{\cdot}72\times10^{-14}$ from the e.m.f. of the hydrogen electrode against $0{\cdot}01N$-KCl and the calomel electrode. The best representative value is $[H^{\cdot}][OH']=0{\cdot}73\times10^{-14}$; hence $[H^{\cdot}]=[OH']=0{\cdot}85\times10^{-7}$. This is taken to mean that in a litre of water, at 18°, 0·000085 milligram of hydrogen is present as free hydrogen ions. The ionization constant for water changes rapidly with temperature. R. Lorenz and A. Böhi computed values from their measurements of electrode potentials, and F. Kohlrausch and A. Heydweiller and A. A. Noyes and co-workers from measurements of the electrical conductivity. The results are by no means concordant. R. Lorenz and A. Böhi give:

	0°	18°	25°	30°	50°	70°	90°	99°
$K\times10^{14}$ . . .	0·14	0·72	1·22	1·74	8·8	21·5	53·5	72·0
$[H^{\cdot}]\times10^{7}$ . . .	0·37	0·85	1·10	1·32	2·96	4·61	7·3	8·49

According to C. W. Kanolt (1907), the ionization constant K for water at 0° is $0{\cdot}089\times10^{-14}$; at 18°, $0{\cdot}46\times10^{-14}$, and at 25°, $0{\cdot}82\times10^{-14}$, while A. A. Noyes, Y. Kato, and R. B. Sosman give the concentration of the hydrogen ion, $[H^{\cdot}]$, and the ionization constant K at different temperatures θ, as

θ	0°	18°	25°	100°	150°	218°	306°
$[H^{\cdot}]\times10^7$	0·30	0·58	0·91	6·9	14·9	21·5	13·0
$K\times10^{14}$	8·089	0·46	0·82	48	223	461	168

The **heat of ionization** Q of one gram-molecule of water calculated from the usual formula $\log (K_2/K_1)=Q(T_2-T_1)/RT_1T_2$, is nearly 14 Cals. when $R=1{\cdot}986$ cals.

F. Kohlrausch assumes that each ion is surrounded by a shell or atmosphere of the solvent which differs in some respects from the rest of the solvent; the dimensions of the atmosphere is determined by the character of the ions. In other words, the ions are hydrated. The electrolytic resistance of an ion is a frictional resistance which increases with the dimensions of the atmosphere. F. Kohlrausch continues:

> The relationship between the mobilities of the ions and their temperature coefficients first led me to seek a general explanation for the electrolytic resistance in the idea of a water atmosphere, in order to escape being compelled to explain this otherwise irreconcilable fundamental characteristic of the ions as a *deus ex machinâ*. Assuming as the single fundamental characteristic of each univalent monatomic ion the formation of a water atmosphere, which varies according to the nature of the ion, the mobility of the complex on the one side, and its temperature coefficient on the other, will be functions of the atmospheric formations, and therefore both quantities must hold functional relations to each other. We know at present too little of the molecular forces to attempt to describe this connection more exactly; but for the case in which the water shell is so thick that the ion exerts no force beyond it, the resistance to motion becomes simply a matter of water friction, which explains the fact that the most sluggish ions have nearly the same temperature coefficients as the viscosity. In the case of smaller aggregations, we must remain content with the fact that we have at least the possibility of a fundamental explanation.

W. Nernst assumes that the solvent water is strongly contracted by the presence of free ions, and the observed contraction which occurs during the dissolution of ionized substances is smaller than the molecular volume of the solid—*e.g.* sodium carbonate, magnesium or zinc sulphate, etc. The electrostriction is caused by electrostatic fields of the ions which make the solvent contract in their immediate vicinity.

In addition to the ionization $H_2O\rightleftharpoons H^{\cdot}+OH'$ in which water acts as if it were a monobasic acid, a second stage in the ionization is conceivable, $H_2O\rightleftharpoons HO'+H^{\cdot}\rightleftharpoons 2H^{\cdot}+O''$. where the water acts as if it were a dibasic acid. Nothing definite is known about this second stage of ionization; if it does occur at all, it must be in exceedingly small proportions because the second stage in the ionization of a dibasic acid is always more difficult than the first stage, and the first stage with water is very small.

Many organic substances—fatty acids, oximes, alcohols, etc.—form complex or polymerized molecules when dissolved in hydrocarbons, chloroform, carbon disulphide, or carbon tetrachloride; the complexes are usually broken down into simpler molecules when these substances are dissolved in water, and to a less extent when dissolved in alcohols, ethers, or phenols. The latter class of solvents is said to be ionizing because when saturated with hydrochloric acid the liquids act as conductors of electricity, whereas the former class of solvents is non-ionizing because the liquids are virtually non-conductors under similar conditions. Water is *par excellence* the ionizing solvent. J. W. Brühl [24] explains this by assuming that water is an unsaturated compound containing quadrivalent oxygen $H_2=O=$, or $H-\overset{\cdot}{\underset{\cdot}{O}}-H$, and that the latent valency of water is the cause of the formation of molecular aggregates which in turn makes water an ionizing solvent. The organic solvents, too, which act in a similar way, usually contain hydroxylic oxygen, while those solvents free from oxygen—hydrocarbons, chloroform, etc.—have usually little or no ionizing power. J. W. Brühl cites in favour of the view that water has an unsaturated molecule: (1) Nearly all substances capable of uniting with water are hygroscopic; (2) Numerous hydrates and compounds of water of crystallization exist; and (3) Water is an unusual solvent.

According to R. Abegg, the **dielectric capacity**[25] of ice at −18° is 3·16 for waves approximately $\lambda=5\times10^3$ cm.; while U. Behn and K. Kiebitz give 1·76 and 1·88 for waves $\lambda=75$ cm. at −190°. According to K. Bädeker, the dielectric constant of water vapour under 3 atm. pressure, at 145° is 1·00705 (vacuum unity) or 1·00646 (air unity); and at θ° the dielectric constant is $1{\cdot}00705\{1-0{\cdot}00014(145-\theta)\}$. M. Jona also measured the dielectric constant of water vapour at temperatures ranging from 17·8° to 178·1°. According to Maxwell's rule, the square of the index of refraction μ^2 is equal to the dielectric capacity K for electric fields alternating with a low frequency. C. B. Thwing (1894) found that the dielectric capacity of liquid water with rapidly alternating oscillations (with a wave-length over 10 m.) rises from 79·46 at 0° to a maximum 85·2 at 4°, and falls to 79·4 at 7°. The refractive index μ for long electrical waves is given by the quotient $\mu=\lambda/\lambda'$, where λ and λ' represents respectively the wave-lengths in air and in the compound under investigation. For sufficiently long waves—about 70 cm.—the square of the refractive index μ is equal to the dielectric constant K, or $\mu^2=K$. At 17°–18°, for water, H. Merczyng, A. Colley, H. Rukop, J. F. Smale, B. B. Turner, and P. Drude found:

λ	3·5	4·5	55·5–68·5	long	c. 10^4
μ	6·54	6·88	8·955	9·0	—
μ^2	42·7	47·3	80·26	81·0	—
K	—	—	80·9–81·1	—	80·0

C. Niven found the dielectric constant decreased with increasing temperatures at 0°, $K=90{\cdot}36$; at 7°, 80·06; at 33°, 69·31; at 58·32°, 59·5; and at 83°, 37·97. B. Hopkinson and E. Wilson found that the dielectric constant of ice is nearly 80 with low frequency electrical oscillations between 10 and 100 per second. From Maxwell's rule, the refractive index of ice is 1·41 corresponding with a dielectric constant of about 2; and the dielectric constant of ice with oscillations of a frequency of a million is a number less than 3. Thus, the refractive index of ice for electro-magnetic waves falls to 1·4 for waves of even moderate frequency under conditions where the refractive index of water still remains at 8·9. This illustrates the general observation that when liquids with a high dielectric constant pass into the solid state, the abnormal refractive index is more easily reduced to approximate with the value of μ for the visible spectrum by increasing the frequency. J. A. Fleming and J. Dewar also found that the dielectric constant of ice falls from 80 at about 0°, to nearly 3 at very low temperatures, say −190°, and the refractive index is then 7·6 with waves of low frequency and wave-length 14 mm. The refractive index of ice for light vibrations of wave-length from 14 mm. to 2088 cm. progressively decreases from 1·76 to 1·50. The latter corresponds with a dielectric constant 2·25. R. Blondlot obtained a value 2·6 for oscillations of still greater wave-lengths. R. Abegg at −18°, found for $\lambda=5\times10^3$, $K=3{\cdot}1$; for $\lambda=75$ at −90°, U. Behn and F. Kiebitz found $K=1{\cdot}76$ to 1·88; and E. Beaulard found at 0° $K=\mu^2=1{\cdot}71$. There is a steady, almost linear, change of dielectric capacity with temperature, such that the dielectric constant at θ° between 0° and 76° is $80{\cdot}6\{1-0{\cdot}004583(17-\theta)+0{\cdot}0000117(17-\theta)^2\}$. With short waves (under 1 m.) the dielectric constant is rather greater than with longer waves—at 17°, 80·6 with a wave-length 200 cm., 81·7 for 74 cm., and 83·6 for 38 cm. E. A. Harrington found the dielectric constant of aqueous solutions of sugar, and methyl alcohol to be less the greater the concentration; with aqueous solutions of urea, the reverse obtains.

The high dielectric constant of water is supposed to give a hint as to the cause of the great ionizing power, when contrasted with other solvents, *e.g.*

	Water.	Methyl alcohol.	Ethyl alcohol.
Dielectric constant	81·7	34	26
Per cent. ionization ($\frac{1}{10}N$) Potassium iodide .	88	52	25
,, ,, ,, Sodium bromide .	86	60	24
,, ,, ,, Potassium acetate .	83	36	16

J. J. Thomson's explanation[26] how a high dielectric constant favours ionization is as follows:

> If we take the view that the forces which hold the atoms in the molecules together are electrical in their origin, it is evident that these forces will be very much diminished when the molecule is close to the surface of, or surrounded by, a conductor, or a substance like water, possessing a very large specific inductive capacity (dielectric constant). Thus, let *A*, *B*, Fig. 24, represent two atoms in a molecule placed near a conducting sphere, then the effect of the electricity induced on the sphere by *A* will be represented by an opposite charge placed at *A′*, the image of *A* in the sphere. If *A* is very near the surface of the sphere, then the negative charge at *A′* will be very nearly equal to that at *A*. Thus, the effect of the sphere will be practically to neutralize the electric effects of *A*; as one of these effects is to hold the atom *B* in combination, the affinity between the atoms *A* and *B* will be almost annulled by the presence of the sphere. Molecules condensed on the surface of the sphere will thus be practically dissociated. The same effect would be produced, if the molecules were surrounded by a substance possessing a very large specific inductive capacity. Since water is such a substance, it follows, if we accept the view that the forces between the atoms are electrical in their origin, that when the molecules of a substance are in aqueous solution, the forces between them are very much less than they are when the molecule is free, and in a gaseous state.

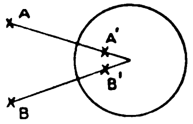

FIG. 24.

P. Dutoit and E. A. Aston[27] suggest that the ionizing power of a solvent is dependent on its degree of polymerization; they show that only polymerized solvents conduct electricity.

Ice is diamagnetic.[28] The coefficient of magnetization when referred to unit mass is $0·7193\times10^{-6}$ at 20° with a temperature coefficient of 0·00013 at 20°; P. Sève found $0·725\times10^{-6}$ at 22°. A. Piccard found that the diamagnetic coefficient of water at 0° is $0·7174\times10^{-6}$, and it changes with temperature, until, at 100°, it attains the constant value $0·7228\times10^{-6}$. The curves showing the relation between the variation of the coefficients of **magnetization** of water with respect to temperature, led A. Piccard (1912)[29] to infer that "in water at ordinary temperatures there are two substances in equilibrium." Determinations of the **magnetic susceptibility** of water[30] by different investigators give numbers ranging from $6·4\times10^{-7}$ to $8·4\times10^{-7}$ for temperatures approximating 20°. A. Piccard's value at 20° is $7·193\times10^{-7}$, and C. H. Hayes' value at 24° is $7·26\times10^{-7}$. The **magneto-optic rotation** of liquid water for a wave-length $\lambda=0·2496\mu$ is 0·1042′ per cm. per unit magnetic field; for $\lambda=0·4046\mu$, the rotation is 0·0293′; for $\lambda=1·000\mu$, the rotation is 0·00410′; and for $\lambda=1·300$, the rotation is 0·00264′. L. H. Siertsema's value[31] for **E. Verdet's constant** for water at 13·4° and the *D*-line is 0·01302; F. Agerer's value at 18°, 0·01309; G. Quincke's value at 21·81° is 0·01414; and L. Arons' value at 23°, 0·01293. J. W. Rodger and W. Watson give for θ° between 3° and 98°, $0·01311\,(1-0·0000305\theta-0·00000305\theta^2)$. L. H. Siertsema calculated the ratio of E. Verdet's constant for light of wave-length λ to the value for the *D*-line at 20°; for $\lambda=0·405\mu$, the ratio is 2·218; for $\lambda=0·589$, unity; and for $\lambda=0·701\mu$, the ratio is 0·700. J. W. Rodger and W. Watson also calculated the molecular rotation for the *D*-line between 4° and 90°, and they also found that the magnetic rotary power of unit depth of water in a magnetic field of unit strength at a temperature θ between 4° and 98° is $0·01311-0·0_64\theta-0·0_74\theta^2$. J. Kerr found that when the wire terminals of an induction coil were embedded in a block of glass placed between crossed nicols, there was a restoration of the light. The restored light could not be extinguished by rotation of the analyzer, and the phenomenon was not therefore a simple rotation of the plane of polarization, but an elliptical polarization resulting from the fact that the medium had become doubly refracting. The phenomenon also occurs with isotropic liquids. It is called **Kerr's electro-optic effect.** If D denotes the path-difference measured in wave-lengths of the two components of the vibration, K the strength of the electric field, then for unit length of fluid, $D=jK$, where j is the so-called Kerr's constant.[32] For light of wave-length $680\mu\mu$, at 20°, G. Lemoine found Kerr's constant to be $3{\cdot}70\times10^{-7}$, which is nearly the value found by R. Leiser for water. W. Obolensky[33] found that water gives a maximum **photo-electric effect** with the extreme ultra-violet rays in the neighbourhood of $\lambda=130\mu\mu$; and, becoming less as the wave-length increases, vanishes completely, when $\lambda=202{\cdot}5\mu\mu$. Ice is more sensitive than water; with rays in the neighbourhood of $\lambda=130\mu\mu$, the activity of water is $\frac{1}{400}$th of that of cupric oxide, and for rays approximating $\lambda=190\mu\mu$, ice surpasses cupric oxide.

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§ 9. The Chemical Properties of Water

Water is formed by the direct union of the two elements, such as when one of the elements is burnt in the presence of the other; by the combustion of compounds containing hydrogen in air or oxygen; by the action of hydrogen on certain oxides or compounds containing oxygen; and by the decomposition of many organic and inorganic compounds containing hydrogen and oxygen. Water formed by the combustion of hydrogen in oxygen is reported to contain sometimes hydrogen peroxide, and ozone; and if the oxygen contains nitrogen, both nitric acid and ammonium nitrite may be formed. M. Berthelot[1] has reported that when a gram of hydrogen was burnt in air, 0·000075 grm. of nitric acid, HNO_3, was simultaneously formed; and in oxygen containing 8 per cent. of nitrogen, 0·017 grm. of nitric acid was obtained with a small flame, and 0·071 grm. with a large flame.

A mixture of two volumes of hydrogen and one volume of oxygen is variously styled *detonating gas*, *electrolytic gas*, *gaz tonnant*, and *Knallgas*. The constituents of detonating gas unite to form water (i) when *heated*; (ii) when exposed to an *electric spark*, or to the *silent electrical discharge*;[2] (iii) when merely *in contact with certain metals*—particularly the platinum family—charcoal, etc.; (iv) when directly exposed to *radium rays*;[3] but, according to W. P. Jorissen and W. E. Ringer, there is no perceptible action if the detonating gas in a glass vessel be exposed to radium rays. S. C. Lind found that the velocity of combination of hydrogen and oxygen under the influence of radium emanation is proportional to the amount of emanation present at any time, and to the gas pressure such that $\log (p/p_0)=kE(e^{-\lambda t}-1)$, where E_0 denotes the initial amount of emanation expressed in curies which is decaying proportionally to the factor $e^{-\lambda t}$; k is a constant; and p_0 and p mm. are respectively the initial pressure and the pressure at the time t. Increasing the volume of the gas decreases the velocity constant such that in a spherical bulb of diameter d, $k=84{\cdot}1d^{-2}$. An excess of oxygen gives a velocity constant higher than normal; an excess of hydrogen acts in the opposite direction. For each pair of ions produced by the emanation, about 3·9 molecules of water are formed. From A. T. Cameron and W. Ramsay's measurements, S. C. Lind showed a parallelism between chemical action and ionization, but O. Scheuer found about 5·5 molecules of gas combined for each pair of ions produced, and E. Wourtzel found that in general, the amount of reaction is in excess of ionization. This led

A. Debierne to reject the assumption that ionization is the primary cause of the reaction, and he suggested that the passage of an α-particle through a gas may thermally decompose molecules lying outside the ionization zone. S. C. Lind explains the apparent discrepancy on the assumption that the *recoil atoms* contribute to the ionization. When an atom emits an α-particle at a high speed, the residual atom recoils with a velocity about $\frac{1}{50}$th of that of the emitted particle, and the velocity and corresponding kinetic energy suffice to give the recoil atoms ionizing properties. The resulting calculation shows that there is a statistical agreement between the actual number of ions produced and the number of reacting molecules.

According to T. de Saussure,[4] (v) various organic substances (peas, corn, and humus) in the act of decomposition may stimulate the union of hydrogen and oxygen gases. (vi) J. B. Biot (1805) found that detonating gas combined under *pressure* in an iron tube, but heat developed by the compression may have raised the mixture to the temperature of ignition, for F. de la Roche (1811) observed no combination under a pressure of 50 atm. applied gradually; nor did A. F. E. Degen (1836) observe any signs of the recombination of the gases from the electrolysis of sulphuric acid, at a pressure of 150 atm. H. N. Warren (1893) states that an explosion with the production of flame occurs under these conditions at 180 atm. pressure, but it is not clear from his account whether or not combination occurred—his tubes always burst—he may have simply compressed the gas to the bursting pressure of the tube. (vii) Electrolytic gas may be confined an indefinite time over water or mercury, at ordinary temperatures, in darkness, with no tangible sign of chemical action, but according to H. B. Baker, if detonating gas be ***exposed to sunlight***, there is a slow combination. This no doubt explains the contradictory observations of B. Hooke (1803) and T. de Saussure (1815), for the former claimed that the gases slowly combine on standing some months, while the latter contradicted this statement.

V. Meyer and W. Raum[5] could detect no sign of combination when a mixture of hydrogen with half its volume of oxygen was heated in glass bulbs for 218 days at 100°; at 300° the formation of water could just be detected after 65 days; at 350°, in four bulbs, between 0·5 and 1·9 per cent. had combined in 5 days, and in one bulb 16·4 per cent. in the same time. W. A. Bone attributes this to a slight devitrification of the glass because he found similar accelerations in the speed of the reaction with bulbs partially devitrified. At 400°, says W. A. Bone, we are on the border line where the formation of water may be recognized within a week, but hardly within three days. The reaction then progresses the faster the higher the temperature. H. Helier passed the mixed gases through a glazed porcelain tube packed with pieces of porcelain so as to present a large surface to the gas; he could detect but a slight combination at 180°, and found that the reaction progresses faster and faster as the temperature is raised. At any assigned temperature, there is a limit beyond which no further combination ensues. For example, the percentage amount of water formed at different temperatures was found to be as follows:

200°	260°	300°	311°	376°	498°	637°	825°
0·12	1·6	3·8	9·8	25·1	56·4	85·6	96·1

At 840° the mixture exploded. Water vapour does not dissociate at these temperatures, and accordingly there appear to be two equilibrium states for the reaction: $2H_2O \rightleftharpoons 2H_2 + O_2$, according as equilibrium is approached by decomposing water vapour, or by uniting the elementary gases. Does not this conflict with the general theory of mass action? M. Bodenstein believes that a true state of equilibrium was not obtained by H. Helier, and that if he had heated his mixtures longer, no discrepancy would have been detected. On the other hand, P. Duhem believes that the system in H. Helier's experiment acquired a passive condition called a state of *false equilibrium*. Great differences in speed of the reaction have been obtained by different experimenters, and M. Berthelot has shown that this must be largely due to the nature of the surface exposed to the gas. Indeed, there are many reasons for supposing that the reaction takes place only on the surfaces of the solid; but with the facts available it is at present impossible to infer, with any degree of certainty, what would be the course of the reaction in a vessel with walls absolutely inert.

The union of hydrogen and oxygen, and the decomposition of water vapour under the influence of ultra-violet light in quartz vessels at 150° and at 240° shows that a definite equilibrium—the same at both temperatures—is attained, $2H_2+O_2 \rightleftharpoons 2H_2O$. The work done by the light rays in the reaction $2H_2O \rightleftharpoons 2H_2+O_2$ is about 44·5 Cals. per gram-molecule of water. Small quantities of hydrogen disappear owing to the reduction of silica by moist hydrogen when stimulated by active light rays. No signs of hydrogen peroxide have been detected in the equilibrium mixture, but if a fast stream of the two gases passes through the apparatus, hydrogen peroxide can be detected in the water which is formed; this is thought to indicate that the union of hydrogen and oxygen takes place in two stages: $2H_2+O_2=H_2O_2+H_2=2H_2O$.

Ignition temperatures.—H. Davy,[6] and T. von Grotthus found that a mixture of hydrogen gas and air heated to a temperature below visible redness, rapidly unites to form water without the evolution of light or heat. The temperature at which detonating gas inflames has been measured by E. Mallard and H. le Chatelier (1880) and many others. The numbers are widely divergent. By plunging a bulb containing mixed gases in a bath at a constant temperature, numbers ranging from 518° to 650° have been obtained, and higher results are obtained if an excess of either gas be present; by passing a stream of the mixed gases through a tube in a bath heated on a gradually rising temperature, numbers ranging from 550° to 845° have been reported; and by measuring the adiabatic compression required to just ignite the gas, and calculating the corresponding temperature, K. G. Falk obtained 540° for the mixture $2H_2+O_2$; 514°, for H_2+O_2; and 530°, for H_2+2O_2. According to H. B. Dixon (1910), the ignition temperatures of mixtures of 100 vols. of hydrogen with *n* vols. of oxygen, by adiabatic compression, are:

Vols. of oxygen .	33·33	40	50	100	200	300	400
Ignition point .	557°	542°	536°	530°	520°	512°	507°

Hence, the most easily ignited mixture is not one in which the proportion of hydrogen to oxygen is as 2 : 1, but when the ratio is 1 : 4. H. B. Dixon and H. F. Coward showed that the ignition temperature falls with increasing pressures; and that a stream of hydrogen at a normal pressure ignites between 580° and 590° in an atmosphere of oxygen, and virtually the same in air. The hydrogen gas was led through a narrow tube in the axis of a larger porcelain tube through which a slow current of oxygen or air was passed. The outer tube was heated by an electric current traversing a coil of wire. A constant ignition point was obtained when the diameter of the outer tube and the speed of the current of gas surpassed a certain minimum value. With an orifice 1 mm. diameter, and an outer tube 4·5 cm. diameter, the gas had to be passed at a rate exceeding 9 c.c. per minute to give constant results. The ignition temperatures obtained with the gases in sealed bulbs are rather lower than the ignition points of flowing gases. According to H. F. Coward, C. Cooper, and C. H. Warburton, a flame which filled a 570 c.c. globe has been obtained with the electrolytic gas at a pressure of 5 mm., and a flame travelled through a cylinder 2 metres long with a gas at 8 mm. pressure. These pressures are lower than have been obtained by others, for previous records gave minimum pressures between 34 and 146 mm. The ignition temperature is largely determined by the nature of the spark discharge. The small amount of gas—0·3 to 5·5 per cent.—which remained uncombined, presumably owing to the cooling of the walls, varied inversely as the original pressure of the gas, and was greater the larger the globes.

Lord Rayleigh (1875) has shown that energy is dissipated when a mixture of hydrogen and oxygen at atmospheric pressure is exploded by an electric spark. The spark itself can be neglected because any given spark can explode an indefinitely large quantity of the mixture. If the gas is expanded at constant temperature before the explosion, and, after the explosion, brought back to its former volume, the pressure required to compress the steam will be less than that exercised by the same volume of uncombined gas, and accordingly work is gained in the operation, for less energy is dissipated during the explosion of the expanded gas than is dissipated by the explosion of the condensed gases. If the expansion be increased without limit, the amount of energy dissipated during the explosion becomes indefinitely small; otherwise expressed, the tendency to combine diminishes the rarer the gas, and there must be a point where the gas becomes so rare that the explosion will not take place.

According to H. B. Dixon (1884),[7] the **speed of the explosion wave** in long tubes containing mixtures of hydrogen and oxygen, nH_2+O_2, is

n	8	6	4	2	1	$\frac{1}{2}$	$\frac{1}{3}$	
Speed	3532	3527	3268	2821	2328	1927	1707	metres per sec.

The speed is thus greater in an excess of the specifically lighter gas, hydrogen, than in an excess of the specifically heavier gas, oxygen.

The catalytic action of metals, etc., by contact.—The combination of hydrogen and oxygen can be *inaugurated* at ordinary temperatures where the most refined observations show no signs of chemical combination, and, where the temperature is such that the gases are actually combining, the speed is *accelerated* by the mere presence of a number of different substances—by finely divided platinum in particular. The phenomenon was discovered by H. Davy in 1817,[8] for he remarked that platinum foil or wire heated to a temperature " short of redness " will induce the combination of oxygen with other inflammable gases or vapours; and P. Erman (1819) showed that a temperature of 50°–51° suffices. After E. Davy (1820) had shown that when finely divided platinum damped with spirits of wine became incandescent owing to the heat generated by the oxidation of the alcohol, J. W. Döbereiner described in a brochure, *Ueber neu entdeckte höchst merkwürdige Eigenschaften des Platins* (Jena, 1823), how finely divided platinum will spontaneously induce the rapid combination of hydrogen and oxygen gas. A. Pleischl noticed that when platinum wire has been in the hydrogen flame for some time it becomes corroded, dull, and dark grey; and that the corroded part subsequently gets hot quickest in the jet of hydrogen gas. W. A. Bone also found that the appearance of a piece of silver gauze before and after it has acted as a catalytic agent for hydrogen and oxygen at 400° changed so that the wires originally smooth became quite rough. These facts are taken to show that the reacting gases during the catalytic action are in very intimate contact with the surface film of metal. P. L. Dulong and L. J. Thénard found that while a coil of new platinum wire—0·05 mm. diameter—must be heated to 300° to make it effective, after several ignitions, it acts as low as 50° or 60°. If the wire be immersed in hot or cold nitric acid, and dried at 200°, it acts at the ordinary temperature of the air, and becomes red hot in a jet of a mixture of air and hydrogen; sulphuric acid acts similarly but is less effective; and hydrochloric acid is still less effective. Potassium or sodium hydroxide destroy the activity of the metal.

P. L. Dulong and L. J. Thénard reported that the property acquired by platinum, by the acid treatment, persists but a few hours when the metal is exposed to the air, and 24 hours if confined in a vessel. The treated metal loses its property if exposed for five minutes to a current of dry air, oxygen, hydrogen, or carbon dioxide; ammonia or the alkali hydroxides deprive the metal of its peculiar power. Platinum foil and platinum filings when fresh and clean exploded a mixture of hydrogen and oxygen. They lose this quality if exposed to air for an hour or two, but the property is recovered if the metal be ignited in a covered crucible. Platinum filings prepared under water have no action. The less active forms of the metal may induce the combination of the mixture of hydrogen and oxygen without causing explosion. M. Faraday showed that a platinum plate must have its surface rigorously clean if it is to effect the combination of detonating gas, and he described several methods of cleaning platinum plates in order to make them active stimulants of the union of hydrogen and oxygen. He also found that the surface of the plates loses its activity on exposure to air for 24 hours, but regains it when gently ignited. A platinum plate is active when it has been used as the anode in sulphuric, nitric, oxalic, tartaric, citric, or acetic acid, or in a solution of potassium phosphate, chlorate, or nitrate, or of sodium or copper sulphate; it acquires less power in hydrochloric acid, still less in potassium or sodium carbonate, and none at all in potassium hydroxide.

According to J. W. Döbereiner, spongy *platinum* is effective at ordinary temperatures in inducing the combination of hydrogen and oxygen; the action is at first slow, but as the temperature rises, the action is very fast; while A. Pleischl, and A. de la Rive and F. Marcet found the ash of filter paper saturated with ammonium chloroplatinate is even more effective than spongy platinum, for the action was then apparent at —20°. E. Davy and J. W. Döbereiner found that very finely divided platinum—platinum black—is still more active. Hence, the more finely divided the platinum, the greater its efficiency in stimulating the union of a mixture of hydrogen and oxygen. Platinum black which has not been freed from oxygen can induce the union of the two elements at the temperature of liquid air, —190°.

J. W. Döbereiner, P. L. Dulong and L. J. Thénard, M. Faraday, A. Pleischl, W. C. Henry, and A. de la Rive and F. Marcet obtained similar results with *iridium* and *palladium*; *osmium* acts at 40° or 50°; spongy *rhodium* at 240°; *gold* leaf at 260°; gold paper ash at 50°; and *silver* leaf below 357°; silver paper ash, 120° to 150°. W. C. Henry found finely divided *copper* at 264° does not set fire to a stream of hydrogen but the copper oxidizes; at higher temperatures the powder becomes red hot. E. D. Campbell found an alloy of copper with one per cent. of palladium—*palladized copper*—stimulates the union of hydrogen and oxygen; *cobalt* and *nickel* behave similarly; while P. L. Dulong and L. J. Thénard say copper and nickel act at 300°. W. C. Henry found that *iron* reduced from the oxide induces rapid combination of hydrogen and oxygen at the temperature of reduction. Copper or iron turnings, *zinc* foil, and *charcoal* were reported by W. C. Henry to have no action, but P. L. Dulong and L. J. Thénard found charcoal, *pumice stone*, *porcelain*, *rock crystal*, and *glass* to act below 350°; the action of *fluorspar* is very feeble. P. L. Dulong and L. J. Thénard say that angular pieces of glass are twice as active as rounded pieces of equal surface in stimulating the union of hydrogen and oxygen. *Mercury* at its boiling point has no appreciable action. Devitrified glass bulbs were found by W. A. Bone to accelerate the reaction at about 300°; and M. Berthelot found *barium hydroxide*, *alkali salts*, and *manganese salts* raised the speed of the reaction between 250° and 300°.

R. Böttger found that *ammonia* gas destroys the activity of platinum—even a drop of a solution of ammonia evaporating in a room suffices. The vapour of nitric acid or chlorine restores the activity removed by ammonia. J. S. C. Schweigger adds that *hydrogen sulphide*, *ammonium sulphide*, and particularly *carbon disulphide* render the metal inactive, and the activity is not restored by nitric acid or chlorine. W. Artus showed that the activity may be also destroyed by the traces of hydrogen sulphide present as impurities in hydrogen gas, and M. Faraday showed that hydrogen prepared by the decomposition of water by red hot-iron is not affected by either spongy platinum or platinum foil—presumably because the activity of the catalyst is quelled by the impurities in the gas. According to E. Turner, finely divided platinum does not become inactive when confined 24 hours over mercury in an atmosphere of oxygen, hydrogen, carbon dioxide, or air; it loses part of its power after 5 min. exposure to *hydrogen chloride*, still more in *ethylene* or coal gas; and it becomes inactive in *sulphur dioxide*, hydrogen sulphide, or ammonia.

A little moisture favours the action, for W. French (1900) showed that if the mixture be thoroughly dried, finely divided platinum does not start the reaction. If the metal be wet with water, the action is feeble at first but gradually increases as the water evaporates; similar remarks apply if the metal be wetted with alcohol or ether; and if wetted with sulphuric, nitric, or hydrochloric acid, the metal is inert. W. Henry also found that spongy platinum produces its effect if one volume of detonating gas be mixed with ten volumes of oxygen, hydrogen, nitrogen, or methane; or with six volumes of hydrogen chloride; but it is either prevented or very much retarded by 11 vols. of nitrous oxide; 3 vols. of carbon dioxide; 1½ vols. of ethylene; 1 vol. of cyanogen; or 0·5 vol. of carbon monoxide. Spongy platinum is inactive in a mixture of detonating gas with an equal volume of carbon monoxide, hydrogen sulphide, or ethylene, but platinum black becomes red hot and combination rapidly occurs. E. Turner, M. Faraday, and W. C. Henry also made observations on the retarding effects of carbon monoxide, sulphur dioxide, hydrogen sulphide, hydrogen chloride, ammonia, nitrous oxide, carbon disulphide, and ethylene on the union of detonating gas by finely divided platinum.

According to T. Graham, only impure ethylene retards the activity of spongy platinum; the purified gas does not affect the metal, and he states that in a mixture of ethylene, hydrogen, and oxygen, spongy platinum acts only on the hydrogen, not on the ethylene, so that the two gases may be separated by this agent. W. Henry also noticed that if oxygen be mixed with hydrogen, carbon monoxide, methane, and nitrogen gases, and passed over spongy platinum at 177°, the hydrogen and carbon monoxide are alone oxidized. W. Hempel based a method for analyzing certain mixtures of gases on the power possessed by finely divided palladium or platinum of inducing preferential *fractional combustion* in this manner. H. Landolt also found that hydrogen burns more readily than methane or ethylene in a flame when in the presence of platinum, but W. A. Bone has shown the need for a repetition of these experiments. W. A. Bone and his co-workers found that in explosive reactions the affinity of methane is at least 20 to 30 times greater than that of hydrogen for oxygen. At high temperatures the specific nature of the solid catalytic agent becomes negligible because the reaction takes place so rapidly in the gas phase. W. A. Bone found that hydrogen burns more readily than methane at 500° in the presence of broken firebricks (grog); in borosilicate glass tubes, at 300°-400°, methane, ethylene, and acetylene are burned more quickly than hydrogen or carbon monoxide; E. Jäger says that in the presence of copper oxide at 250°, all the hydrogen in a mixture of hydrogen and methane can be burned without decomposing the methane. W. D. Bancroft adds that at low temperatures the nature of the catalytic agent may determine which of two combustible gases will burn the more readily. Since charcoal causes the oxidation of ethylene to carbon dioxide and water, and since charcoal has very little effect on a mixture of hydrogen and oxygen, it is probable that charcoal will cause the preferential combustion of ethylene in a mixture of ethylene and hydrogen.

There have been many attempts to explain **the mechanism of the catalytic activity** of platinum. J. W. Döbereiner and J. S. C. Schweigger vaguely attributed the phenomenon to the electrical reactions between the different substances concerned in the action. One of the oldest hypotheses is due to A. Fusinieri (1825) and M. Faraday (1834). It refers the action to the absorption or *the condensation of the reacting gases on the surface of the metal*, and the enhanced faculty of combination possessed by the gases in this condensed state. J. Babinet, L. Meyer, G. H. Quincke, and J. J. Thomson also attribute the action in part to the change in the physical condition of the molecules of the reacting gases in contact with the catalytic agent. M. Bodenstein's measurements of the rate of the reaction at the higher temperatures (short of explosion) correspond with a termolecular reaction, $2H_2+O_2=2H_2O$, whereas at lower temperatures the reaction is monomolecular, for the rate of the reaction is then proportional to the pressure of the gas—the rate of absorption of each gas is also proportional to its pressure. Hence it is inferred that the main reaction at low temperatures takes place on the surface of the metal, and is dependent on the rates of absorption of the two gases by the metal, and also on the rate of diffusion of the products of the reaction away from the seat of the reaction on the surface of the metal. C. Ernst also found that the rate of combination of hydrogen and oxygen dissolved in water in contact with electrolytic gas is proportional to the rate of solution of the mixed gases, which in turn is proportional to the pressure of the gases lying above the surface of the water. M. Bodenstein found similar results for the action of Bredig's colloidal platinum in water. This agrees with the observations of W. A. Bone and R. V. Wheeler, W. A. Rowe, etc.

Another hypothesis, suggested by A. de la Rive and F. Marcet (1839) and by C. Engler and L. Wöhler (1901), assumes that there is *a rapidly alternating series of oxidations and reductions of the surface of the metal.* A platinum oxide is first supposed to be formed: $Pt+nO_2=PtO_{2n}$; the oxide is immediately reduced: $PtO_{2n}+2nH_2=2nH_2O+Pt$; the reduced metal is re-oxidized, to be reduced again, and so on indefinitely. In support of the view that the formation of an oxide of platinum is an intermediate stage of the catalyzed reaction, oxidized platinum is stated to be a more active catalytic agent than platinum alone. M. Berthelot and P. Sabatier suggested that a hydride, not oxide of platinum, is formed as the intermediate stage in the reaction.

How the metal carries oxygen to the hydrogen or hydrogen to the oxygen has not been definitely established. W. D. Bancroft sums up the evidence by stating that while the effect of platinum may be due to an oxidation, it is doubtful if this is the case with charcoal and oxygen. In general, with contact catalysis: (i) only those substances which are absorbed by a solid are catalyzed by it; (ii) while the catalytic action of solids may be solely the result of the increased surface concentration in some cases, this is not always the only factor; (iii) a solid catalytic agent may be considered as equivalent to a solvent and may therefore displace the equilibrium; (iv) as a result of selective adsorption we may get different reaction products with different catalytic agents; (v) a catalytic agent tends to produce the system which it absorbs the most strongly.

I. Langmuir[9] mounted a short filament of platinum in a 4-litre bulb; this was electrically heated in a mixture of hydrogen and oxygen in the absence of water vapour, at low temperatures and low pressures, and he found that the rate of the reaction V is directly proportional to the pressure of the oxygen, p_2, and inversely proportional to the pressure of the hydrogen p_1, so that $V=k_1p_2/p_1$, where k_1 is a constant; while at higher temperatures the rate varies with the partial pressures of the two gases, so that the speed of the reaction $V=k_2p_1p_2$, where k_2 is a constant. I. Langmuir here assumed that a certain fraction of the hydrogen molecules which strike the surface of the platinum are condensed, and the layer of hydrogen thus formed distils off at a certain rate; he further assumes that the reaction occurs when the hydrogen molecules strike oxygen on the surface, but not when oxygen molecules strike hydrogen molecules.

The energy of the reaction between hydrogen and oxygen.—According to W. G. Mixter (1903), the **heat of combustion** of a gram of hydrogen at constant pressure to form liquid water at 0° is 33993 cals.; and the mean value of the observations of other recent observers is 34022 cals. with a possible error of about $\frac{1}{10}$th per cent. The **heat of formation** Q, of a gram-molecule of water, $H_2+\frac{1}{2}O_2=H_2O$, at atmospheric pressure, and 0°, is, according to M. Berthelot and C. Matignon[10] (1893), 70·4 Cals. for ice; 69·0 Cals. for the liquid; and 58·1 Cals. for the vapour all at 0°. The change in the heat of combination of hydrogen and oxygen to form a gram-molecule of liquid water per degree change of temperature, can be calculated from G. Kirchoff's equation $dQ/dT=\Sigma(C-C_1)$, where ΣC denotes the sum of the specific heats of the reacting products, and ΣC_1 that of the end-products. Taking the molecular heat of hydrogen as 6·8 cals.; of oxygen, 6·96 cals.; of water, 18 cals., it follows that $dQ/dT=6{\cdot}8+3{\cdot}48-18$, and the heat of formation of a gram-molecule of water decreases 7·72 cals. per degree rise of temperature. The heat of formation Q of water vapour decreases perceptibly with a rise of temperature; it is 50·5 Cals. at 2000°, and 37·1 Cals. at 4000°. W. Nernst and H. von Wartenberg found that at constant pressure, $Q_p=57200+1{\cdot}37T-0{\cdot}000365T^2-0{\cdot}0_6312T^3$ cals. per gram-molecule of the gas, and F. Haber and L. Bruner, at a constant volume, $Q_v=57084-2976T-0{\cdot}00125T^2$ cals.

A platinum plate charged with hydrogen, and a platinum plate charged with oxygen, behave in conducting liquids as if they were electrodes made of the respective gases which conduct electrically. If these electrodes be immersed in a solution of an electrolyte, there is formed a voltaic combination, H_2 | Aqueous solution | O_2 known as *Grove's gas cell,* which gives an electromotive force of 1·15 volts, but the calculated value from H. von Helmholtz's equation (1847) furnishes 1·23 volts at 7° on the assumption that the hydrogen and oxygen are under a pressure of one atmosphere. The free energy of the reaction $H_2+\frac{1}{2}O_2=H_2O$ is therefore equivalent to 475,000 joules. The discrepancy has been attributed to the formation of an oxide of platinum at the oxygen electrode. E. Bose obtained 1·1392+0·015 volts from the gas battery, and this makes the heat of formation of water vapour 52·654 Cals. This agrees with G. Preuner's value. M. de K. Thompson calculated from potential measurements 57·5 Cals. for water vapour, and 67·6 Cals. for liquid water at 0°; J. Thomsen gives 68·3 Cals., C. von Than, 68·43 Cals.; A. Schüller and V. Wartha, 68·25 Cals. for liquid water at 0°. The reported values for the heat of formation of water are therefore very concordant, and G. N. Lewis considers the best representative value to be 68·47 at 0°. J. E. Mills calculates for ice at −273°, 71·4 Cals.

According to W. Nernst and H. von Wartenberg (1906), the **free energy of the reaction** $H_2+\frac{1}{2}O_2=H_2O$ when the two gases are at atmospheric pressure, and at 1000° K. is 90·6 Cals., showing that there is a large positive chemical affinity between those gases at this temperature. G. N. Lewis and M. Randall calculate the free energy of the reaction $H_2+\frac{1}{2}O_2=H_2O$ to be $F=-57410+0{\cdot}94T\log T+0{\cdot}00165T^2-0{\cdot}00000037T^3+3{\cdot}66T$. This makes the free energy of formation of a gram-molecule of gaseous water at 25°, *i.e.* 298° K., −54590 cals. If the vapour pressure of water be 23·8 mm. at 25°, barometer 760 mm., the free energy $=-RT\log(760/23{\cdot}8)=-2053$; the free energy of formation of liquid water at 25° becomes −56640 cals. The value calculated from the heat of dissociation of silver oxide is −56530 cals.; from the dissociation of mercuric oxide, −56650 cals.; and from the e.m.f. of the hydrogen: oxygen cell, −54567. The free energy of the formation of a gram-molecule of ice is −56478 cals.; and the free energy of fusion $H_2O_{solid}=H_2O_{liquid}$ is $F=-1022-9{\cdot}0T\log T+54{\cdot}230T$, or −141·6 cals. at 25° when the heat of fusion is 79·7 cals. per gram, or 1436 cals. per gram-molecule.

The decomposition of water.—Water is fairly stable, and even at the high temperature of the oxyhydrogen flame—estimated to be over 3000°—the amount decomposed is small although quite appreciable. Water is decomposed (i) by exposure to very high temperatures; (ii) by the electrolysis of the liquid; (iii) by passing a series of electric sparks or the silent discharge[11] through the vapour; (iv) by the formation of an electric arc under the liquid—as shown by W. Loeb; (v) by the action of the alkali metals at ordinary temperatures or of other metals at higher temperatures whereby *the oxygen of the water is fixed by the metal, and hydrogen gas escapes*; and (vi) by exposing water to the action of fluorine at ordinary temperatures, or of chlorine or bromine light or heat whereby *the hydrogen of the water is fixed by the halogen, and oxygen escapes.* Again, (vii) W. Ramsay found that water is decomposed by the dissolution of radium salts in the water, whereby a stream of hydrogen is continuously evolved; and (viii) M. Kernbaum, that water is decomposed by exposure to ultra-violet light: $2H_2O=H_2O_2+H_2$.

W. Ramsay and F. Soddy decomposed water acting as solvent with a radium salt as solute, and W. H. Bragg noted what he called "a curious parallelism in numbers" in that the number of molecules of water decomposed was almost exactly equal to the number of ions which would have been produced in air by the emanation employed. K. Bergwitz noted the decomposition of water by the α-rays of polonium deposited on copper, and M. le Blanc showed that the results closely approximated to the requirements of Faraday's law—the ionization and chemical action are of the same statistical order. W. Duane and O. Scheuer also found a close equivalence between ionization and the amount of water decomposed. S. C. Lind showed that the recoil atoms also play a part in producing ionization, and that if ionization by α-particles be alone considered, the chemical effects produced appear greater than corresponds with ionization.

In 1847, W. R. Grove described in a paper, *On the decomposition of water into its constituent gases, by heat*,[12] an experiment in which hydrogen and carbon dioxide were heated in a tube by means of a wire heated white hot by means of an electric current. Carbon monoxide and water were formed, $CO_2+H_2=CO+H_2O$. If carbon monoxide be similarly heated under precisely similar conditions, carbon dioxide and hydrogen are formed $CO+H_2O=CO_2+H_2$. Now, added W. R. Grove,

> It appeared to me ultimately that the ignited platinum had no specific effect in producing either composition or decomposition of the water, but it simply rendered the chemical equilibrium unstable, and that the gases then restored themselves to a stable equilibrium according to the circumstances in which they were placed, with regard to surrounding affinities ; that if the state of mixed hydrogen and oxygen were, at a certain temperature, more stable than that of water, ignited platinum would decompose water as it does ammonia. . . . It now appeared to me that it was possible to effect the decomposition of water by ignited platinum : that supposing the atmosphere of steam in the immediate vicinity of platinum were decomposed, or the affinities of its constituents loosened, if there were any means of suddenly removing this atmosphere, I might get the mixed gases ; or secondly, if quantity had any influence, that it might be possible to so divide the mixed gases by a quantity of neutral ingredient as to obtain them by subsequent separation (or as it were filtration) from the neutral substance.

W. R. Grove then related that when the incandescent wire converted water into steam, some steam was always decomposed, and a small bubble of mixed hydrogen and oxygen gases was formed.

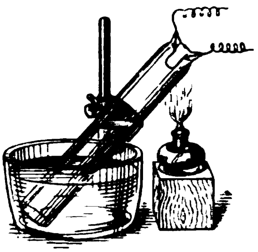

FIG. 25.—W. R. Grove's Experiment.

A glass tube with a piece of platinum wire sealed at the upper end and filled with water, is placed in an inclined position, and heated in its upper part by means of a spirit-lamp as shown in Fig. 25. The platinum wire is heated to incandescence by a suitable battery. In a few moments the lamp is removed, and the water is again allowed to fill the tube. A bubble of mixed gas remains in the tube, and it can be examined. However long the heating be continued no further decomposition occurs, for the equilibrium conditions between the water vapour and the products of decomposition are established immediately the wire becomes incandescent. The experiment was repeated with a similar result when electric sparks were passed from one wire to another inside the tube ; and also when a platinum tube was heated with a blowpipe flame, and no electrical heating employed.

W. R. Grove's work was undoubtedly the starting point of the modern theory of dissociation, even though his explanations are couched in different terms. Ten years after W. R. Grove, the subject was resumed by H. St. C. Deville,[13] who, in 1857, repeated Grove's experiments on a larger scale, and introduced many other ingenious modifications. He was able to collect a relatively large amount of the mixture of oxygen and hydrogen by pouring one to three kilograms of molten platinum into a vessel of water.

H. St. C. Deville also passed the vapour of water through a porous tube of earthenware, placed in the axis of a wider glazed porcelain tube, and passed a current of carbon dioxide in the annular space between the two tubes. The whole was heated in a furnace to about 1300°. The gases from the water dissociated in the inner tube, passed through the porous walls at different rates, and were carried away before they had the chance of recombining in the cooler parts of the tube. The carbon dioxide was removed by absorption in potash. There are two important objections to this experiment—first, it is doubtful if the temperature was high enough to give an appreciable amount of decomposition, and second, there is a possible reaction between the hydrogen and carbon dioxide. In A. W. Hofmann's experiment (1890), a stream of water vapour is quickly passed through a tube containing a strip of platinum foil heated to incandescence by an electric current, and the resulting hydrogen and oxygen are prevented from recombining on cooling. The mixed gases are collected in a cylinder over water.

The word **dissociation** was coined by H. St. C. Deville (1857) and was used synonymously for *decomposition*, but three years later, he used the term to characterize the temporary disjunction of the molecules of certain bodies into their elements at elevated temperatures. He assumed that bodies possess, at a temperature below their decomposing point, a certain tendency to decompose which he called their *dissociation tension*.

E. Mallard and H. le Chatelier (1881) showed that the pressure developed during the explosion of a mixture of hydrogen and oxygen is rather less than that calculated on the assumption that combustion is complete. It was therefore inferred that a small proportion remains uncombined. It will also be observed that the back-reaction, $2H_2O=2H_2+O_2$, the un-burning, so to speak, sets a limit to the temperature attainable in a combustion dependent on the reaction symbolized: $2H_2+O_2=2H_2O$. W. Nernst and H. von Wartenberg were able to show that steam dissociates by heat, and that the reaction is balanced by the recombination of the products of decomposition to re-form water vapour: $2H_2O=H_2+O_2$. Only about 0·00003 per cent. is dissociated at 1000° and 3·98 per cent. at 2500°. The equilibrium constant, K, for the reaction $2H_2O\rightleftharpoons 2H_2+O_2$ is $[H_2]^2[O_2]=K[H_2O]^2$, where the bracketed terms denote concentrations—say partial pressures. If a gram-molecule of water be decomposed into two gram-molecules of hydrogen, and one of oxygen, and if x denotes the degree of dissociation, there will be present $1-x$ gram-molecules of water, x of hydrogen, and $\frac{1}{2}x$ of oxygen. The total volume will be $1-x+x+\frac{1}{2}x=1+\frac{1}{2}x$, and if p denotes the total pressure, the partial pressure of water will be $[H_2O]=p(1-x)/(1+\frac{1}{2}x)$; of hydrogen, $[H_2]=px/(1+\frac{1}{2}x)$; and of oxygen, $[O_2]=\frac{1}{2}px/(1+\frac{1}{2}x)$. By substitution, therefore, the equilibrium equation reduces to

$$K=\frac{px^3}{(2+x)(1-x)^2}$$

If x is small, $K=\frac{1}{2}px^3$, or $\log K=3\log x-\log 2$, at atmospheric pressures when $p=1$. In that case W. Nernst gives $3\log_{10}x=-25050T^{-1}+1{\cdot}75\log_{10}T+0{\cdot}00028T+0{\cdot}1$. W. Nernst and H. von Wartenberg[14] further obtain

$$\log K=11{\cdot}46-\frac{25030}{T}+2{\cdot}38\log\frac{T}{1000}-1{\cdot}38\times10^{-4}(T-1000)-6{\cdot}85\times10^{-8}(T^2-1000^2)$$

The calculated degrees of dissociation at different pressures and temperatures are indicated in Table XVII.

TABLE XVII.—DEGREE OF DISSOCIATION OF WATER AT DIFFERENT TEMPERATURES.

θ° C.	Degree of dissociation, x per cent.			
	$p=10$ atm.	$p=1$ atm.	$p=0{\cdot}1$ atm.	$p=0{\cdot}01$ atm.
727°	0·0000139	0·00003	0·0000646	0·000139
1227°	0·0103	0·0221	0·0476	0·103
1727°	0·273	0·588	1·26	2·80
2227°	1·98	3·98	8·16	16·6

The values agree satisfactorily with W. Nernst and H. von Wartenberg's observations below 2000° and with N. Bjerrum's above that temperature:

	1124°	1288°	1984°	2369°	2488°	2656°
x . .	0·0073	0·034	0·77	4·3	8·6	11·1 per cent.

I. I. Andréeff found that a mixture of hydrogen and oxygen, when exposed to the ultra-violet light from a mercury lamp, unite to form water at a constant speed, which is independent of the concentration of the reacting gases, but is almost proportional to the intensity of the light. Water is also decomposed under the influence of ultra-violet light. The same condition of equilibrium is attained whether a mixture of hydrogen with half its volume of oxygen, or water-vapour be exposed to the light. With an increase in the intensity of light, the equilibrium is displaced in favour of dissociation.

The electrolysis of steam.—In 1858, A. Perrot [15] noticed that when an electrical discharge is passed through steam, there is a kind of electrolysis, and J. J. Thomson found that with *short* sparks, the gases which collect at the negative electrode contain an excess of oxygen, and those at the positive, an excess of hydrogen—the total gas collected corresponds with that obtained in the voltameter exactly as would be obtained with a true electrolysis. It was therefore inferred that the current is conveyed through water vapour in the same manner as through water. With *long* sparks this state of things is reversed and the excess of hydrogen changes over to the negative electrode, and the excess of oxygen to the positive electrode—the hydrogen collected is less than would correspond with a true electrolysis. Hence, adds J. J. Thomson,

> There is this remarkable difference between the electrolysis of steam and water, that whereas in the case of water, the hydrogen always comes off at the negative, and the oxygen at the positive electrode ; in the case of steam, the hydrogen and oxygen come off sometimes at one terminal, sometimes at the other, according to the nature of the spark.

According to D. L. Chapman and F. A. Lidbury, the electrolysis of water vapour does not take place in such a manner that the hydrogen appears at one pole and oxygen at the other, but when water vapour is decomposed by electric sparks, the hydrogen separates at both electrodes, and it has a tendency to accumulate in the neighbourhood of the two electrodes, while the oxygen is driven towards the middle of the spark gap. The nature of the gases collected at the respective electrodes is determined by the velocity of the current of steam, as well as by the nature of the sparks. Hydrogen can diffuse against the stream of water vapour much faster than oxygen. When electric sparks are passed through steam (or other compound gases), the distribution of the products of decomposition is not always the same as when the corresponding liquid is electrolyzed. The decomposition may occur in the entire path of the spark as well as in the neighbourhood of the electrodes. The distribution of the decomposition products about the two electrodes is determined by the position of the tube bringing the current of steam to the electrodes and the relative rates of diffusion of the constituent gases.

Water is *par excellence* a solvent. Aqueous solutions of certain salts can dissolve some substances not soluble in pure water—*e.g.* salts of benzoic, salicylic, and benzenesulphonic acids on certain alkaloids, fats, alcohols, and carbohydrates. The phenomenon is termed *hydrotropism* by C. Neuberg (1916).[16] The **metals** act as reducing agents towards water forming an oxide—usually basic—and liberating hydrogen ; or reciprocally, water acts as an oxidizing agent on the metals—*e.g.* it has been shown that with sodium, $2Na+2H_2O=2NaOH+H_2$; and with iron, $3Fe+4H_2O=Fe_3O_4+4H_2$. The behaviour of the metals towards water was used as an important criterion in L. J. Thénard's and H. V. Regnault's systems of classifying the metals.[17] They first attempted a dichotomous separation into metals whose oxides can be decomposed by heat alone, and those whose oxides cannot be so decomposed. The metals were then arranged in five sub-groups : (1) metals which decompose cold water—*e.g.* the metals of the alkalies and of the alkaline earths ; (2) metals which decompose hot water between 50° and 100°—*e.g.* beryllium, magnesium, etc. and a number of the rare earth metals, etc. ; (3) metals which decompose water at a red heat—*e.g.* zinc, cadmium, tin, iron, nickel, cobalt, chromium, osmium, etc. ; (4) metals which decompose water only at a white heat—*e.g.* copper, lead, etc. ; (5) metals which do not decompose water at any temperature—*e.g.* mercury, silver, gold, and members of the platinum family excepting osmium.

The **halogens** act as oxidizing agents on water liberating oxygen ; or reciprocally, water acts as a reducing agent on the halogens—*e.g.* with chlorine, $2Cl_2+2H_2O=4HCl+O_2$. With **sulphur** and **phosphorus** the hydrogen of the water forms a hydride and the oxygen forms an oxide which may unite with water furnishing an acid: *e.g.* with sulphur over 100°, $2H_2O+3S=2H_2S+SO_2$; and with phosphorus at 250°, $3H_2O+2P=PH_3+H_3PO_3$—if air be present the action occurs at a lower temperature. Some of the non-metals act like the metals and form an oxide—usually acidic—and liberate hydrogen—*e.g.* carbon and **boron** at a red heat. The reaction with **carbon** is symbolized: $C+H_2O=CO+H_2$ and $C+2H_2O=CO_2+2H_2$; there is also a reversible side reaction, $CO_2+H_2\rightleftharpoons H_2O+CO$. Some oxides react with water liberating hydrogen—for instance, in the reaction last symbolized carbon monoxide is decomposed by water vapour forming carbon dioxide and hydrogen; similarly, **manganous oxide** forms the brown oxide, Mn_3O_4, and hydrogen, $3MnO+H_2O=Mn_3O_4+H_2$; **uranium oxide,** UO_2, gives the green oxide, U_3O_8, and hydrogen; **chromous oxide** in acid solution is oxidized by water and hydrogen is slowly evolved; **potassium cobaltocyanide,** K_4CoCy_6, on oxidization by water to the cobalticyanide, K_3CoCy_6, gives off hydrogen [18]; when an alkaline solution of **molybdenous chloride,** Mo_3Cl_6, is warmed, a black precipitate of $Mo(OH)_3$ is produced, and hydrogen is evolved: $2Mo_3Cl_6+18H_2O=6Mo(OH)_3+12HCl+3H_2$. Neither **iodine** nor **aluminium** alone acts chemically on water. but remarkably enough, conjointly these elements attack water with the evolution of hydrogen. J. H. Gladstone and A. Tribe [19] consider that there is first formed a little aluminium iodide, AlI_3, which is immediately decomposed by water whereby aluminium hydroxide, $Al(OH)_3$, and hydriodic acid, HI, are produced: $AlI_3+3H_2O=Al(OH)_3+3HI$; the hydriodic acid immediately attacks the metal re-forming aluminium iodide with the evolution of hydrogen: $2Al+6HI=2AlI_3+3H_2$. Water also reacts with many **metal dioxides** forming hydroxides. For example, with the oxides of the alkalies and alkaline earths a base is formed—thus, with calcium oxide the reaction is symbolized, $CaO+H_2O=Ca(OH)_2$. With the **non-metallic oxides** an acid is formed—thus, the products with sulphur trioxide, SO_3, and water, are sulphuric acid, H_2SO_4, in symbols: $SO_3+H_2O=H_2SO_4$.

Water reacts with many metal **phosphides, silicides,** or **carbides**, respectively forming hydrogen phosphide, silicide, or carbide (hydrocarbon), and the metal oxides or hydroxides: *e.g.* calcium carbide, CaC_2, gives acetylene, C_2H_2, and calcium hydroxide: $CaC_2+2H_2O=C_2H_2+Ca(OH)_2$; similar remarks apply to the carbides of the alkali and alkaline earth metals; aluminium or beryllium carbides give methane, CH_4; and other carbides give various mixtures of hydrogen and hydrocarbons. The **sulphides** and **selenides** of boron, silicon, aluminium, and magnesium are decomposed by water furnishing hydrogen sulphide or selenide, and the metal hydroxide, or, in the case of the non-metals, an acid and the metal hydroxide. The **nitrides** of the metals usually give ammonia with cold or hot water; the metal **hydrides** give hydrogen under similar conditions—the metal hydroxide is formed simultaneously. The **organo-metallic compounds** of the more oxidizable metals give the corresponding hydrocarbon and the metal hydroxide—*e.g.* zinc methide, $Zn(CH_3)_2$, gives methane, CH_4, and zinc hydroxide, $Zn(OH)_2$.

Many **halogen compounds** give the haloid acid and either an oxyhaloid or hydroxide of the other element, *e.g.* with phosphorus pentachloride, PCl_5, hydrochloric acid, HCl, and phosphoric acid, H_3PO_4, are formed: $PCl_5+4H_2O=5HCl+H_3PO_4$; with antimony chloride, antimony oxychloride, $SbOCl_3$, and hydrogen chloride, HCl, are formed by a reversible reaction: $SbCl_5+H_2O=SbOCl_3+2HCl$. The **esters**—studied by M. Berthelot and L. P. de St. Giles [20] in their *Recherches sur les affinités* (1861-3)—are broken down by water—preferably in dilute acid solution; *e.g.* ethyl acetate, $CH_3COOC_2H_5$ forms acetic acid, $CH_3CO.OH$, and alcohol, C_2H_5OH. The reaction gradually slows down, and finally comes to a standstill, when a certain proportion of the four components of the reaction are present:

$$\underset{\text{Ethyl acetate.}}{CH_3CO\,OC_2H_5}+\underset{\text{Water.}}{H\,OH}=\underset{\text{Acetic acid.}}{CH_3CO.OH}+\underset{\text{Ethyl alcohol.}}{C_2H_5OH}$$

The distribution of these four components when the system is in equilibrium depends on their concentration, and on the temperature. The work on this reaction is classical, and it played an important *rôle* in the evolution of the law of mass action. Reactions like the so-called **hydrolysis** of potassium cyanide, KCy, symbolized, $KCy+H_2O=KOH+HCy$; and of ammonium chloride, $NH_4Cl+H_2O=NH_4OH+HCl$, are similar in character, and the ionic hypothesis attempts to describe the mechanism in still more detail. Water also forms a series of hydrated compounds with the elements—*e.g.* $Br_2+10H_2O=Br_2(H_2O)_{10}$, or $Br_2.10H_2O$—or with compounds—*e.g.* $FeSO_4.6H_2O+H_2O=FeSO_4.7H_2O$; and also $Na_2SO_4+10H_2O=Na_2SO_4.10H_2O$. The relations of the water in these compounds to the rest of the molecule has been much discussed.

The different behaviour of one of the two hydrogen atoms in water towards sodium, ethyl iodide, C_2H_5I, and phosphorus trichloride, PCl_3, led W. Ganswindt (1891)[21] to assume that water is hydrogen hydroxide, H—(OH). The argument, however, is rather weak, because it is possible that there is an equal probability of, say, sodium displacing either of the hydrogen atoms in water, H.O.H, but that as soon as one hydrogen atom has been replaced by sodium, the molecule with its one hydrogen atom becomes more resistant. J. W. Brühl (1896) assumed that water contains quadrivalent unsaturated oxygen because water exhibits, beyond most other substances, an unsaturated character—as exemplified by its faculty of forming hydrated and crystalline compounds, and its great solvent and ionizing powers. Hence, J. W. Brühl represents the molecule of water by the formula $H\cdot\dot{O}\cdot H$.

The adsorption of water by solids.—Probably many substances adsorb water vapour, so that after exposure to air, they are covered with a film of moisture which they retain so very tenaciously that it can be removed only by heating to a temperature short of dull redness in vacuo. R. Bunsen estimated that 2·11 sq. metres of glass surface, dried at 20°, lost 22·3 mgrm. of water when heated to 500°. The adsorption of water vapour by glass surfaces has been studied by R. Bunsen,[22] E. Warburg and T. Ihmori, C. J. Parks, etc.; quartz by A. von Dobeneck, L. J. Briggs, etc.; and charcoal by H. W. Foote. The penetration of adsorbed water into insulating materials has been studied by C. J. Rottmann. T. Ihmori also investigated the adsorption of water vapour by platinum, shellac varnish, brass, etc. It has long been known that old soda-glass tubing which has stood in the laboratory some time, becomes very rough when suddenly heated owing to the development of innumerable spits. This is probably due to adsorbed water.

E. Warburg and T. Ihmori divide the water film condensed on the surface of glass into a temporary portion which disappears when the vapour pressure is reduced to zero, and a permanent portion which remains. According to L. J. Briggs, the adsorption of water vapour by quartz is less than with amorphous silica. At 30°, the permanent film condensed on quartz from an atmosphere within one per cent. of saturation, corresponds with a film $2{\cdot}66\times10^{-6}$ cm. thick on the assumption that the film is uniform and has unit specific gravity. C. J. Parks found for glass wool in a saturated atmosphere at 15° a thickness $13{\cdot}3\times10^{-6}$ cm. H. W. Foote and B. Saxton found that the water adsorbed by lampblack is essentially the same as other water, only it does not freeze in the capillary pores until a low temperature, about —35°, is attained.

Pouillet effect.—In 1822, G. S. N. Pouillet[23] showed that porous substances—paper, wool, etc.—and fine powders—glass, charcoal, alumina, etc.—become heated when they are wetted with water—a liquid which exerts no solvent or chemical action on the solid. The phenomenon is now known as the *Pouillet effect.* The rise of temperature amounts to about 1°, and by suitably varying the conditions a rise of nearly 30° has been recorded. One gram of powdered charcoal, according to P. Chappius, evolves 7·425 cals. when wetted with water, and 24·36 cals. when wetted with carbon disulphide, while a gram of powdered alumina evolves 2·747 cals. when wetted with water. For the same liquid and the same powder, the quantity of heat evolved is proportional to the mass of the powder. According to G. Schwalbe, 10 grms. of washed sand gives 0·3 cal., when wetted with 0·5 grm. of water, and 0·8 cal. when wetted with 2 grms. of water, but no further rise of temperature occurred when more water was used; with silicic acid, 1·89 cals. were developed with 5 grms. of water, and 6·16 cals. with 20 grms. of water. T. Tate referred the cause of the Pouillet effect to chemical action, but this hypothesis was considered to be out of the question; G. S. N. Pouillet himself referred the effect to capillary action; C. G. Jungk showed that the effect is possibly due to the exercise of a pressure at the surface of the powder and liquid. C. Cantoni (1866) and L. Meslens (1874) assumed that the water passes into a different state of aggregation when it wets a powder—either into the solid state or some intermediate state between solid and liquid. T. Martini holds that just as a gas becomes a liquid when dissolved by a liquid, so does a liquid become solid when dissolved by a solid; and accordingly, the Pouillet effect is due to the latent heat of solidification. This hypothesis was discountenanced when M. Bellati and L. Finazzi (1902) showed that the specific heat of the water was not diminished by adsorption, as would have been the case if the water was solidified. They also stated that the grain-size of the powder had no influence on the result, but this statement proved to be erroneous; for C. J. Parks (1902) showed that when powdered and dry silica, sand, or glass are wetted with water at the same temperature the heat evolved is proportional to the exposed area of the solid, and is nearly equal to 0·00105 cal. per sq. cm. when the temperature is 7°. G. Schwalbe (1905) then demonstrated that if the temperature is below 4°, there is a negative Pouillet effect, for the water is cooled and not heated; and at 4°, there is neither heating nor cooling. This is in agreement with Lord Kelvin's proof that the temperature change dT due to the change of pressure dp on a liquid whose coefficient of thermal expansion is a, specific gravity D, absolute temperature T, and specific heat at constant pressure C_p, is

$$dT=\frac{aT}{C_pD}dp$$

Since the coefficient of expansion of water changes sign at 4°, there should be a change of sign in the Pouillet effect at the same temperature. Lord Kelvin computes there is a cooling of 0·00026° when a cubic centimetre of water at 0° is subjected to a pressure of 10 atm., and at 10° a rise of temperature of 0·0040°. It is also possible to calculate the compression of the water adsorbed by the powder from the Pouillet effect. The formation of ice within fissures and caves whose mean temperature is not below the freezing point of water, has also been explained by assuming that water below 4° is cooled instead of heated in percolating through the sandy walls of the cave.

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§ 10. Hydrates and Hydrated Salts

The term **hydrate** is not used very definitely in chemistry. . It is sometimes loosely employed in contrast with anhydrous. In addition, there are at least three different meanings to the word: (1) *Hydrated colloids* or *colloidal water.*—Silica, and the hydroxides of many of the metals—iron, chromium, aluminium, etc.—pass out of solution in a more or less gelatinous or colloidal condition associated with an *indefinite* amount of water. When dried, the water usually passes off continuously with rise of temperature without any signs of the existence of definite chemical compounds. (2) *Hydrated salts* or *water of crystallization.*—The very *definite* amount of water which is contained in many salts which crystallize from aqueous solutions—*e.g.* sodium carbonate, $Na_2CO_3,10H_2O$, etc.—is called water of crystallization, and several other synonyms have been employed. It is often stated that the molecules of water in compounds containing *water of crystallization* belong to the molecular structure or else exist in them entirely among the other molecules, and belong only to the crystalline structure; on the other hand, the molecule of *water of constitution* is not supposed to exist as such but to be formed when the mineral is decomposed owing to the union of the contained hydrogen with oxygen or hydroxyl groups contained in the molecule. (3) *Hydroxides—acids, alkalies, alcohols*, etc.—The water of hydration appears to be an integral part of the molecule, and it cannot usually be removed without changing the character of the substance. Examples are indicated above, to these are sometimes added the alcohols which are related to water and the ethers as previously indicated by graphic formulæ.

Both hydrate and hydroxide contain the elements of water which can usually be recovered as water when the substance is heated or subjected to the action of a dehydrating agent. It is sometimes assumed that the molecules of water in a hydrated colloid or salt have entered into combination as a whole; while in hydroxides, the constituent atoms have been rearranged, to form quite a different compound. The two terms are therefore used to distinguish two conceptions regarding the relation between the properties and composition of compounds containing water. In the case of hydroxides, the atoms of water and of the oxide are rearranged during the union so as to form hydroxyl or HO-groups. In hydrates the atoms of water either combine as a whole with the compound or enter into some new relation with the rest of the molecule which is different from that which obtains in the case of hydroxides. It is difficult to apply the definitions, hydrate and hydroxide, in practice, for they are largely theoretical; a true hydroxide may be so unstable that it decomposes into water, etc., far more readily than a true hydrate. For example:

Hydroxide . .	$Au(OH)$	$Ag(OH)$	$Tl(OH)_3$	$Zn(OH)_2$	$Al(OH)_3$	NaOH
Decomposes at .	15°	150°	230°	585°	850°	very high

T. Carnelley and J. Walker [1] tried to measure the affinity of the oxides for water by measuring the temperature of dehydration of the hydroxides. They showed that the members of the *even* series of Mendeléeff's table, exhibit an increase in the temperature of dehydration with an increase in atomic weight; and with the *odd* series, there is a decrease in the temperature of dehydration with increasing atomic weight. In the same series of elements, the temperature of dehydration of the hydrated oxides diminishes to the middle member and then increases.

To distinguish hydroxides from hydrates.—The specific or *molecular volume* of compounds formed by the interaction of water has been suggested as a means of throwing light on the difference in the effect produced by water in forming hydrates and hydroxides. The specific or molecular volume is the quotient of the molecular weight by the specific gravity. F. W. Clarke[2] found that in the hydrated chlorides, MCl_2nH_2O, the difference in the molecular volumes of the hydrates and anhydrous salts divided by the number of molecules of water in the hydrated salt, varies from 12·5 to 15·0—average 13·76. If oxides be substituted for chlorides, the corresponding quotient varies from 7·4 to 19·4. Hence, it was inferred that while the specific volume of each H_2O molecule in hydrated chlorides has a mean value 13·74, no simple relations can be traced with the hydrated oxides in which presumably a rearrangement of the atoms of the water molecule has taken place.

W. J. Perkin [3] attempted to distinguish the two types of combined water by measurements of the *magnetic rotatory power*. If the value of this constant for water be unity, and for an anhydrous compound be x, then if the molecular rotatory power of the hydrated compound be increased by unity for each molecule of combined water, it might be concluded that the compound is a hydrate. Thus, the product of the union of formic acid, H.COOH—molecular rotatory power 1·67—with water, 1·676+0·995, and hence the product is a hydrate. With sulphuric acid

	H_2SO_4		$H_2SO_4+H_2O$		$H_2SO_4+2H_2O$
Molecular rotatory power . . .	2·315		3·188		4·113
Difference per molecule of H_2O . .		0·873		0·925	

Hence, W. J. Perkin concluded that the first hydrate of H_2SO, *viz.* $H_2SO_4.H_2O$, is a chemical compound—a hydroxide—which he symbolized, $SO(OH)_4$, while the second hydrated compound, $H_2SO_4.2H_2O$, is a hydrate : $SO(OH)_4.H_2O$.

The period of free vibration of molecular aggregates can be studied by *absorption or emission spectra*. The high temperature generally required to produce emission spectra may complicate the phenomena owing to the dissociation of the radiating body; on the other hand, absorption spectra can be obtained at low temperatures, and this gives more definite knowledge of the molecular complexity. The period of free vibration of an atomic group or radicle is not always greatly modified as the molecular complexity of a series of compounds containing that radicle increases. In 1882, W. de W. Abney and E. R. Festing [4] found that certain radicles showed distinctive absorption bands at particular parts of the spectrum; and ten years later, W. H. Julius demonstrated that a chemical atom may lose its identity in a compound, for the effect is not additive but constitutive; and the absorption spectrum of a compound cannot be predicted from the spectra of the constitutive elements. The intra-molecular character of the certain absorption bands, however, is evidenced by the fact that the important groups of atoms and radicles which occur in chemical compounds have a definite or specific effect upon radient energy, particularly upon the so-called low frequency or infra-red radiation. This effect is manifest by intense absorption bands which occur in definite positions characteristic of the radicle or group of atoms causing these bands.

W. W. Coblentz further argues that the absorption spectrum of a compound with water of constitution will not be the composite spectrum of the anhydrous substance plus water, because the combination with water completely changes the physical character of the molecule; on the other hand, if the molecules or groups of atoms which cause the absorption band undergo no physical change when they combine to form a crystal, or when they enter into solution, the absorption spectrum will be a composite of the absorption bands of the constituents. The heat of hydration, in this latter case, might lead to the inference that a new compound is formed although the bands due to the anhydrous substance and to water are the same in magnitude and position as that which the constituents possessed before they united. The radiometric test makes no distinction between water of crystallization, dissolved or absorbed water, and water of solid solution. The behaviour of water in crystals and in solid solution is identical with that of water in its free liquid state. In illustration, the absorption spectra of selenite, opal, and the zeolites are identical with those characteristic of free liquid water, and therefore it is inferred that the water in these minerals remains intact as a group of molecules; on the other hand, in brucite, $Mg(OH)_2$; diaspore, $AlO(OH)$; bauxite, $Al_2O(OH)_4$; göthite, $FeO(OH)$; muscovite mica, $H_2KAl_3(SiO_4)_3$; tremolite, $CaMg_3(SiO_3)_4$, the water is not present in solid solution or as absorbed water, but is rather constitutional, being an integral part of the molecule. Many of these minerals show a clear absorption band characteristic of the OH group in alcohol.

The infra-red absorption spectra show that the following compounds probably contain *water of crystallization :* heulandite; stilbite; potassium alum; natrolite; scolecite; analcite; colemanite; hexahydrated calcium chloride—$CaCl_2.6H_2O$; trihydrated potassium ferrocyanide, $K_4FeCy_6.3H_2O$; apophyllite; deweylite; thomsonite; gismondite;

blödite; thaumasite; hydrotalcite; varescite; wavellite; vivianite; mellite; and Rochelle salt; while the following compounds contain *water of constitution*: manganite; göthite; bauxite; turquoise; lazulite; hydrargillite; diaspore; datolite; azurite; brucite; prehnite; hydronephelite; pectolite; chloritoid; clinochlore; penninite; tourmaline; the micas; muscovite; biotite; serpentine; talc; epidote; sodium metaphosphate; meta- and ortho-phosphoric acids.

C. Schaefer and M. Schubert[5] have studied the natural infra-red vibrations of solids by the *reflection method* in preference to the absorption method. They obtained characteristic reflection maxima for the SO_4-group in 34 sulphates; and for the CO_3-group in 15 carbonates. In agreement with W. W. Coblentz, they also found that substances containing water of hydration show a reflection maximum between 3·0 and 3·5μ, and a long-wave maximum between 15 and 20μ. The former is displaced in salts like cupric sulphate and the alums containing water of hydration. Water of hydration seems to adapt itself to the symmetry of the crystal, and it is anisotropic in anisotropic crystals, uniaxial in uniaxial crystals, and biaxial in biaxial crystals. L. Vegard and H. Schjelderup studied the structure of crystals by means of the X-ray reflection method with a view of elucidating the *rôle* of the water of crystallization.

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§ 11. The Vapour Pressure of Hydrated Salts

If a substance can form a number of definite hydrates, **at any given temperature, each hydrate has its own characteristic vapour pressure.** For instance, from the work of W. Müller-Erzbach, H. Lescœur, and J. L. Andreae,[1] it appears that copper sulphate forms three hydrates with vapour pressures, at 50°:

	Water.	$CuSO_4.5H_2O$	$CuSO_4.3H_2O$	$CuSO_4.H_2O$
Vapour pressure . .	92·0	47·0	30·0	4·5 mm.

Suppose water vapour be slowly admitted to a suitable vessel containing anhydrous copper sulphate at 50°. The two-component system has two solid phases and one vapour phase; accordingly, the system will be univariant, and the vapour pressure will remain *constant and fixed* at 4·5 mm. until *all* the anhydrous copper sulphate has been transformed into a monohydrate: $CuSO_4+H_2O \rightleftharpoons CuSO_4.H_2O$; the system is now bivariant because but one solid phase—the monohydrate—is present, and this can exist in contact with a vapour pressure which varies within certain limits. Hence, further addition of water vapour will be followed by a rise in the vapour pressure. At 30 mm. pressure the bivariant system becomes univariant owing to the appearance of a second phase—the trihydrate. The vapour pressure will then remain constant and fixed at 30 mm. until all the monohydrate has been transformed into the trihydrate: $CuSO_4.H_2O+2H_2O=CuSO_4.3H_2O$. Further additions of water vapour will be attended by a rise of the vapour pressure to 47 mm., and the vapour pressure will then remain stationary until all the trihydrate has been transformed into the pentahydrate: $CuSO_4.3H_2O+2H_2O \rightleftharpoons CuSO_4.5H_2O$. Any further addition of water vapour will raise the vapour pressure until the water condenses to a liquid and gives the vapour pressure of a saturated solution of copper sulphate at 50°. Further additions of water vapour will simply increase the amount of condensed water. When all the copper sulphate has dissolved, the vapour pressure will be determined by the concentration of the solution of copper sulphate.

Conversely, starting with the pentahydrate, the reverse change will occur if water be continually withdrawn from the system. The vapour pressure of the pentahydrate, 47 mm. at 50°, will be maintained as long as the system contains any of the pentahydrate. When all the pentahydrate has decomposed, the vapour pressure will drop suddenly to 30 mm. and remain stationary until all the trihydrate has decomposed; the vapour pressure will then fall abruptly to 4·5 mm. and remain at that value until all the monohydrate has decomposed into anhydrous copper sulphate. These changes are usually shown diagrammatically by curves resembling Fig. 26. Amounts of water, expressed in gram-molecules, are represented on the horizontal axes, and the vapour pressures along the vertical axes. The constancy of the vapour pressure of each hydrate is emphasized by the horizontal terraces on the vapour pressure curve.

This step by step dissociation of the hydrates furnishes a method which is sometimes available for deciding whether or not definite compounds exist at definite temperatures. If definite compounds are produced, the gradual addition or removal of water vapour will alter the vapour pressure curve until a pressure is reached which remains constant for a certain period, and then suddenly assumes a new constant value. It must be added that some (*e.g.* P. Blackman, 1911) consider the dehydration of copper sulphate pentahydrate is comparable with the removal of water from an ordinary aqueous solution; that the alleged breaks in the curve are due to a malinterpretation of imperfect experiments; and that the observed vapour pressures are points on a continuous curve. This, however, does not interfere with the principle involved.

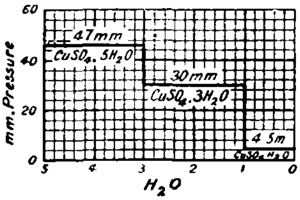


FIG. 26.—Vapour Pressure Curves of the Hydrates of Copper Sulphate.

By measuring the rate of decomposition of hydrated aluminium and ferric hydroxides, W. Ramsay inferred the non-existence of definite hydrates because no signs of any discontinuity was observed in the rate of evolution of water; but he concluded that two were formed with lead oxide—$2PbO.H_2O$ and $3PbO.H_2O$. J. M. van Bemmelen, for similar reasons, believed in the non-existence of definite hydrates of silicic acid. The underlying hypothesis is that differences in the tenacity with which the constituents of water are retained by the molecule, as evidenced by the temperatures at which the water is expelled, are the result of differences in the structure; and that molecules of water which are simultaneously expelled at a definite temperature occupy a similar position in the molecule.

Each hydrate has its own specific vapour pressure at a particular temperature, The average vapour pressure of the water vapour in atmospheric air is equivalent to 8 or 9 mm. of mercury. If the vapour pressure of the hydrate be greater than the vapour pressure of the atmospheric moisture, the hydrate will *lose* water on exposure to the air—in other words, the salt will be **efflorescent;** on the contrary, if the vapour pressure of the hydrate be less than that of the atmospheric moisture, the salt will *absorb* moisture from the atmosphere, and be **deliquescent.** A few illustrations are indicated in Table XVIII.

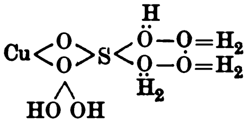
TABLE XVIII.—VAPOUR PRESSURES OF HYDRATES.

Salt.	Vapour pressure, mm.	Property.
$CaCl_2.6H_2O$	3·2	Deliquescent
$FeCl_3.6H_2O$	6·0	Deliquescent
$Na_2SO_4.10H_2O$	27·8	Efflorescent
$Na_2CO_3.10H_2O$	24·2	Efflorescent

Whether a salt effloresces or deliquesces depends on the humidity of the atmosphere in which it is confined. Thus, A. Vogel found that while hydrated copper sulphate may be preserved unaltered for years, it effloresces rapidly in air dried by sulphuric acid or calcium chloride. H. Watson also showed that sodium carbonate does not effloresce between 6° and 12° in air with the dewpoint at 3° or 4°, but it does effloresce in air at 14·4° when the dew point is at 8·9°; Glauber's salt effloresces in air at 14·4° when the dew point is at 9·4°, but not when the dew point is over 10°. According to H. Lescœur,[2] the vapour pressure for the deliquescence of hexahydrated strontium chloride is 11·5 mm., and for efflorescence 5·6 mm. at 20°. It is therefore possible to predict whether or not a salt will have a tendency to efflorescence or deliquescence in an atmosphere of known humidity when the vapour pressure of the hydrate is known.

A. C. Cumming, J. R. Partington, W. N. Rae, and F. Ephraim have shown that when certain crystalline salts are dehydrated, the vapour pressure may rise very slowly or even remain constant for a time, and then rise rapidly to the normal value required for the given temperature. The suspended transformation, lagging, or period of induction is shown by copper sulphate, $CuSO_4.5H_2O$; sodium carbonate, $Na_2CO_3.10H_2O$; barium chloride, $BaCl_2.2H_2O$; racemic acid, $C_4H_6O_6.H_2O$; the double sulphates, $M'_2SO_4.M''SO_4.6H_2O$; some ammino-salts; etc. M. Faraday showed that a perfectly sound crystal of hydrated sodium carbonate, phosphate, or sulphate does not effloresce readily on exposure to the atmosphere; indeed, M. Faraday found such crystals may be kept for years in an open dish without efflorescing. If, however, the change has commenced at any point, it will spread quickly throughout the whole mass; and this is in accord with the phase rule $F=C-P+2$. In the perfect crystal there are two phases P, namely, sodium sulphate, $Na_2SO_4.10H_2O$, and water vapour; and two components C, namely, Na_2SO_4 and H_2O. Hence the system is bivariant ($F=2$), so that the pressure of the water vapour and the temperature can be arbitrarily within certain limits without altering the state of the system. If, however, some efflorescent salt be present, there will be three phases, and the system will be univariant ($F=1$), so that for every temperature there is one and only one vapour pressure for equilibrium. The phase rule is only concerned with the conditions of equilibrium, and has nothing to say about how that state will be obtained.

The study of copper sulphate, which is typical of numerous other hydrates, shows that the molecules of the combined water may differ in the tenacity with which they are retained by the molecule of copper sulphate. The older books on chemistry drew fine distinctions between the different combinations of water with a salt; it is now believed that the water of one hydrate does not differ in kind from that of the other hydrates. The water is sometimes conventionally styled "constitutional water," "water of crystallization," "water of hydration," or "water of combination." The actual term used does not matter very much provided it is not misunderstood. The proportion of water in the different hydrates is in accord with the law of multiple proportions—if not, the water is arbitrarily said not to be chemically combined. The mode of writing the formulæ—$CuSO_4.5H_2O$; $Na_2SO_4.10H_2O$—and the ease with which the hydrates dissociate into water, etc., might give rise to the idea that the water molecule exists in the hydrate ready-made. There is, however, no evidence how the elements of water are combined in the hydrate, and consequently, following the old adage—truth is to be found within ourselves; it takes no rise from outward things—many suggestions have been made to represent the constitution of the hydrates graphically. The application of the theory of valency to explain the composition of salts does not usually include water of crystallization; and in order to extend that theory to salts with water of crystallization, it is usually assumed that all or some of the contained oxygen atoms are quadrivalent. For instance, assuming that in copper sulphate (1) the oxygen is quadrivalent; (2) one water molecule is associated in the molecule differently from the other four molecules because it is not expelled except at a much higher temperature; (3) two of the remaining four molecules are more strongly attached than the other two as is evidenced by the step by step dehydration of the pentahydrate→trihydrate→monohydrate→anhydrous salt, one of the many formula which can be devised is:



If all four water molecules were united in the same way it is further assumed that they would be liberated together, or set free individually one after the other forming respectively penta-, tetra-, tri-, di-, and mono-hydrates. There is some evidence to show that when a double salt is formed containing the solvent, the latter is an essential constituent of the salt, for the substitution of one solvent for another may prevent the formation of a particular double salt. Thus H. W. Foote (1910)[3] found that potassium and mercuric chlorides form the following double salts with water, alcohol, C_2H_6O, and acetone, C_3H_6O:

Water.	Alcohol.	Acetone.
. . .	. . .	$KCl.5HgCl_2.C_3H_6O$
$KCl.2HgCl_2.2H_2O$	. . .	. . .
. . .	$5KCl.6HgCl_2.2C_2H_6O$	$5KCl.6HgCl_2.2C_3H_6O$
$KCl.HgCl_2.H_2O$	. . .	. . .
$2KCl.HgCl_2.H_2O$	. . .	. . .

We know very little beyond the simple facts that (1) water is a product of the dissociation of the hydrates; (2) the water of the hydrate is given off at comparatively low temperatures; (3) the water is not an essential part of the reacting unit in its most characteristic transformations; (4) the water is not generally necessary for the formation of the salt itself since the water of crystallization can generally be removed by suitable means leaving behind the anhydrous salt; and (5) the water can often be replaced by an organic solvent so that a salt crystallizing with a definite number of molecules of water at a given temperature will crystallize from one organic solvent with the same or a smaller number of molecules of the solvent.

There is much cogent evidence leading to the inference that water is a ternary substance containing molecules H_2O, $(H_2O)_2$, and $(H_2O)_3$, and A. Rosenstiehl (1911) considers that in salts containing water of crystallization, the water may be present as H_2O, $(H_2O)_2$, or $(H_2O)_3$, or a mixture of these different groups. The effect of temperature on the dehydration of the hydrated salts will show the state of the polymerization of the bound water. Salts containing 1, 2, or 3 molecules of water of crystallization usually lose water in one step. Salts with 3, 6, 9, 12 molecules of water on hydration lose water as $3H_2O$ or multiples of this; and salts with 4, 5, 7, 8, or 10 molecules of water furnish evidence that two kinds of molecules of water are involved. For instance, the dehydration of $CuSO_4.5H_2O$ behaves as if the molecule contained $CuSO_4.H_2O+2(H_2O)_2$; $MgSO_4.7H_2O$, as if it were $MgSO_4.H_2O+3(H_2O)_2$; while $Na_2CO_3.10H_2O$ behaves as if the molecules contained $Na_2CO_3.H_2O+3(H_2O)_3$.

If the term "water of crystallization" be carelessly employed it may suggest that crystallization is somehow dependent on the presence of water, and this the more, as efflorescent salts appear to lose their crystalline character when water is lost. Crystals of gypsum—$CaSO_4.2H_2O$—form a white chalky powder when the water is driven off; crystalline sodium carbonate, and Glauber's salts, likewise produce white powders when their combined water is expelled. The powdered dehydrated substances are all crystalline. Several zeolites may lose their combined water without losing their crystalline form. In fact, practically all chemical compounds can be crystallized. Crystallization is not dependent upon the presence of water. Sulphur, common salt, iodine, potassium chlorate, potassium sulphate, and numerous other crystalline substances do not contain the elements of water.

Again, crystalline calcspar does not contain the elements of water, and yet when calcined it gives a white powder. The calcspar loses carbon dioxide, not water.

Alcohol, C_2H_5OH, has a constitution similar to water, but one of the hydrogen atoms of water is replaced by the radicle C_2H_5. Alcohol, ammonia, and hydrogen peroxide can combine with certain other molecules to form complexes, and thus we speak of "alcohol of crystallization," "ammonia of crystallization," "hydrogen peroxide of crystallization," etc.

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CHAPTER X

SOLUTIONS

§ 1. The Solubility of Solids in Water

> In a strictly scientific sense of the word, insolubility does not exist. Even those substances which are characterized by the most obstinate resistance to the solvent action of water should probably be regarded as extraordinarily difficult of solution, but not insoluble.—O. N. WITT (1905).

WATER is one of the most active of solvents, and, in consequence, it has been styled *the universal solvent*, but not in the same sense as the visionaries' *alcahest* (universal solvent) so often mentioned in the writings of mediæval alchemy. It is remarkable that a belief in this, Paracelsus' menstruum, was fairly prevalent towards the beginning of the eighteenth century. R. Boyle[1] said: "He that hath seen it, hath more reason to believe it, than he that hath not." J. Kunckel[2] said that some derive the term alcahest from the Latin *alkali est*, others from the German *all geist*—all spirit—and yet others from the German *alles est*—it is all. J. Kunckel also expressed his surprise that it does not seem to have occurred to the old alchemists that no vessel on earth could hold their universal solvent, because a universal solvent would also dissolve its containing vessel.

For convenience, the dissolved substance is often called the **solute,** and the liquid in which the solute is dissolved the **solvent.** When no solvent is mentioned, water is usually understood; the list of possible solvents is almost as extensive as the list of chemical compounds. If potassium chloride be added to water kept at a constant temperature the salt is gradually dissolved, and the process of solution continues until a definite amount has dissolved. Any solid in excess of this will remain an indefinite time without further change, provided the temperature remains constant, and no solvent is lost by evaporation, or gained by absorption. The solid and solution are then in equilibrium. As in the analogous case of the pressure of a liquid, the equilibrium between a saturated solution and a solid is dynamic, not static. Accordingly, with the preceding notation the equilibria with solid and liquid solutes respectively are represented:

$$\text{Solute}_{\text{solid}} \rightleftharpoons \text{Solute}_{\text{dissolved}}\ ; \quad \text{or } \text{Solute}_{\text{liquid}} \rightleftharpoons \text{Solute}_{\text{dissolved}}$$

A solution in equilibrium with its solid is said to be **saturated** with the solid at the temperature of experiment. **The weight of salt dissolved by 100 c.c. of the solvent so as to make a saturated solution at any assigned temperature is called the solubility of the salt.** Thus, 100 c.c. of water at 20° will dissolve 35 grams of potassium chloride, and accordingly, 35 is the solubility of potassium chloride in water at 20°.

J. L. Gay Lussac (1819)[3] expressed the solubility as parts of the substance in 100 parts of water. Other modes of representing solubility are more convenient in special cases—*e.g.* the percentage amount of salt in a given weight of the solution may be employed, and A. Etard (1884) represented the solubility in terms of the weight of the solvent in 100 parts of solution. With the latter mode of representation, the solubility curves are usually straighter, and very great solubilities cannot exceed 100, whereas with J. L. Gay Lussac's method they may become infinite. For example, at 310° a saturated solution of sodium hydroxide has 22,222·2 parts of the solid in 100 parts of water, and 99·45 grms. of the hydroxide in 100 parts of solution. E. Cohen and E. H. Buchner, however, have shown that A. Étard's rule (1898)—to the effect that if the solubility be defined as the weight of salt in 100 grms. of saturated solution, the solubility-temperature curves are straight lines—is not in accord with facts.

It is common in studying the physical properties of solutions, to represent the ratio in terms of the number of gram-molecules of the dissolved substance per 100 of the solvent, or of the solution; or as the *molecular fraction* as it is called, that is, the ratio of the number of gram-molecules of the solute to the number of gram-molecules of the solvent and solute. If S denotes the quantity of the substance by weight dissolved in 100 parts by weight of the *solvent*, and W the quantity by weight in 100 parts by weight of the solution; then, if S parts of the substance are contained in 100 parts of the solvent, the S parts of the substance are contained in $100+S$ of the solution; and consequently, 100 parts of the solution will contain $W=100S/(100+S)$ parts of the dissolved substance. Conversely $S=100W/(100-W)$. This gives a relation between S and W, provided no marked change in volume occurs on solution.

There are also many ways of respresenting the concentration of a solution, for example, the concentration of ordinary sulphuric acid can be represented: (1) By the specific gravity (or density) 1·161. This mode of representation must be supplemented by tables relating concentration and specific gravity. (2) By the stoichiometric proportion of H_2SO_4—(i) 22·27 per cent. by weight of H_2SO_4; (ii) 258 grms. of H_2SO_4 per litre; (iii) $258\div98=2·63$ gram-molecules per litre; or (iv) $H_2SO_4+19H_2O$. (3) By the normality of the solution $258\div49=5·26N$—that is, 5·26 equivalents of H_2SO_4 per litre. (4) Molecular fraction 0·05, meaning that 0·05 gram-molecule of H_2SO_4 is mixed with $1-0·05=0·95$ gram-molecule of water.

It is important in measuring the solubility of a salt to make sure that the solution is really saturated because some salts dissolve very slowly. Many of the older determinations are vitiated by failure to guard adequately against supersaturation,[4] and by using inadequately purified salts.

The **concentration** of a solution is determined by the relative amount of solute in solution—if but a small proportion is present, the solution is said to be *weak* or *dilute*; if a relatively large amount of solute is dissolved, the solution is said to be *strong* or *concentrated*. We can thus see with C. L. Berthollet (1803) a close analogy between the solution of a salt in water, and of water by air. In each, the quantity dissolved at a given temperature is always the same—in the case of a solution of salt in water, this constant is called *the solubility of the salt*, and in the case of a liquid in air, *the vapour pressure of the liquid*.

J. H. van't Hoff's definition (1890) [5] of a solution is one of the best yet suggested. It runs somewhat as follows: **A solution is a homogeneous mixture of two or more substances; the composition of the mixture can vary within certain limits**—the limits of its existence; or, as C. L. Berthollet expressed it in 1803: *Les sels s'unissent à l'eau en toute proportion, jusqu'au point de la saturation.* It has been conventionally agreed to call solutions mixtures because their composition can vary in the way just described and not *per saltum* as is characteristic of that mode of chemical combination defined by the laws of constant and multiple proportion. F. Wald distinguishes a chemical individual as a substance which persists as a phase of constant composition when the conditions of temperature, pressure, and composition of the other phases present, undergo continuous alteration within certain limits—the limits of existence of the substance.

Pliny commented on the limited solubility of salts in water. In his *Historia naturalis* (**31.** 34) of the first century, he said:

> It is a singular fact that if more than one sextarius of salt be put into four sextarii of water, the solvent action of the water will be overpowered, and no more will dissolve.

N. le Febure [6] in the seventeenth century stated the law of saturation very clearly:

> Digest four ounces of ordinary salt in eight ounces of water, and you will find that the water will dissolve three ounces of the salt, and that it will take up the other fourth if the water be boiled and the liquid agitated. . . . When a menstruum is fully saturated—either cold or hot—it is impossible by any art to go further, because it is charged conformably with *le poids de nature*, which cannot be transgressed.

The numbers expressing the solubility of a salt were thus regarded as natural constants—*le poids de nature.*

Speaking in terms of the phase rule, the solubility of a solid in a liquid is the saturation concentration, and at an assigned constant temperature the system is invariant; and, with liquid-liquid systems, two liquid layers are necessary for invariance; and, in dealing with gas-liquid systems, the pressure of the gas must be specified. It is also necessary to consider the formation of compounds of solute and solvent, for, at a given temperature, some compounds with the solvent may be stable, others unstable. When a compound is decomposed by water, its solubility has no more meaning than to speak of the solubility of zinc in dilute sulphuric acid. The term solubility is loosely applied to both phenomena because in each case the solid phase disappears, and the material passes into the liquid until the liquid is saturated. In a rough way the term *dissolution* is applied when the substance dissolved is decomposed by the solvent, and *solution* when it is not decomposed.

Are all substances soluble in water?—Excluding chemical action, so-called, there are three possible ways in which two substances can behave: (1) One substance may be quite *insoluble* in the other—*e.g.* platinum in water; (2) One substance may be *partially soluble* at a given temperature—*e.g.* salt in water; (3) The two substances may be *completely miscible* in all proportions—*e.g.* alcohol and water; fused cobalt and nickel. It might be argued that a substance must either be soluble or insoluble in a given menstruum—either it will be diminished in mass by the solution of a portion in the menstruum, or it will suffer no change after prolonged contact therewith. Very exact investigations have shown that few substances considered by the chemist to be *insoluble* really are so. The so-called **insoluble substances** obtained as precipitates in analysis are in reality substances with a very low solubility. It is all a question of measurement. As the methods of observation become more and more precise, so does the list of insoluble substances grow less and less. The general use of the term *insoluble* must, in consequence, give way to *sparingly soluble*. In illustration, the three precipitates obtained in the first group of the regular scheme for qualitative analysis are usually said to be insoluble, but they are not really insoluble in water because their solubilities, per 100 c.c. of water, at 20°, are represented by the following numbers: silver chloride, 0·00016 gram; mercurous chloride, 0·00031 gram; and lead chloride, 1·18 gram. In some cases the alleged solubility—*e.g.* platinum in water—cannot be proved directly, but requires involved reasoning which appears to be subtle sophistry of no substance or profit.

The influence of the grain-size of solids on the solubility.—In 1813, W. H. Wollaston noted that finely-divided substances suspended in a solvent not only dissolve more rapidly but they may have an even greater solubility than coarse-grained powders; in 1870, E. Divers also made the same observation with respect to calcium carbonate; and G. A. Hulett found that a litre of water at 25° will dissolve 2·085 grms. of gypsum when particles have an average diameter of about 0·0004 cm. and 2·476 grms. when the average diameter is about 0·00006 cm. The theory was worked out by J. W. Gibbs [7] in 1876, and by J. J. Thomson in 1888. J. W. Gibbs' theory is embodied in the expression

$$\log\frac{S_2}{S_1}=\frac{2M\sigma}{RTD}\left(\frac{1}{r_1}-\frac{1}{r_2}\right)$$

where R denotes the gas constant, *viz.* $8{\cdot}315\times10^7$ ergs per degree; T, the absolute temperature; D, the specific gravity of the solid; M, the molecular weight of the solute; σ the energy per unit area of the surface of separation between the solid and solution; and S_1 and S_2 denote the concentrations of saturated solutions in contact with spherical particles of the respective radii r_1 and r_2. If r_2 be indefinitely large, the expression reduces to that employed by G. A. Hulett, for S_2 then denotes the ordinary or normal solubility of the substance. For calcium sulphate, where $D=2{\cdot}33$; $M=136$; $\sigma=1050$ ergs per sq. cm. at 25°,

$$\log\frac{S_1}{S_2}=\frac{2M\sigma}{RTDr_1};\ \text{or}\ \log\frac{S_1}{S_2}=\frac{14{\cdot}69\times10^{-4}}{r_1T}$$

if D and σ are independent of temperature. On calculating the solubilities of gypsum for different values of r and T it is found that the solubility curve for $r = 50{\cdot}0\mu$ is virtually the same as when r is infinite. The results shown in Fig. 1 represent the solubility curves (milligram-molecules per litre) for $r=0{\cdot}5\mu$; $r=1{\cdot}0\mu$; $r=3{\cdot}0\mu$; and $r=50{\cdot}0\mu$.

A solution in equilibrium with fine-grained particles, say $0{\cdot}5\mu$, is super-saturated with respect to coarser-grained particles, say 50μ. Consequently with a mixture of coarse and fine grains, the coarse grains will grow at the expense of the fine grains. In illustration, a fine-grained precipitate, after standing some time in contact with its solution, becomes coarser-grained, so that the freshly-made precipitate readily passes through the filter paper, while the older precipitate does not pass.

E. Podszus found that certain oxides—alumina, thoria, and zirconia—usually not acted upon by the hydrochloric acid are dissolved by this reagent when they have been reduced to a fine state of subdivision so that the particles have a diameter of the order 1μ. The dissolution of the oxides in hydrochloric acid is a phenomenon different in kind from the solution of, say, gypsum in water. W. Herz calculated the molecular diameter, d, of liquids from the equation $d=2\gamma v/L$, where γ denotes the capillary constant, v the specific volume, and L the latent heat of evaporation per gram. He then examined the relation between this magnitude and the solubility of the liquids in water, and found that in general the solubility is greater the smaller the diameter. The rule can be entirely altered by specific chemical properties.

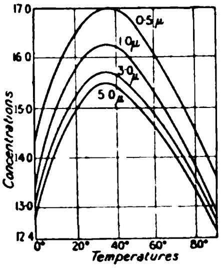

FIG. 1. — Solubility Curves of Calcium Sulphate of Different Grain-size.

The effect of grain size on solubility recalls the fact that when drops of liquid are suspended in air or other gas, the smaller drops of liquid grow smaller and disappear, so that the larger drops grow larger at the expense of the smaller drops. The vapour pressure of a liquid depends on the curvature of its surface; the greater the curvature the greater the vapour pressure, and hence the vapour from the smaller drops is distilled on to the larger drops—**1.** 9, 6. The two phenomena are not strictly analogous except in this way. The boundary-surface between a liquid and a solid is the seat of a certain amount of energy—the so-called free surface energy of the liquid. The greater the curvature of a liquid, the greater the surface energy. The greater the free surface energy of a substance, the greater the solubility—*e.g.* the allotropic forms of a substance have different solubilities, the less stable is always the more soluble. Hence, P. Curie inferred that the greater the free surface energy between a solid and its solution, the greater the solubility.

Is water in aqueous solutions identical with water alone ?—When the absorption of light by a given layer of an aqueous solution is compared with that of a layer of water of the same depth, it cannot be assumed that the water in the aqueous solution absorbs as much light as pure uncombined water; and that the difference between the light absorption of the aqueous solution and of pure water is due to the dissolved substance. The different transparency of the water in a solution as compared with water alone must be ascribed to a relation between the dissolved substance and the solvent water; part, at least, of the water must be different from water alone, and the most probable hypothesis is that the water is partly depolymerized by the solute or that part of the water present in a solution is in combination with the dissolved substance. Of the salts examined by H. C. Jones (1913) and his co-workers, those which do not form hydrates absorb practically the same amount of light as a corresponding layer of water. A difference in light absorptive power is only exhibited by solutions of those substances which form hydrates; this is taken to mean that the difference between light absorbing power of solutions of hydrated salts and the corresponding amount of the solvent is not fully explained by the depolymerization or the breaking down of associated molecules of water by the dissolved substance.

The influence of temperature on solubility.—The solubility of most substances increases with the temperature; the higher the temperature, the greater the solubility. **Graphs obtained by plotting the relation between the solubility of solids and temperature are called solubility curves.** The solubility curve presents a graphic picture which enables the relation between solubility and temperature to be seen at a glance. In illustration, the upward left-to-right slope of the solubility curve of calcium sulphate shows that the solubility of this salt *increases* with a rise of temperature up to about 40°, and the downward left-to-right slope over that temperature shows that the solubility then decreases as the temperature rises. Sodium chloride is but slightly more soluble in hot than in cold water. The solubilities of a few typical salts at 0°, 50°, and 100° are as follows:

Solubility of	0°	50°	100°
Potassium hydroxide, KOH	97·00	140·00	178·00
Sodium chloride, NaCl	35·63	36·67	39·12
Calcium hydroxide, $Ca(OH)_2$	0·14	0·10	0·06
Calcium chromate, $CaCrO_4$	4·50	1·12	0·42
Cerium sulphate, $Ce_2(SO_4)_3$	19·09	4·78	0·78

The solubility of a substance depends on so many complex factors that a satisfactory quantitative theory has not yet been established. E. Clapeyron and R. Clausius' equation can be written:

$$\frac{d\log S}{dT}=-\frac{Q}{RT^2};\text{ or }\frac{1}{S}\frac{dS}{dT}=-\frac{Q}{RT^2}\quad .\quad .\quad .\quad .\quad (1)$$

so as to show the relation between the absolute solubility, S, and the temperature coefficient, dS/dT, of the solubility—*i.e.* approximately the change in solubility per degree—and the reversible heat of solution, Q. The gas constant R is nearly 2 calories. It is usual to represent the observed data between the concentration S and the temperature $\theta°$ by an empirical formula of the type, $S=a\theta+b\theta^2+c\theta^3+. . .$, where a, b, c are constants to be evaluated from the measurements of the solubilities S at temperatures θ_1, θ_2, θ_3, . . . R. T. Hardmann and J. R. Partington[8] used the empirical expression $\log S=A-BT^{-1}-C\log T$, which contains three constants like the simpler relation, $S=a+b\theta+c\theta^2$.

Starting from F. M. Raoult's vapour pressure law, G. Bodländer calculated the solubilities of some very sparingly soluble salts from the heats of formation Q of an equivalent amount of the salt, and the electrode potentials of their ions—$E^{\bullet}$ for the cation, E' for the anion:

$$0\cdot058\left(\frac{1}{n^{\bullet}}+\frac{1}{n'}\right)\log S=E^{\bullet}+E'\frac{Q}{230}$$

where $n^{\bullet}$ and n' respectively denote the valencies of cation and anion, and the solubility S is expressed in gram-equivalents per litre. It is here assumed that the free energy of the reaction is equal to the total energy change. F. Dolezalek also calculated the solubility of gases in liquids on the assumption that Raoult's law is valid. J. H. Hildebrand deduced the following expression for the solubility N of a solid at the absolute temperature T:

$$\log\frac{n}{N}=-\frac{\lambda TT_m}{4\cdot58(T_m-T)}$$

where n/N denotes the solubility of the compound expressed in terms of the molecular fraction—n representing the number of gram-molecules of the solute in the solution, and N the total number of gram-molecules of solvent and solute; λ denotes the heat of fusion per gram-molecule assumed to be independent of the temperature; T_m, the absolute melting temperature of the solute. It follows from this conclusion that the solubility of a solid is smaller the greater the heat of fusion, and the higher the melting point over $T°$.

D. Tyrer assumes that the solubility of a given substance depends not only upon the temperature and nature of the solvent, but also on the mass of the solvent contained in unit volume of the solution. The solubility of a substance in a given solvent is always diminished when the solvent is diluted with a liquid in which the given solute is insoluble. On this assumption he deduces the relation, $S^n = a(V/v)^n - b$. which also contains three constants, n, a, and b. V represents the total volume of the solution and v the specific volume of the solute. Sufficient data have not been published to establish this relation.

The influence of pressure on solubility.—The effect of pressure on solubility in condensed systems—liquids and solids—is relatively small—one per cent. per 1000 atm.—when contrasted with the effect of temperature, and it may be either positive or negative. Pressure has but a slight influence on binary condensed systems generally. The most accurate work on the effect of pressure on solubility is that by E. Cohen and co-workers[9] on the solubility of sodium chloride and mannite; when at 24·05°, it was found:

Pressure	1	250	500	1000	1300 atm.
Solubility	26·41	26·60	26·76	27·02	27·20 per cent.

and H. F. Sill's work on sodium chloride and barium hydroxide, $Ba(OH)_2.8H_2O$, where it was found, for the latter, at 25°:

Pressure	1	25	490 atm.
Solubility	8·299	8·790	9·366 per cent.

In 1862, K. Möller stated that that pressure must exercise an influence on the solubility of a salt; and in 1863, H. C. Sorby[10] made some remarks on the subject. The solubility of a salt is increased by pressure if, during solution, a contraction occurs; and conversely, the solubility of a salt is decreased by pressure if an expansion occurs during solution. For example, the percentage changes in the volumes of solid sodium and ammonium chlorides over their volumes in a saturated solution are respectively +13·57 and −15·78; the percentages changes in solubilities per atmosphere increase of pressure are respectively +0·00419 and −0·00638, when the + signs denote increases, and the − signs decreases. In 1870, C. M. Guldberg deduced a general expression for the change of solubility S which occurs when the pressure changes by an amount dp. This is usually expressed in the form:

$$\frac{d \log S}{dp} = \frac{\delta v}{RT}; \text{ or, } \frac{1}{S} \cdot \frac{dS}{dp} = \frac{\delta v}{RT} \quad . \quad . \quad . \quad . \quad (2)$$

These expressions follow directly from Clapeyron's equation. The observed results are in agreement with these formulæ when δv denotes the change in volume which occurs during the solution of the solid, and dS/dp, the pressure coefficient of the solubility—that is, the change of solubility which occurs when the pressure changes one unit. F. Braun made a special study of the subject in 1870, and this work has crystallized in the statement: **The solubility of a salt will increase with pressure if the solution occupies a less volume than the sum of the volumes of its constituent parts; while the solubility will diminish if the solution occupies a greater volume than the sum of the volumes of its constituent parts.** This is but a specialized form of the so-called generalization of G. Robin in 1879: At constant temperature there is one definite pressure at which a system will be in equilibrium; on raising the pressure, the reaction will take place in that direction which is produced with a decrease in volume; while if the pressure be reduced, the reaction will proceed in that direction which has the greater volume. This, again, is a special case of J. H. van't Hoff's law of mobile equilibrium; which in turn is a special case of the principle of least action, foreshadowed in a vague sort of way by

Maupertius in 1747—all natural changes take place in such a way that the existing state of things will suffer the least possible change.

By division of the expression (1) for the relation between the temperature coefficient of the solubility, dS/dT, and the heat of solution Q by the above expression, (2) for the relation between the pressure coefficient of solubility, dS/dp, and volume change dv, it follows that

$$Q\frac{dS}{dp}=-\frac{dS}{dT}(v_2-v_1)T \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where v_2-v_1 represents the change in volume, in c.c., which occurs when a gram-molecule of the solid is dissolved at the temperature T in an unlimited quantity of the saturated solution; Q represents the heat of solution under these conditions. The term dp may be taken to represent the increase in pressure necessary to cause one gram more of the solute to pass into solution and dT the increase in temperature necessary to produce that result; or dS/dT, the temperature coefficient of the solubility represents the change in solubility per degree change of temperature, and ds/dp the pressure coefficient of the solubility. Values of Q for barium hydroxide calculated from this equation agree well with the observed.

Since chemical equilibrium [11] is determined only by the relative concentration of the different kinds of molecules concerned in the reaction, the equilibrium can be altered by pressure only by changing the relative concentration of the substance concerned in the reaction; but the compressibility of liquids and solids is small, and differences in the compressibility of the components in a reaction must therefore be very small. Consequently, the effect produced by changes of pressure on chemical equilibrium in condensed systems must be small. When one of the components is a gas, the case is different because gases are highly compressible, and their reactivity is almost proportional to the pressure. A compound involving a volatile component will not be formed in a reaction unless the concentration or partial pressure exceeds a certain limiting value which is mainly dependent on the temperature. For instance, liquid water will not be formed at 200° if the pressure is less than 15 atm., and at 300° if the pressure be less than 100 atm. Calcium hydroxide in an atmosphere of steam at 550° and one atm. pressure, does not dissociate into water and calcium oxide, but at 750° a pressure of 15 atms. is required to prevent dissociation.

According to G. Tammann,[12] if a solvent and a solution be subjected to a certain pressure p, it is sufficient to raise the pressure on the solvent by a certain amount of δp in order that it may behave like the solution with respect to volume, temperature, and pressure. The extra pressure δp required to make the coefficient of thermal expansion of the solvent, or the coefficient of compressibility of the solvent, equal to that of the solution under the standard pressure, depends upon the concentration and nature of the solute. G. Tammann explains the phenomenon by assuming that internal pressure is raised by the solution of a substance in the solvent, so that the solvent requires an additional external pressure to compensate the extra internal pressure of the solution. Under these circumstances the equations of state of solution and solvent are the same.

Transition temperatures.—Some solubility curves exhibit irregularities at certain temperatures. The solubility curve may change its direction, as calcium sulphate does at 35°, and barium butyrate at 45°. The solubility curve of sodium sulphate is a very trite illustration, but none the less instructive on that account. It is shown in Fig. 2.[13] The solubility of sodium sulphate, said J. L. Gay Lussac, follows *une marche très singulière* for the solubility of the salt, $Na_2SO_4.10H_2O$, *increases* rapidly with rise of temperature, as shown by the slope of the curve EO, Fig. 2. There is an abrupt change in the direction of the solubility curve at 32·383°, O, Fig. 2. Above that temperature the solubility *decreases* with rise of temperature. This, said J. L. Gay Lussac in 1819, is the second example of a body whose solubility decreases with a rise of temperature, for J. Dalton had previously shown that lime behaves in a similar manner.

The break—*point de rebroussement*—in the solubility curve of sodium sulphate, the first of its kind, was discovered by J. L. Gay Lussac in 1819, and in 1839 he recognized that the breaks in the solubility curves of some substances can be accounted for by assuming that at this point it is no longer the same substance which dissolves further. In 1840, H. Kopp showed that the solubility curves above and below the *point de rebroussement* are two distinct curves representing the solubility of two different substances. The one curve below the transition point can be represented by the formula $S_1=5{\cdot}02+0{\cdot}30594\theta-0{\cdot}000410\theta^2+0{\cdot}0009977\theta^3$; and the other by $S_2=58{\cdot}50-0{\cdot}27783\theta+0{\cdot}0006900\theta^2+0{\cdot}0000049802\theta^3$. At the transition point $S_1=S_2$, and θ then becomes 32·93°. The observed value is a little lower than this, *viz.* 32·383°. At the transition temperature, adds H. Kopp, the crystallized sodium sulphate passes into the anhydrous salt. Consequently, the curve of increasing solubility of temperature below 32·383° represents the solubility of curve of the decahydrate, $Na_2SO_4.10H_2O$; and the curve of decreasing solubility with rise of temperature represents the solubility curve of the anhydrous salt, Na_2SO_4. The decahydrate, at 32·383°, is transformed into the anhydrous salt. The decahydrate is not stable above 32·383°; the anhydrous salt is not stable below 33°. This temperature is called the *transition temperature* or *transition point*, and the change is symbolized :

$$Na_2SO_4.10H_2O \overset{32{\cdot}383^\circ}{\rightleftharpoons} Na_2SO_4+10H_2O$$

The solubility curves, it will be observed, represent the conditions of equilibrium between the solvent and salt. It makes no difference whether we start with the anhydrous sulphate or the decahydrate. When in equilibrium, the solution in contact with the solid will contain the amounts of sodium sulphate—Na_2SO_4—indicated by the solubility curves, Fig. 2. The saturated solutions, when in equilibrium, have the same concentration and are identical in every way. We cannot continue the observation of the solubility of the decahydrate beyond 32·383°, because it *immediately* splits up either into a less hydrated form—*e.g.* $Na_2SO_4.7H_2O$—or the anhydrous form, Na_2SO_4. The solubility curve of the heptahydrate meets the solubility curve of the anhydrous sulphate in the region of instability; the transition point from the heptahydrate to the anhydrous salt is 34°, or

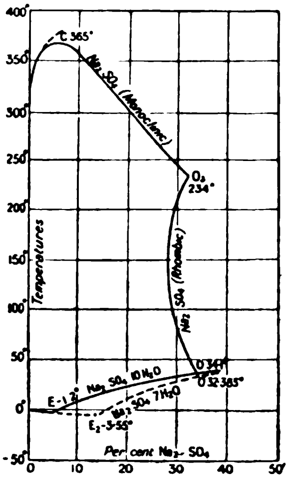

FIG. 2.—Solubility Curve of Sodium Sulphate.

$$Na_2SO_4.7H_2O \overset{34^\circ}{\rightleftharpoons} Na_2SO_4+7H_2O$$

The so-called eutectic points E and E_2 will be discussed later, but since the transformation of the anhydrous salt into the hydrate takes an appreciable time, it is possible to measure the approximate solubility of the anhydrous salt below 32·8. This is indicated by the dotted line in the diagram. In saturated solutions of hydrates, a definite hydrate is in dynamic equilibrium with the solution; if the hydrate changes as shown by E. Demarçay's study (1883) of the hydrates of thorium sulphate, the maximum amount of a salt which can enter into solution depends on its temperature and on its state of hydration; the solubilities of the different hydrates of a salt are different, and at the transition temperature, there is a break in the continuity of the solubility curve. H. W. B. Roozeboom's studies of the hydrates of a number of salts show that the solubility curves of the different hydrates of a salt indicate the limits of their stability.

The solubilities of the two sodium sulphates—anhydrous and decahydrate—are quite different. If the solid decahydrate were in contact with a saturated solution at 20°, and some of the anhydrous sulphate were added to the solution, some of the latter would dissolve and be deposited later as the decahydrate. The final result would be a transformation, through the medium of the solution, of the anhydrous salt into the decahydrate. Although 100 c.c. of water at 0° can only dissolve about 5·0 grams of the decahydrate, the same quantity of water can dissolve much more of the anhydrous sulphate. The general result of a multitude of experiments is to show that salts which crystallize in two or more different forms with different amounts of combined water, have different solubilities; and at certain temperatures a solution may be saturated with either of two different hydrates, *e.g.* $Na_2SO_4.10H_2O$, or $Na_2SO_4.7H_2O$; it is therefore necessary to specify which sodium sulphate is in question when reference is made to a saturated solution of sodium sulphate. Of two hydrates that containing the less water is usually the more soluble at any temperature below the transition temperature—H. le Chatelier's rule. For instance, sodium sulphate forms the hydrates, $Na_2SO_4.7H_2O$ and $Na_2SO_4.10H_2O$, and 100 grams of a saturated solution of the former at 10° has 23·1 grams of the former and 8·3 grams of the latter. The rule is not general; the hydrates of manganous sulphate do not fit the rule.

The solubility curve of anhydrous rhombic sodium sulphate progresses from O_3 into the metastable region. The solubility curve is at first retrograde—decreasing with rise of temperature—and it then becomes normal—increasing with rise of temperature. A. Smits explains the retrograde solubility curve of rhombic sodium sulphate by assuming a retrogression of the degree of hydration of the salt in solution with a rising temperature. At the transition point, 234°, the rhombic crystals of sodium sulphate pass into the monoclinic form:

$$Na_2SO_{4\,\text{rhombic}} \overset{234^\circ}{\rightleftharpoons} Na_2SO_{4\,\text{monoclinic}}$$

The solubility of anhydrous monoclinic sodium sulphate is wholly retrograde, and at the critical temperature (365°) the concentration of the solution is so small that the critical temperature is virtually the same as that of water. A. Smits assumes that the strongly retrograde solubility of monoclinic sodium sulphate indicates that the latent heat of liquefaction of this salt is much less than that of the rhombic salt. In the diagram, the concentration near the point C is on a much enlarged scale in order to make the relations clear, for the curve up to C represents the solubility of sodium sulphate in the vapour phase, and hence this curve virtually coincides with the H_2O axis. At the critical temperature of the solution, the liquid and vapour perhaps have the same composition, and the two curves join up with one another.

Is a heterogeneous solution to be regarded as a phase?—In heterogeneous solutions there are an infinite number of phases because every different degree of concentration can be regarded as a phase. **The phase rule is concerned with conditions of equilibrium,** and a heterogeneous solution is not in equilibrium because there is a tendency to diffusion. Hence, the phase rule is not needed to determine if such a solution is in equilibrium. If sulphur be placed in contact with iron, it might be said that, neglecting vapour, there are two components, and two phases, and therefore the system is univariant. Hence, sulphur and iron will not interact when heated. It will be noticed, however, that the mixture of sulphur and iron is not a system in equilibrium; the two elements are not phases of a prior system, or molten ferrous sulphide, FeS, on cooling would separate into particles of free sulphur and free iron. Consequently, the phase rule does not apply.

Is a solution to be regarded as a one-phase or as a two-phase system?—The decrease in the solubility of a substance with rise of temperature is due to the solute changing its nature thus, the diminishing solubility of sodium sulphate, $Na_2SO_4.10H_2O$, above 33° is referred to the passage of the decahydrate into the anhydrous salt, Na_2SO_4; with calcium hydroxide, $Ca(OH)_2$, too, the change is usually attributed to the transformation of some hydroxide into oxide, CaO. In general, **a turning point in the solubility curve shows that the solid phase in the saturated solution is changing.** From this it follows that the molecules of a substance in solution may retain their individuality and that they can undergo changes in the solution similar to those they suffer when heated alone. H. C. Jones and J. S. Guy[14] showed that water which is combined with salts in solution is far more transparent than pure water; and J. E. L. Holmes and H. C. Jones, that the rate of saponification of methyl acetate or formate is likewise faster with combined than it is with free water.

While a solution in equilibrium can be said to have the same composition in all its parts, so that it cannot be separated by mechanical or physical operations into different individual parts, yet, according to the molecular theory, there must be a limit to the subdivision beyond which the solution can no longer be regarded as homogeneous. Consequently, there is no clearly defined line of demarcation between heterogeneous and homogeneous mixtures. A so-called homogeneous solution, for instance, can sometimes be separated into its component parts by certain membranes, just as a mixture of gases can sometimes be separated into its constituent parts by atmolysis. A homogeneous solution, or a mixture of gases, however, is considered to be a homogeneous one-phase system because diffusion maintains one uniform concentration throughout its mass.

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§ 2. The Freezing of Solutions

> Proof or disproof of the existence of many compounds must be sought in the physical properties and in the behaviour of mixtures at different temperatures.—L. W. Andrews (1907).

The curve *OB*, the *salt line*, Fig. 3, represents the solubility of sodium chloride at temperatures ranging from —23° to +40°; the observation cannot be continued below —23°, because the whole mass freezes at or above that temperature; the upward curve would probably stop only at the melting point of sodium chloride, 801°, if it were not for the volatilization of the water. Hence, to determine the solubility, the pressure would have to be very great at this high temperature to prevent the water leaving the salt.

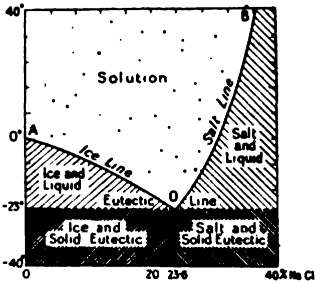

Fig 3.—Solubility and Freezing Curves of Sodium Chloride: Water Solutions.

The freezing temperature of a solution is generally lower than that of the pure solvent. More than a century ago, C. Blagden (1788)[1] cited a number of observations which led him to the belief that the lowering of the freezing point is proportional to the amount of substance in solution. In his own words: **The effect of a salt is to depress the freezing point in the simple ratio of its proportion to water.** This generalization is sometimes called **Blagden's Law.** The freezing point of an aqueous solution of sodium chloride, that is, the temperature at which *ice* begins to separate, is gradually reduced by the continued addition of small quantities of sodium chloride, and reaches its lowest value, —23°, when the solution has nearly 23·5, say 24, per cent. of sodium chloride; further additions of the salt raise the temperature at which the solid is deposited. Solid sodium chloride, not ice, separates from the solution. F. Guthrie's measurements (1875)[2] of the relation between the freezing point and the concentration of aqueous solutions of sodium chloride are shown graphically by the *ice line*, *AO*, Fig. 9, Cap. IX.

Impurities included in crystals.—It has long been known, even as far back as Aristotle's day, that drinkable water could be obtained from frozen sea-water; and that if an aqueous solution of salt be gradually cooled, comparatively pure ice first separates from the solution. The work of F. Rüdorff (1861) and of J. Fritzsche (1863)[3] on the freezing of coloured solutions clearly established this fact. Thus, magnesium cyanoplatinate forms a colourless solution from which colourless ice separates, whereas, if solid magnesium cyanoplatinate separated, the colour would be intensely red.

Faraday's experiment.—Water coloured with sulphindigotic acid is placed in a test-tube and immersed in a freezing mixture; the water on freezing near the walls of the tube drives the colouring matter to the axis of the tube. The coloured liquid is poured away, and when the cavity is rinsed out, a plug of transparent colourless ice is obtained. The trace of salt which is generally found in the ice which separates from a salt solution is merely the mother liquid or solute which is mechanically entangled in the crystals of ice.

The freezing curves of binary mixtures which do not form compounds.—A solution of sodium chloride in water may be taken as an example. It may be assumed that these substances are but partially soluble in the liquid state and insoluble in the solid state. Imagine a 5 per cent. solution of salt subjected to a gradually diminishing temperature. Start at 0°. When the temperature reaches, say, —3·4° ice separates from the solution. The mother liquid remaining has therefore more than 5 per cent. of salt in solution; as the temperature falls, more ice separates. The further concentration of the mother liquid and the separation of ice continue until the mother liquid has about 23·6 per cent. of salt, when the whole remaining liquid freezes *en bloc* at —23°. The solid now consists of crystals of ice embedded in a matrix of ice and salt. Quite an analogous sequence of changes occurs if solutions containing more than 23·6 per cent. of salt be gradually cooled. This time, however, instead of pure ice, pure salt separates until the residual liquid has 23·6 per cent. of salt. The whole solidifies *en masse* at —23°. If the cooling solution has just 23·6 per cent. of salt, neither ice nor salt separates, until the temperature has fallen to —23°, when the whole freezes to a solid mass. No other mixture of water and salt freezes at a lower temperature than this. Hence a solution containing 23·6 per cent. of salt is called a **eutectic mixture** or simply a **eutectic**; —23° is the **eutectic temperature**; and the general phenomenon is called **eutexia**—from the Greek εὐ, easily, and τήκω, I melt. Hence *eutectic* means "that which is easily melted." The word εὔτηκτος was used by Aristotle (*Problemata*, **1**. 50) in the sense of easily soluble or digestible. The nature of the cooling liquid, or of the solid of any given composition, is also shown by the shaded areas in Fig. 3. F. Guthrie used to think that this mixture—water with 23·6 per cent. of salt—corresponded with the formation of a definite compound of sodium chloride and water—$NaCl.10H_2O$—stable only at low temperatures. Hence his designation **cryohydrate** for the alleged compound. A. Ponsot (1896)[4] called the substance a **cryosel.** The term eutectic mixture is preferred in place of cryohydrate or cryosel. The eutectic temperature, —1·2°, represented at *E*, Fig. 2, corresponds with the eutectic mixture of 3·85 per cent. of Na_2SO_4 in 100 grams of solution when the decahydrate, $Na_2SO_4.10H_2O$, is the stable phase; and with the heptahydrate, $Na_2SO_4.7H_2O$, the eutectic mixture contains 12·7 per cent. of Na_2SO_4, and the eutectic temperature is —3·55°. The same type of curve is illustrated in Fig. 4—two separate branches meeting in a eutectic is characteristic of binary metal alloys which form neither compounds nor solid solutions—*e.g.* alloys of tin and bismuth, tin and zinc, cadmium and zinc, lead and antimony, etc.

Cryohydrates and eutectics.—We now know that Guthrie's cryohydrates are nothing but mechanical mixtures of ice and salt. The one is entangled with the other. The more salient characteristics of eutectics are: (1) They have a lower melting point than mixtures with a greater or less quantity of one component; (2) They freeze at a constant temperature; and (3) They have a constant composition. With these qualities, it is easy to understand how eutectic mixtures were mistaken for true chemical compounds. No matter what the original composition of the salt solution, the last fraction to solidify always has the same composition; and a constant melting point. Both these qualities are often stated to be characteristics of true chemical compounds. The inference that eutectics or cryohydrates of sodium chloride and numerous other salts are not chemical compounds is based on the following evidence: (1) The heterogeneous structure is frequently apparent under the microscope. The crystals of ice can often be seen lying in a matrix of salt, especially if a coloured salt like potassium permanganate, copper sulphate, or potassium dichromate be employed. Indeed, the eutectic sometimes forms definite patterns, with iron and carbon, the eutectic consists of alternate bands of the two components—*lamellar eutectic*; with copper and aluminium, one component forms globules embedded in a matrix of the other—*globular eutectic*; with copper and antimony, the one component appears like small polyhedral crystals arranged in matrix of the other—*polygonal eutectic.* (2) Unlike true crystalline compounds, the cryohydrates are generally opaque and ill-defined. (3) Alcohol may dissolve the solvent, leaving behind a network of salt. (4) There are no special signs of chemical change during the formation of the cryohydrate. (5) The physical properties of the cryohydrate—*e.g.* heats of solution, specific gravities—are a mean of those of the corresponding constituents. This is not usually a characteristic of chemical combination. (6) The ratio of salt to solvent is not always in molecular proportions. The agreement in some cases is merely a coincidence. (7) The composition of a cryohydrate is different when the solidification takes place under different pressures. Hence, added A. Ponsot (1896), the eutectics or " cryohydrates of F. Guthrie are not chemical compounds, they are mechanical mixtures of pure ice and the solid salt. The salt may be anhydrous like potassium nitrate, KNO_3, or hydrated like copper sulphate, $CuSO_4.5H_2O$."

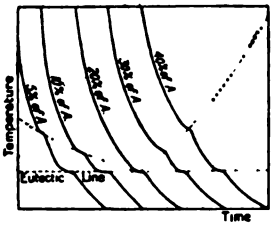

FIG. 4.—Cooling Curves of Binary Mixtures of *A* and *B* with a Eutectic.

There is another kind of eutectic which is formed in a solidified, congealed, or supercooled solution, at the time of solidification. In the case of a solidified solution; to distinguish this mixture from a true eutectic it is sometimes called a **eutectoid**. The only difference between a eutectoid and a eutectic is that the former is formed *after*, and the latter *at* the time of solidification. In the case of a solidified solution of carbon in iron, the eutectic—called pearlite—is formed after the metal has become solid. The conglomerate or impure ice formed by the freezing of a solution with less than 23·5 per cent. of sodium chloride is called a **hypo-eutectic** because it contains less than the eutectic percentage of the salt; likewise also the conglomerate formed by the freezing of a solution with more than 23·5 per cent. of salt is called a **hyper-eutectic** because it contains more salt than the eutectic proportion. The hypo-eutectic is a mixture of the eutectic with an excess of the frozen solvent; the hyper-eutectic is a mixture of the eutectic with an excess of solute.

Cooling and heating curves.—If a thermometer or thermocouple be placed in a cooling solution, and the time be plotted against the temperature, three main types of cooling curve may be obtained: (1) *Pure liquids* show a break in the continuity of the curve at the freezing point corresponding with the evolution of heat—latent heat of solidification—middle curve, Fig. 4. (2) *Mixed liquids*—binary alloys and solutions—show two breaks in the continuity of the curve: (*a*) when the solvent begins to separate and there is a change in the direction of the cooling curve, *B*, and (*b*) when the eutectic freezes *en masse*, Fig. 4. (3) *Eutectic mixtures* have a cooling curve with one break corresponding with the evolution of heat when the whole mass solidifies (20 per cent. *A*, Fig. 4). These phenomena are reversed when the corresponding solids are heated. The observation of the heat changes which occur when a metal, alloy, or other substance is cooled from an elevated temperature or raised to a higher temperature is called **thermal analysis,** and it has played a great part in studying the constitution of metals and alloys.[5]

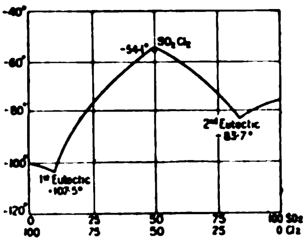

FIG. 5.—Freezing Curve of Mixtures of Chlorine and Sulphuric Dioxide showing Two Eutectics.

The freezing curves of binary mixtures which form compounds.—T. P. van der Goot (1911)[6] found that when a mixture of sulphuryl chloride, SO_2Cl_2, melting at —54·1°, and of sulphur dioxide, SO_2, melting at —75·1°, be treated as in the case of the above mixture of sodium chloride and water, a eutectic melting at —87·3° is obtained, while a mixture of sulphuryl chloride and chlorine—Cl_2, melting at —100·9°—furnishes a eutectic melting at —107·5°. A mixture of sulphur dioxide and chlorine furnishes two eutectics melting at —83·7° and —107·5° respectively with a maximum point at —54·1°, corresponding with the formation of the compound

SO_2Cl_2 from the components in question, $SO_2+Cl_2=SO_2Cl_2$, and the eutectic at −107·5° is characteristic of a mixture of sulphuryl chloride and chlorine. These results are summarized in Fig. 5.

The raising of the melting or freezing point of one substance by the addition of another often indicates that a compound is being formed. The freezing point of zinc is depressed by addition of tin, bismuth, thallium, cadmium, lead, antimony, magnesium, or aluminium; and elevated by additions of silver, copper, gold, or platinum. In general, when a pair of metals, minerals, or salts furnish a freezing curve with a number of branches dependent on the number n of compounds formed, the curve will have $2n+1$ branches and there will be $n+1$ eutectics. *E.g.* alloys of copper and antimony; nickel and tin; silver and aluminium; zinc and antimony; lead and copper; lead and aluminium; bismuth and copper; aluminium and gold; aqueous solutions of ammonia, nitric, hydrochloric, or sulphuric acid; etc. If one or more of the compounds forms a solid solution with one of the other metals, this would modify the character of the curve as indicated in the first type of freezing curve.

J. P. Cooke (1855)[7] and N. S. Kurnakoff (1912) have concluded from a study of alloys—zinc and antimony, in the former case; and thallium and bismuth in the latter—that there is a class of **indefinite compounds** which are not described by the laws of definite and multiple proportions, and they support the view of C. L. Berthollet in his controversy with J. L. Proust:

> The result of the different circumstances which modify chemical action is sometimes a combination whose proportions are constant, and sometimes, on the contrary, the proportions of the combinations which are formed are not fixed, but vary according to the conditions under which they are formed.

N. S. Kurnakoff has pointed out that the composition of a compound is determined by the position of singular points on the curve representing physical properties; these points most frequently correspond with simple formulæ, but there are exceptions. For example, a maximum occurs on the freezing-point curve of mixtures of thallium and bismuth with a mixture containing 62·8 atomic per cent. of bismuth, but solid solutions at ordinary temperatures extend from 55 to 64 atomic per cent. of bismuth, and there is a cusp in the electrical conductivity curve with 64 atomic per cent. of bismuth. N. S. Kurnakoff recommends naming compounds whose composition does not change with changes in the equilibrium conditions of a system, **daltonides**; and compounds whose composition varies with a variation in the conditions under which they are formed, **berthollides.** He considers that solid solutions, brasses and bronzes, zeolites, metal ammines, etc., are representative berthollides. This is a direct attack on constant composition as a test for chemical action, and if it were accepted as an arbitrary definition, convention would return a different answer from that previously obtained for the question: Are solutions chemical compounds?

The freezing curves of binary mixtures which either form or do not form continuous series of mixed crystals.—When two substances are reciprocally soluble in all proportions and solidify to form solid homogeneous solutions—also called mixed crystals—but not chemical compounds, a continuous curve will connect the freezing points of the pure components. The properties of the mixtures will vary in a continuous manner from one end of the series to the other. The freezing points of all possible mixtures will be represented (i) by a straight (or almost straight) line between the freezing points of the pure components as is the case with mixtures of albite and anorthite. The pyrophosphates of manganese and magnesium are miscible in all proportions and belong to Roozeboom's type I:

Manganese pyrophosphate .	100	75	50	25	0 per cent.
Magnesium pyrophosphate .	0	25	50	75	100 ,,
Melting point . . .	1196°	1242°	1286°	1340°	1383°
Refractive index (mean) .	1·70	1·67	1·65	1·63	1·60

Other examples are lead bromide and iodide ; lead and stannous chlorides ; alloys of gold and silver ; gold and platinum ; copper and nickel ; palladium and silver ; palladium and gold ; palladium and copper ; and usually, with pairs of metals of high melting points, but the further apart the melting points of the two components the less the probability of this linear relation. (ii) By a continuous curve which rises through a *maximum*, as is the case, for instance, with mixtures of organic compounds which show optical isomerism—*e.g.* *d*- and *l*-carvoxime (J. H. Adriani, 1900),[8]—but has not been otherwise verified. (iii) By a continuous curve which drops down through a *minimum* as is the case with mixtures of silver and cuprous sulphides—Ag_2S—Cu_2S ; copper and manganese sulphites, $CaSO_3$ and $MnSO_3$; iron and vanadium ; manganese and nickel ; and copper and gold. Mercuric bromide melts at 23·5° and the iodide melts at 255·4° ; the system $HgBr_2$—HgI_2 has a minimum point with 59 per cent. gram-molecules of the bromide (41 of the iodide) and melts at 216·1°. The dotted line, Fig. 6, shows the solidus curve—W. Reinders (1899).

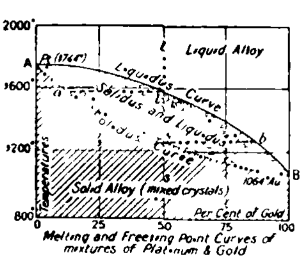

FIG. 6.—Melting and Freezing Point Curves of Mixtures of Platinum and Gold—Roozeboom's Type I.

Consider the first case. The freezing and melting point curves do not coincide, so that these two curves divide the region, Fig. 6, into three parts ; above the freezing-point curve *AlbB*—the **liquidus curve** of H. B. Roozeboom—all possible mixtures of platinum and gold are completely liquid ; below the melting point curve *AasB*—the **solidus curve** of H. B. Roozeboom—all possible mixtures are solid ; and in the part *AlbBsa*, bounded by the liquidus and solidus curves, the mixture is partly liquid and partly solid. If a molten mixture of 50 gram-atoms of each of the two metals at a temperature represented by the point *l* be allowed to cool. the temperature of the system will be represented by a point travelling down *llss*, and mixed crystals, that is a solid solution of the two metals, will begin to separate when the temperature drops to *l*. It is very unlikely that the reciprocal solubility of the two metals will be equal in the solid and liquid states ; in most cases, the solubility will be different, and be more complete in the liquid state so that mixed crystals of an alloy richer in the less fusible metal and with a composition represented by the point *a* will separate, and the mother liquid will have a composition richer in the more fusible metal and be represented by the point *b*. As the freezing continues, the composition of the mixed crystals which separate will be represented by a point travelling along the line *as*, and the composition of the mother liquid by a point travelling along the line *lb*. The process of diffusion, however, will tend to make the composition of the solid solution more and more like that of the mother liquid. With complete diffusion, the solid solution at the end of the process will be homogeneous in composition ; but since diffusion in a solid is a very slow operation, in practice, diffusion will be incomplete, and the mass will be more or less heterogeneous. If there were no diffusion, the final mass would have a composition ranging from that represented by the point *a* (in the centre of

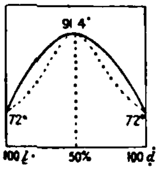

FIG. 7.—Roozeboom's Type II of mixed Crystals of Carvoxime.

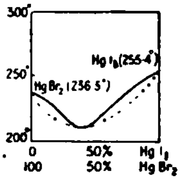

FIG. 8.—Roozoboom's Type III of mixed Crystals.

the mass) to b (on the outside). By reheating the alloy (below its melting point) diffusion may take place, and such a process—called *annealing*—is necessary to make the solid mass approximate more and more to the homogeneous condition. The alloy solidifies completely when the temperature has fallen to s, and is partly liquid and partly solid in the temperature interval ls. Hence, says H. M. Howe (1916), the liquidus traces the history of the liquid or mother liquor; the solidus, the history of the frozen or solidified part during freezing and melting.

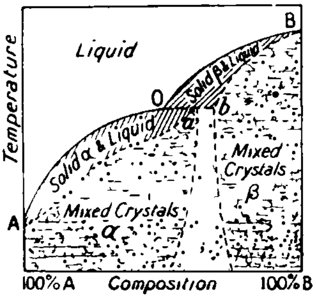

FIG. 9.—Diagrammatic—Type IV.

In addition to the three types of mixed crystal formation just considered, there are two others in which the two substances are completely soluble in the liquid state, but in one type (IV), the liquidus curve shows a transition point, O, Fig. 9, and the solidus is compounded of two disconnected curves Aa and Bb with a hiatus ab. The range of composition of mixed crystals α and β is respectively represented by the abscissæ of Aa and Bb. *A magma of composition corresponding with the transition point O is in* equilibrium with the mixed crystals α or β. Mercury and cadmium alloys investigated by H. C. Bijl (1902) illustrate the type—mercury melts at —38·8°, cadmium at 320·8°. The transition point corresponding with 61 per cent. of cadmium occurs at 188°, a corresponds with 61·7 per cent. of cadmium and b with 65·2° per cent. Fig. 9 is based on this example. Other examples are mixtures of enstatite and diopside; sodium and silver nitrates; and, according to G. Scarpa (1915), mixtures of potassium hydroxide and chloride.

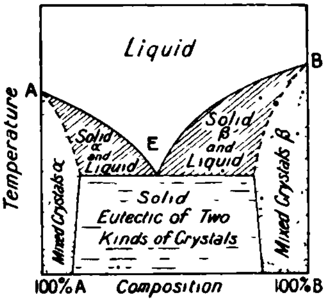

FIG. 10 —Diagrammatic—Type V.

In the next type (V), the liquidus consists of two curves meeting in a eutectic E, and the solidus likewise consists of the two dotted curves A and B, Fig. 10. Mixed crystals can exist only in the range indicated. Fig. 10 is based on C. Sandonnini's work (1911) on mixtures of silver chloride melting at 455°, and cuprous chloride melting at 422°; the eutectic is at 260°. Other examples are potassium and thallium nitrates, orthoclase and albite, cuprous and sodium chlorides, thallium chloride and iodide, calcium and lithium silicates —$CaSiO_3$ and Li_2SiO_3; mercuric chloride and iodide; aluminium and zinc, gold and nickel, etc.

To summarize the five types of mixed crystal formation, in which chemical compounds are not formed:

Liquid state.	Solid state.	Liquidus.	Figure.
Completely soluble	Completely soluble, continuous series of mixed crystals	no max. or min.	6
		maximum	7
		minimum	8
	Partially soluble limited range mixed crystals	transition point	9
		eutectic	10

Modifications of the two latter types are exhibited when the substances are only partially soluble in the liquid state, and when they are partially or wholly insoluble in the solid state. The case of salt and water, Fig. 3, illustrates the former; and copper and cuprous sulphide, iron and ferrous sulphide, and zinc and lead illustrate the latter. Very complex curves may be obtained as a result of complications introduced by the formation of chemical compounds which may or may not form mixed crystals with one another or with the pure components; the chemical compounds formed may dissociate below the freezing temperature; the solubilities in the liquids and solid states may vary; and transition points may appear in the cooling solid.

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§ 3. The Solubility of Liquids in Liquids

Mixtures of liquids like benzene and water or carbon disulphide and water are mutually insoluble, and they are said to be *immiscible* or *non-miscible*. Each liquid then behaves as if it were present alone, the vapour pressure of the mixture corresponds with the sum of the saturation pressure of each. Each of the two liquids may be partially soluble in the other as in the case of ether and water, phenol and water, or aniline and water, and the liquids are then said to be *partially miscible*; or the two liquids may be miscible in all proportions—*completely miscible*—as in the case of alcohol and water. With partially miscible liquids, the composition of each solution, per unit volume, is independent of the masses of the two components—provided both are present. Thus, when ether is gradually added to water, a solution of ether in water is formed, which becomes more and more concentrated. When the aqueous solution is saturated any further addition of ether forms a saturated solution of water in ether, and with further additions of ether, the ethereal solution remains saturated with water until, finally, the ether has dissolved all the water. Any further addition of ether simply dilutes the ethereal solution of water. Consequently, partially miscible liquids have a sharply defined limiting surface furnishing a heterogeneous two-phase solution; with completely miscible liquids, a homogeneous one-phase solution is formed.

When two liquid phases are present in a system—*e.g.* ether and water—the system has the following characteristic properties: (1) The composition of each phase is constant at any assigned temperature and pressure, and is independent of the relative amounts of the two phases, and independent of the mode of preparation. (2) The composition of each phase changes with temperature changes. (3) The vapour pressure of both liquid phases are equal both as to the total pressure and to the pressure of each constituent. If in the system ether and water, the water is withdrawn continuously, the pressure will remain constant so long as both liquid phases are present. When the water disappears, the pressure of the water vapour begins to fall, and becomes zero simultaneously with the disappearance of the water phase, and the residue will be a saturated solution of water in ether. At any assigned temperature, the composition of the liquid will have one constant value, but it will vary with variations of temperature.

In 1835, M. L. Frankenheim[1] noticed that while a variety of creosote and water are only partially miscible at 0°, at 22° the two liquids are mutually soluble in all proportions; and in 1857, D. Absaheff investigated the mutual solubility of a number of pairs of liquids, and showed that the composition of partially miscible liquids changes with a rise of temperature, so that the composition of the two layers becomes more and more nearly alike until a point is reached at which the liquids become completely miscible. A few exceptions have been encountered. For example, for mixtures of water and ether E. A. Klobbie found that the solubility of ether in water *decreases* with rising temperature, while the solubility of water in ether *increases*, as indicated in Table I.

TABLE I.—MUTUAL SOLUBILITIES OF ETHER AND WATER.

Temperature.	Grams of ether per 100 grms. of aqueous solution.	Grams of water per 100 grms. of ethereal solution.
−4°	12·63	0·92
0°	12·17	1·00
10°	9·02	1·12
20°	6·48	1·23
30°	5·04	1·33

This was further investigated by W. Alexejeff [2] between 1876 and 1885; F. Guthrie in 1884, F. A. H. Schreinmakers in 1897, etc. W. Spring and S. Romanoff observed that certain pairs of molten metals presented a similar phenomenon to that observed by M. L. Frankenheim. For instance, mixtures of zinc and bismuth which, below 800°, form two layers, like mixtures of ether and water at ordinary temperatures, but are completely miscible above 900°. W. Alexejeff's data for the mutual solubilities of aniline and water are indicated in Table II.

TABLE II.—MUTUAL SOLUBILITIES OF ANILINE AND WATER.

Temperature.	Grams of aniline per 100 grms of aqueous solution.	Grams of water per 100 grms. of aniline solution.
20°	3·1	5·0
40°	3·3	5·3
60°	3·8	5·8
80°	5·5	6·5
100°	7·2	8·4
120°	9·1	11·9
140°	13·5	16·9
160°	24·9	28·8
167°	48·6	51·4

The temperature at which the two liquids become mutually soluble in all proportions is called the **critical solution temperature,** and the corresponding concentration of the solution, the **critical concentration.** Thus the critical solution temperature of aniline and water is 167°; and the critical concentration is a liquid containing 48·6 grms. of water and 51·4 grms. of aniline. The analogy between the critical solution temperature and the critical state of gases was pointed out by O. Lehmann in 1888,[3] and by O. Masson in 1891, and it is illustrated by the curves, Fig. 11. There has been some discussion as to whether the observed data lie on one continuous curve, or form two curves which intersect one another at the critical point.[4]

The determination of the critical solution temperature is effected by plotting the solubility curves of the two liquids—*A* in *B* and *B* in *A*; or by heating a mixture of the two liquids until a homogeneous solution is obtained, and noting the temperature at which a turbidity appears. The blue opalescence is due to the separation of minute drops of liquid; and their appearance is evidence that the liquid is saturated with respect to large drops, since E. Warburg[5] has shown that small drops of liquid are more readily dissolved than large ones, just as Lord Kelvin has shown that small drops of liquid appearing in vapour are absorbed by the larger one owing to the greater vapour pressure of the former.

According to C. S. Hudson[6] nicotine and water are miscible in all proportions at ordinary temperatures, but at temperatures exceeding 60°, the solution becomes turbid owing to incomplete miscibility; at 210° the two liquids again become completely miscible. The solubility curves of the binary system nicotine and water thus appear to form a closed curve with an upper and a lower temperature of complete miscibility. A similar closed curve has been observed with secondary butyl alcohol and water. According to W. Dolgolenko, the lower temperature limit of complete miscibility in the latter case is due to the presence of traces of tertiary alcohol as an impurity; if these be eliminated, the lower critical temperature does not occur. The phenomenon of a closed solubility curve is taken to be characteristic of a ternary, not a binary, system. In the case of nicotine and water, the third constituent is supposed to be a hydrate of nicotine—such a system is called a *pseudoternary system* by H. W. B. Roozeboom.[7] The hydration of nicotine is evidenced by a considerable contraction and evolution of heat when nicotine is mixed with water.

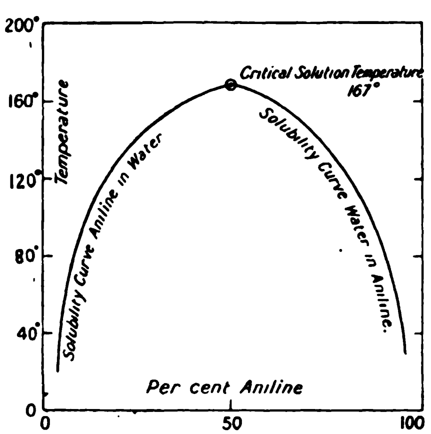

FIG. 11.—Reciprocal Solubility Curves of Aniline and Water.

The kinetic theory of the critical temperatures, and the critical solution temperature.—As the temperature of a liquid is gradually raised, the average kinetic energy of the molecules increases, and a greater and greater proportion of the molecules overcomes the cohesive forces holding the particles of liquid together, and escapes as vapour. The thermal expansion of the liquid is due to the increasing velocity of the vibrating molecules, which makes them behave *as if* they were actually repelled from one another by a force which increases in magnitude as the temperature is raised. Consequently, as the temperature is raised, the repellent forces become stronger and the cohesive forces weaker. When the two forces are just balanced, the liquid can expand indefinitely and the surface separating liquid and vapour vanishes. The properties of liquid and gas are then the same. This is the critical temperature; and the critical pressure has been taken to represent the magnitude of the quasi-repulsive force between the molecules at the critical temperature. When two liquids are in contact, molecules pass from one to the other by a process which is analogous with vaporization, except that the vibratory motions are slower owing to frictional forces. When the average speed of the molecules is great enough just to balance the physical cohesive forces between the molecules of the liquid, the surface of separation between the two liquids vanishes, and the system becomes homogeneous. Hence, in both cases, the critical temperature is due to the balancing of the cohesive forces of the liquid by the quasi-repulsive force due to the increasing velocity of its particles.[8]

Assuming that the critical pressure of a gas is that at which the repellent forces between the molecules are just equal to the forces of attraction at the critical temperature, E. C. Bingham argues that the critical pressure of a gas is a measure of the molecular attraction. Again, since Avogadro's rule applies very well for gases whose particles are so far apart that the time during which they are within the range of one another's attraction is negligible in comparison with the time the particles are independent. The closer the particles are together the more does the intermolecular attraction predominate. If the deviations of a gas from Avogadro's rule are a measure of molecular attraction, the attractive forces will be inversely proportional to the molecular volume, and consequently, the product of the molecular volume M/D and critical pressure p_c should be a constant. E. C. Bingham has worked out Table III. in confirmation of these hypotheses.

TABLE III.—INTERMOLECULAR ATTRACTION AND SOLUBILITY.

	M	D	M/D	p_c	$p_c M/D$	b	$p_c b$
H_2O .	18	1	18	197	3500	0·00150	0·295
NH_3 . .	17	0·6089	28	114	3200	0·00162	0·285
H_2S . .	34	0·91	37·4	90	3370	0·00189	0·170
HCl . .	36·4	0·835	43·6	86	3750	0·00173	0·149
SO_2 . .	64·1	1·3769	46·5	78·9	3670	0·00249	0·196
N_2O . .	44	0·758	52·6	75	3940	0·00189	0·141
CO_2 . .	44	0·8267	53·2	73	3800	0·0019	0·138
CS_2 . .	76·1	1·2922	58·9	75	4400	0·0033	0·247
Cy_2 . .	52·1	0·866	60·2	61·7	3710	0·0029	0·179
$SnCl_4$ . .	260·8	2·28	114·4	36·9	4220	0·00733	0·271
$GeCl_4$.	214·3	1·887	113·6	38	4300	0·00663	0·255
$(C_2H_5)_2O$.	76·1	0·7191	103·4	37·8	3890	0·00563	0·202
$CHCl_3$.	119·4	1·5039	79·4	54·8	4350	0·00445	0·244
C_2H_5OH .	46	0·7942	57·9	62·8	3640	0·00377	0·237
CCl_4 . .	153·8	1·5947	97·1	45	4370	0·00434	0·195

Roughly, the product of the critical pressure and molecular volume is a constant. The molecular volumes should be observed at the critical temperature, but very few data are available. The magnitude b of J. D. van der Waal's equation is proportional to the volume of the particles, and it has been compared with the quotient M/D. The agreement is not so good on account of large experimental errors.

Substances with a large molecular volume have a small intermolecular attraction —*e.g.* ether and carbon tetrachloride—and hence such substances are more likely to be miscible than if one is replaced by a substance like water with a small molecular volume and a large intermolecular attraction. Two substances with a small intermolecular attraction mix readily; no two substances are miscible when their molecular volumes differ very much, since molecular volumes are inversely as molecular attractions. V. Rothmund gives Table IV. indicating the order of solubility of a number of substances in water:

TABLE IV.—THE RELATION BETWEEN MOLECULAR VOLUME, DIELECTRIC CONSTANT, AND SOLUBILITY.

	Molecular volumes.	Dielectric constants.
Water, H_2O	18	81
Formic acid, H.COOH	37·7	57
Methyl alcohol, CH_3OH	39·5	32·5
Acetone, $CH_3CO.CH_3$	72·5	20·7
Aldehyde, $CH_3.COH$	55·6	21·1
Propionitrile, C_2H_5CN	68·8	27·7
Phenol, C_6H_5OH	90	9·7
Benzaldehyde, $C_6H_5.COH$	100	18
Ether, $(C_2H_5)_2O$	103	4·36
Carbon tetrachloride, CCl_4	97·1	1·00
Carbon disulphide, CS_2	58·9	2·64
Hexane, C_6H_{14}	129·9	1·86

Pairs of substances near each other in the list are completely miscible, and the mutual solubility is less, the greater the distance of the two liquids apart. With three or four exceptions, the order of the molecular volumes (E. C. Bingham) and the order of the dielectric constants (V. Rothmund) agree fairly well with the order of solubility. So also the work of A. Christoff shows that the solubility of a gas increases as the cohesion (or surface tension) of the solvent decreases, and that with mixtures of sulphuric acid and water, the solubility of the gases reaches a minimum as the surface tension attains a maximum. I. Traube has made analogous observations by showing that the more a solute decreases (or increases) the surface tension of a solvent, the less (or greater) the force with which it is attracted by the liquid.

The analogy between the critical solution temperature and the critical temperature led W. Alexejeff to try if L. Cailletet and E. Mathias' rule for the relation between temperature and the density of a liquid and of its saturated vapour—a straight line is obtained by joining the mid-points of the ordinates lying between two branches of the curve—is applicable to the mid-points of the line between the two branches of the curve representing the solubilities of one liquid in the other, and he did obtain an approximation to a straight line. W. Rothmund attributed the irregular deviations from a straight line to experimental errors. In cases where accurate data are available the law of rectilinear diameters applies for pairs of liquids with an upper critical solution temperature, so that if C_1 and C_2 be the two concentrations at the same temperature θ, and A and B are constants, $\frac{1}{2}(C_1+C_2)=A+B\theta$, and the concentrations at any temperature θ can be calculated from one another when the constants A and B are known. When there is a lower critical solution temperature, the line is not always straight—but then the lower solution temperature is regarded as a proof that there is some disturbing factor such as the presence of a third component as an impurity or as a compound of the two liquids, or a polymeric modification of one or both of the liquids.

J. Holmes[9] has advanced the hypothesis that the intermiscibility of liquids is a function of the molecular volume which is independent of chemical constitution, and which therefore offers a means of ascertaining the molecular weights of liquids comparable perhaps with the methods which are based on Avogadro's hypothesis for the gaseous state. The molecular volume in question, referred to water unity, is not that deduced from the regular formula. Carbon disulphide and ethyl alcohol, for instance, have the same molecular volume from this point of view, but one liquid is insoluble in water while the other liquid is miscible in all proportions. If allowance be made for the degree of association of the molecules in the liquid state, it is found that *an increase in molecular volume is attended by a decrease in miscibility with water*. Assuming that the liquid molecule consists of a nucleus of great density and an outer envelope or sphere of influence, then in the absence of chemical change, the more nearly equal the radii of the molecular spheres, the greater the miscibility of the two substances. With spheres of different sizes, then, as the ratio of the radius of the larger to that of the smaller sphere increases, the dimensions of the interspaces also necessarily change, and a point is reached when the close packing of spheres is a maximum. In an equimolecular mixture this occurs when the radii are as 1·618 to 1. It is suggested that when these conditions are fulfilled the liquids are on the border line between complete as compared with partial miscibility, and that so long as this or a smaller ratio exists, the liquids will be mutually miscible. When, however, the ratio becomes greater than this value, a complex is formed which will allow of the same close-packing, but results in the formation of two layers of liquid, in each of which the distribution of molecules depends on the further change in this ratio until it reaches 2·414, when, the smaller spheres being able to pass completely through the interspaces between the larger spheres, the liquids should be now wholly immiscible.

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§ 4. The Solubility of Gases in Liquids—Henry's Law

The absorption of gases by liquids began to attract attention towards the end of the seventeenth century; and later the subject was investigated by J. Priestley and H. Cavendish. The solubility of gases in liquids depends upon the nature of the gas and of the solvent, as well as upon the temperature and pressure of the system. No common solubility has been observed, and we have no generalization of such wide applicability as Boyle's and Charles' laws. Some gases are only slightly soluble in water, others dissolve very copiously. One volume of water, at normal temperature and pressure, will dissolve 1200 volumes of ammonia, and but 0·210 volume of hydrogen.

The changes in the volume of the solvent.—There is usually a small expansion when gases are dissolved in water. The phenomenon was noticed by T. Bergmann [1] near the end of the eighteenth century; and the change was investigated by a few workers during subsequent years. Thus, T. Thomson, J. J. Mackenzie, and E. L. Nichols (1878) found that the expansion which occurred when water is saturated with carbon dioxide is almost proportional to the absorption coefficient at the specified temperature. K. Angström (1882) found the increments in the volume of a liquid following the absorption of its own volume of gas:

	N_2	Air.	CO	O_2	H_2	CO_2
Volume increment .	0·00145	0·00140	0·00127	0·00115	0·000106	0·00125

The general results show that **the specific gravity of the absorbed gas is nearly proportional to its specific gravity in the free state**; and the less compressible the gas the greater the volume increment when it is dissolved in water. Concentrated aqueous solution of some of the readily absorbed gases—*e.g.* hydrogen chloride—contract when diluted with water, showing that the volume increment on absorption cannot be proportional to the quantity of gas absorbed.

Two systems have been much employed for representing the solubility of gases in liquids. R. Bunsen (1857) [2] applied the term **absorption coefficient**, β, to the volume of a gas reduced to 0° and 760 mm. which is absorbed by unit volume of liquid when the pressure of the overlying gas on the liquid is 760 mm. and the temperature, at the time of absorption, is $\theta°$. For instance, suppose 20 c.c. of a dry gas at 10° be confined over mercury in a tube such that when the barometric pressure is 750 mm. the upper level of the mercury is 200 mm. above the lower level in the trough; further, let 2·5 c.c. of water be introduced into the tube, and, after shaking, absorption reduces the volume of the gas to 18 c.c. when the barometer remains at 750 mm., the height of the column of mercury in the tube is 204 mm. The volume of dry gas before absorption at 0° and 760 mm. is $20 \times 550/760 \times 273/283 = 13·96$ c.c.

The pressure of aqueous vapour at 10·5° is 9·5 mm. The volume of dry gas at a pressure of 536·5 mm. remaining after absorption by the water and reduced to 0° and 760 mm. is $18 \times 536{\cdot}5/760 \times 273/283{\cdot}5 = 12{\cdot}4$ c.c. Hence, the volume of gas measured at 0° and 760 mm. which is absorbed by 2·5 c.c. of water under a pressure of 536·5 mm. is 13·96 less 12·24, that is 1·72 c.c. Had the pressure at the time of absorption been 760 mm. then, by Henry's law, the 2·5 c.c. of water would have absorbed $1{\cdot}72 \times 760/536{\cdot}5 = 2{\cdot}436$ c.c. Hence, 1 c.c. of water absorbs $2{\cdot}436/2{\cdot}5 = 0{\cdot}974$ c.c. of gas; or $\beta = 0{\cdot}974$. The effect of the slight pressure due to the height of the column of water on the volume of the gas has been here neglected. To put this result in general terms, if v_0 be the initial volume of dry gas at 0° and 760 mm.; v_1, the volume of the dry gas remaining after absorption by V volumes of liquid; and p, the observed pressure of the gas remaining after the absorption, the

$$\text{Coefficient of absorption, } \beta = \frac{v_0 - v_1}{V} \cdot \frac{760}{p}$$

W. Ostwald (1888) represented the **solubility** of a gas, S, as the volume of gas absorbed by unit volume of the liquid all at the temperature of the experiment. Consequently, if S_1 volumes of gas are absorbed at a pressure p, and temperature θ, by V volumes of liquid, then the solubility $S = S_1/V$, and

$$\text{Coefficient of absorption, } \beta = \frac{S_1}{V} \cdot \frac{1}{1+\alpha\theta}; \text{ or } \beta = \frac{S_1}{V} \cdot \frac{273}{T}$$

where α denotes the coefficient of thermal expansion of the gas, approximately 0·00367; T the absolute temperature; and V is usually taken to be 100 c.c. Hence, the solubility, S, of a gas differs from Bunsen's absorption coefficient, β, in that in the former case the volume of the dissolved gas is not reduced to 0° and 760 mm. Again, $1+\alpha\theta$ times the coefficient of absorption β represents the solubility S of the gas, or, $\beta(1+\alpha\theta) = S$, and $\beta = S/(1+\alpha\theta)$, since both the solubility and the absorption coefficient are independent of the pressure. Sometimes the solubility of a gas is expressed as the weight w of the gas in grams which is absorbed by 100 grms. of pure solvent at the indicated temperature and a total pressure made up of the partial pressure of the gas plus the vapour pressure of the liquid at the temperature of the absorption. Thus for ethane at 10°, $\beta = 0{\cdot}0656$; $S = 0{\cdot}0648$; and $w = 0{\cdot}0087$. The concentration of the gases in a solvent can also be treated as in the case of solids. For example, O. F. Tower (1906) found that 27·22 c.c. of 98 per cent. sulphuric acid at 18·5° and 714·6 mm. barometric pressure absorbed 0·58 c.c. of nitrogen. The solubility of nitrogen in the acid at 18·5° is therefore $0{\cdot}58127{\cdot}22 = 0{\cdot}0213$; and the absorption coefficient is $0{\cdot}0213 \div (1 + 0{\cdot}00367 \times 18{\cdot}5) = 0{\cdot}0199$.

J. Dalton ascribed the absorption of a gas by a liquid as being due to the penetration of the particles of the gas between the molecules of the liquid, just as E. Swedenborg[3] in 1721 said that the particles of a salt which dissolve in a liquid cannot add to the bulk but only to the weight, because they occupy the spaces between the particles of water. J. Dalton, however, said that the greatest difficulty attending the mechanical hypothesis arises from the different gases observing different laws. Why does water not admit to its bulk every kind of gas alike? The fact that absorption decreases as the temperature increases and as the intermolecular spaces increase is opposed to the idea that absorption is due to a simple penetration of the gas molecules between the molecules of the solvent.

The kinetic theory of gaseous solution.—The kinetic theory of gases furnishes a mental picture of the process of solution of a gas in water. Suppose that a gas-free liquid be brought into a vessel containing a gas. The molecules of gas impinging upon the surface of the liquid will be absorbed. The dissolved molecules move about in the liquid in all directions, a small number escape back into the gas above. As the molecules of the gas crowd more and more in the liquid, the number of molecules absorbed by the liquid becomes more and more nearly equal to the number which escapes back into the superincumbent gas. If the pressure of the gas remains constant, a time will come when the number of gas molecules which leave the liquid will be equal to the number absorbed. The system is then in a state of dynamic equilibrium resembling the equilibrium of a vapour in contact with its own liquid, and the solution is saturated with the gas under the given conditions of temperature and pressure. The solution of oxygen, for example, can be symbolized: $O_{2\text{gas}} \rightleftharpoons O_{2\text{solution}}$. The surface of the liquid in contact with a dissolving gas must be very quickly saturated with the gas, and the rate of absorption of a gas by a liquid at rest is is really a measure of the rate of diffusion of the gas from the surface through the body of the liquid. The molecules of the liquid must have some attractive influence on the molecules of the dissolved gas.

It is probable that the attractive forces between the molecules of the liquid and the dissolving gas determine the solubility, otherwise we should expect the solubility of certain groups of gases to be the same. True enough, as M. Kofler (1913)[4] has shown, *the critical temperature of the gas* is a controlling factor because the solubilities of different gases in a given solvent are approximately the same at corresponding temperatures. M. Kofler assumed that the solubilities of gases in liquids is dependent upon the magnitude of the intermolecular spaces, and that the latter in turn are dependent on the *compressibility of the liquid solvent;* if so, the greater the compressibility of a liquid the greater its solvent action on gases. Similarly, assuming that a high dielectric constant is associated with small intermolecular spaces, the solubility of a gas should be related with the *dielectric constant of the liquid solvent.* On comparing these deductions with observations, it was found that some qualitative relations could be detected; but the greater variations in the solubility of different gases in the same liquid show that the properties of the gases themselves play a most important part. A. Ritzel assumed that the solubility of a gas in a liquid is proportional to the compressibility β of the solvent, and inversely proportional to the change in volume δ which accompanies the absorption of the gas; or $S=k\beta/\delta$, where k measures the solution pressure of the gas.

The influence of pressure on the solubility of gases.—With gases which are not very soluble in liquids, the greater the pressure, the more soluble the gas; that is, the greater the pressure, the greater the concentration of the gas in the solution. W. Henry (1803)[5] discovered an important relation between the pressure and the solubility of a gas. A specified quantity of liquid under a total pressure, p, of 2 atmospheres, holds in solution twice as much gas by weight, w, as under a total pressure of 1 atmosphere. Otherwise expressed, $w/p=w_1/p_1=\ldots$; or $w/p=$a constant, or, **the weight of gas absorbed by a specified volume of liquid is directly proportional to the pressure.** According to Boyle's law, the concentration of a gas, or the amount of v in an enclosed space, is proportional to the pressure or $pv=$constant; combining these two relations, $w/v=$constant. This means that a gas will distribute itself so that its concentration in the liquid is proportional to that in the space above—and this occurs whatever be the superincumbent pressure. One volume of a gas at atmospheric pressure will contract to half a volume at a pressure of two atmospheres. Under a pressure of 2 atmospheres, a saturated solution of gas holds twice as much gas in solution as it did under a pressure of 1 atmosphere, but two volumes of gas at atmospheric pressure occupy but one volume at a pressure of 2 atmospheres. Hence follows **Henry's law: under equal circumstances of temperature, water takes up in all cases the same volume of the condensed gas as it would if the gas were under ordinary pressure.** That is to say,

$$\frac{S}{p}=\frac{S_1}{p_1}=\ldots;\ \text{or}\ \frac{S}{p}=\text{Constant}$$

The proportion of gas and liquid do not matter so long as a sufficient quantity of each is present to allow the measurements to be made. The law thus describes the behaviour of the less soluble gases very well—carbon monoxide, nitrogen, hydrogen, oxygen—but not the more soluble gases like ammonia, hydrogen, chloride, sulphur dioxide. The deviation is not very great with carbon dioxide,[6] though it is appreciable:

Pressure, p . . .	1	5	10	15	20	25	30 atms.
Solubility, S . . .	1·80	8·65	16·03	21·95	26·65	30·55	33·74
Constant, S/p . . .	1·80	1·73	1·60	1·46	1·33	1·22	1·12

The graph, Fig. 12, represents the observed values of p and S; and the dotted curve in the same diagram represents what the graph would have been had carbon dioxide behaved as described by Henry's law. The value of S/p is not therefore quite constant. If the volume of absorbed gas is referred to the volume of the solution instead of the solvent alone, the constant works out better. The failure arises from the fact that carbon dioxide reacts chemically with water. For the very soluble gases S_i/p = constant, where i is a constant characteristic of the gas.

Henry's law refers to gases which do not act chemically on the solvent. When carbon dioxide dissolves in water, one portion enters into combination to produce a new substance—carbonic acid—while the other portion dissolves in the physical sense as carbon dioxide. The latter portion alone comes within the province of Henry's law. The condition of the carbon dioxide which reacts with the water is represented by $CO_2+H_2O=H_2CO_3$. With a rise of temperature the equilibrium is displaced from right to left, corresponding with the fact that the higher the temperature of observation, the more nearly does Henry's law approximate to the truth. Thus, H. E. Roscoe and W. D. Dittmar (1869) found that the law applies very well for sulphur dioxide at 40°, and for ammonia near 100°. At 100°, also, the solubility of carbon dioxide is proportional to the pressure. If the partial pressure of the hydrate $CO_2.H_2O$ is proportional to the concentration of the dissolved carbon dioxide, *the presence of the hydrate has no influence on the law of absorption*[7] provided there is no change in the gaseous molecule, resulting in the formation of molecules of the type $(CO_2)_n.H_2O$. Suppose the initial value of n is unity. If S_1 be the concentration of the gas CO_2; S_2, that of the water; and S, that of the hydrate, then the condition of equilibrium in the solution $CO_2.H_2O \rightleftharpoons CO_2+H_2O$ is, according to Gulberg and Waage's law, $S_1S_2=K_1S$. If the solubility of the gas is not great the solution will be dilute, and the water will be in so great an excess that its concentration will be virtually constant, and therefore $S_1=K_2S$, where $K_2=K_1S_2$. From Henry's rule, the partial pressure p of the gas will be $p=K_3S_1$, and therefore by substitution for S_1, $p=K_2K_3S$; or, substituting the constant $K=K_2K_3$, it follows that $p=KS$, or the concentration of the hydrated molecules is proportional to the pressure of the gas, just as is the case with the unhydrated molecules. Consequently, assuming that the partial pressure of the hydrate is proportional to the concentration S of the dissolved gas, S/p=constant, just as would be the case if the carbon dioxide were all dissolved in the form of CO_2, and none as $CO_2.H_2O$.

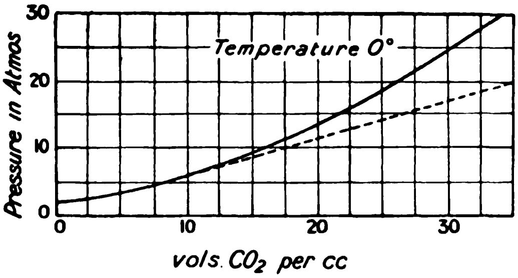

FIG. 12.—Solubility Curve of CO_2 in Water.

Henry's law also assumes that the molecular weight of the dissolved gas is the same in solution and in the gaseous state. If the gas A be polymerized in solution so that $2A_{gas}=A_{2solution}$; then, if S_1 be the concentration of the free gas, and S the concentration of the dissolved gas, by the law of mass action, $S_1^2=k_1S$, where k_1 is a constant. Accordingly, $S_1=\sqrt{k_1S}$, and Henry's law assumes the form $p=k\sqrt{S}$, where k is constant, p the pressure of the gas, and S the solubility—all expressed in proper units. Analogous remarks apply if the gas in solution is polymerized to a higher degree, say n; or if the gas is depolymerized or decomposed.

Since the concentration of a substance is understood to refer to the quantity of substance in unit volume, Henry's law means that in a closed vessel, containing gas and liquid, the gas will distribute itself so that its concentration in the liquid is proportional to that in the superincumbent space. Hence it may be inferred that **if a gas obeys Henry's law, it will have the same molecular weight in solution and in the gaseous condition.** Henry's law is therefore to be regarded as a link connecting the molecular weight of gaseous and dissolved substances with one unit of measurement. If 32 grams of oxygen depress the freezing point to the same extent as 342·2 grams of cane sugar, it would be inferred that the molecular weights of oxygen and cane sugar are related as 32 : 342·2 ; and since oxygen gas has a molecular weight of 32, it is assumed that cane sugar if it could be vaporized, and if its gas obeyed Henry's law, would have a molecular weight of 342·2, because, as indicated above, the molecular weights of a substance in solution and in the gaseous state are assumed to be the same.

It might be emphasized, in passing, that when a gas is dissolved in a liquid at a given temperature, the ratio between the concentration of the gas in the liquid and in the space above is always the same. Thus, Henry's law is a law of distribution for gases because it describes the way a gas distributes itself between the solvent and the space above. Henry's law also describes the condition of equilibrium of a gas whose molecules are physically and chemically independent of each other, and of the solvent.

EXAMPLE.—Show that the absorption coefficient is independent of pressure. If S volumes of gas at a pressure p are absorbed by unit volume of liquid, S_1 vols. by Henry's law will be absorbed at 760 mm. such that $S_1p=760S$. Again, if S_1 volumes of gas at a pressure p and temperature θ, become S_0 volumes at 760 mm. and 0° ; by Boyle's and Charles' laws, $S_1p=760S_0(1+\alpha\theta)$. Substituting for S_1 from the preceding expression and solving for S_0, it follows that $S_0=S/(1+\alpha\theta)$, which is independent of p. If V volumes of liquid have been treated, $S_0=S/V(1+\alpha\theta)$, which is Bunsen's coefficient of absorption, β.

Solids and liquids dissolve in a vacuum or in a dilute indifferent gas in accord with their vapour pressure,[8] but if the indifferent gas be strongly compressed, say at 100 atm., a specific solvent action appears. Thus, compressed oxygen has a greater solvent action on bromine vapour than oxygen under reduced pressure, and at 300 atm. pressure, the colour of the vapour is six or seven times as dense as under atmospheric pressure; while compressed hydrogen has but a smaller solvent action. Iodine imparts an intense violet colour to methane under 300 atm. pressure. Camphor and paraffin likewise dissolve in compressed methane or ethylene gas, and on removing the pressure, the iodine, camphor, or paraffin are deposited as crystals on the walls of the vessel.

The applicability of Henry's law for solvents other than water was proved by R. Bunsen[9] for alcohol; by M. Woukoloff, for chloroform and carbon disulphide; and for petroleum by S. Gniewosz and A. Walfisz. The absorption coefficients of a gas in different solvents are not proportional to one another. In order to test the applicability of Henry's law, W. Sander examined the solubility of carbon dioxide in water and in a number of organic liquids at temperatures between 20° and 100° and at pressures between 20 and 170 kgrms. per sq. cm. He found that Henry's law is the more nearly followed the higher the temperature; at the lower temperatures, the solubility of the gas in alcohol, benzene, chloro-, bromo-, and nitrobenzene, and toluene increases faster with increasing pressure than corresponds with Henry's rule, and with ethyl ether, ethyl acetate, and water, the increase is slower than Henry's law requires. The law is more nearly followed when the volume of gas absorbed is referred not to the volume of the solvent (coefficient of absorption) but to the volume of the solution (Ostwald's solubility). With carbon dioxide in ether, and ether vapour in carbon dioxide, Henry's law is not approximately valid in the neighbourhood of the critical point. O. Sackur and O. Stern have likewise examined the effect of pressure on solutions of this same gas in methyl and ethyl alcohols and acetates between —59° and 78°, and between 50 and 700 mm. pressure.

Henry's law and the kinetic theory.—The gas is in equilibrium with its own solution when the number of molecules which escape from the solution is the same as those which are captured by the solution in a given time. By, say, doubling the pressure the molecular concentration will be doubled, the gas molecules will be crowded more closely together, and the rate at which the solution captures the molecules will be increased twofold for the new state of equilibrium. Similarly the rate of escape will be doubled. Hence **variations of pressure do not alter the relative number of molecules per unit volume of solution and of gas** ; and the *volume* of gas dissolved will be independent of the pressure on the gas, while the *weight* of gas dissolved will be directly proportional to the pressure.

It will be observed that in the relation showing the influence of pressure on the solubility $(d \log S)/dp = \delta v/RT$, the magnitude δv may be interpreted to mean the change in volume which occurs during the process of solution. The volume of the gas is so great in relation to the solution that the volume v of the gas can be substituted for δv, and assuming Boyle's law is applicable $pv = RT$, and substituting for v

$$\frac{d \log S}{dp} = \frac{1}{p}$$

which, on integration, furnishes $S = kp$, that is, Henry's law.

The influence of temperature on the solubility of gases.—The solubility of a gas in a liquid is very sensitive to changes of temperature. The higher the temperature, the less the solubility of the gas. R. Bunsen's measurements agree with the assumption that the absorption coefficient of hydrogen in water and of oxygen in alcohol are not affected by changes of temperature between 0° and 20°; but W. Timofejeff found that R. Bunsen's results were not confirmed by a more sensitive method of measurement.[10] The solubility curve of helium is not much affected by changes of temperature up to 50°, but what little effect there is seems to indicate that the solubility of the gas *increases* as the temperature rises from 25° to 50°. Hydrogen was once supposed to behave in a similar way, between 0° and 25°, but later, more careful measurements show that the solubility decreases steadily from 0·0214 at 0° to 0·0171 at 26°. The solubility of carbon dioxide in nitrobenzene is nearly the same at 100° as it is at 60°.

A. Imhof represented the solubility, S, of a gas (litres of gas in a litre of water) by the expression:

$$S = e^{\frac{T}{27\cdot4}}; \text{ or } T = 27\cdot4 \log S$$

where T denotes the absolute boiling temperature in degrees reckoned from the point where $S = 1$ and $\log S = 0$, namely, $-100°$. T is positive if higher than $-100°$, and negative if below $-100°$. The results have less than a 2 per cent. error with all the gases tried excepting methane, where the error is 5·3 per cent., and hydrogen and helium where the errors are respectively 16·1 and 18·9 per cent. For oxygen, $S = 0\cdot049$; $T = -82\cdot66°$ (observed $-82\cdot5°$); for acetylene, $S = 1\cdot73$; and $T = -15\cdot02$ (observed $+16\cdot0$).

The influence of the surface tension of the solvents has been previously discussed.

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§ 5. The Solubility of Mixed Gases in Liquids—Dalton's Law

When a mixture of two gases is exposed to the action of a solvent, the quantity of each gas dissolved by the liquid depends upon the amount and the solubility of each gas present. The amount of each gas determines its partial pressure, and since the partial pressure of each gas is independent of the others, it follows that **when a mixture of gases is exposed to the action of a solvent, and no chemical action intervenes, the amount of each gas which is dissolved by the solvent is proportional to the partial pressure of the gas.** Each gas behaves as if the others were absent. This is called **Dalton's law,** after its discovery by J. Dalton,[1] 1805; it is obviously a special case of Henry's law.

J. Dalton's idea was that the gases dissolved in water retain their elasticity or repulsive power among their own particular molecules the same in the water as out of it, the intervening water having no other influence in this respect than a mere vacuum. The idea that the solvent water is wholly passive cannot now be maintained. J. Dalton further showed that each gas is retained in water by the pressure of gas of its own kind incumbent on the surface; abstractedly considered, no other gas with which it may be mixed has any permanent influence. J. Dalton also had wrong ideas of the numerical relation between the gas dissolved and that incumbent on the liquid. R. Bunsen[2] studied the solubility of mixed gases, and, in his *Ueber das Gesetz der Gasabsorption,* pointed out:

Let v vols. of a mixture of gases at a pressure P, containing, per unit volume, v_1 volumes of a gas A, v_2 vols. of a gas B, v_3 vols. of a gas C, . . . with the respective coefficients of absorption $\beta_1, \beta_2, \beta_3$, . . . be agitated with V vols. of a liquid, so that there remains u vols. of the gaseous mixture containing u_1, u_2, u_3, . . . respectively of the gases A, B, C, . . . per unit volume at a pressure P_1. The temperature remains constant at 0°. The mixture contains v_1v vols. of the gas A at a pressure P, or $v_1vP/760$ vols. at a pressure 760 mm. This volume of gas is divided into x_1 vols. of gas which remain unabsorbed and y_1 vols. which are absorbed by the v vols. of liquid; but from the law of absorption, unit volume of liquid absorbs β_1 vols. of gas at 760 mm. pressure, or V vols. of liquid absorb $\beta_1 Vp_1/760$ vols. at a partial pressure p_1. The gas A_1, however, expands from x_1 to $up_1/760$ vols. when admixed with the other gases, so that the quantity absorbed by V vols. of liquid in virtue of the partial pressure $\beta_1 Vx_1/u$ is y_1, or $y_1 = \beta_1 vx_1/u$; or the volume of the component A is $x_1 + \beta_1 Vx_1/u = v_1vP{:}760$; or $x_1 = v_1vP/760(1+\beta_1 V/u)$; and generally,

$$x_1 = \frac{v_1vP}{760\left(1+\frac{\beta_1 V}{u}\right)};\quad x_2 = \frac{v_2vP}{760\left(1+\frac{\beta_2 V}{u}\right)};\quad \ldots$$

The volume of residual gases remaining when a gaseous mixture of volume $v = v_1 + v_2 + \ldots$ has been exposed to v vols. of a solvent is $u = (u_1 + u_2 + \ldots$, where

$$u_1 = \frac{x_1}{x_1+x_2+\ldots};\quad u_2 = \frac{x_2}{x_1+x_2+\ldots};\quad \ldots$$

J. Dalton believed that the influences of temperature on the amounts of various gases dissolving in the same liquid is proportional to the influence of each as separately, so that the composition of the gas dissolved by a specified liquid acting on a mixture of gases is independent of the temperature. This statement is not strictly accurate.

When air containing, say, 79 volumes of nitrogen (neglect the argon and rare gases) and 21 volumes of oxygen, and 0·04 volume of carbon dioxide, is skaken up with water, the amount of each gas absorbed by the water can be approximately computed in the following manner: The relative solubilities are: nitrogen, 0·02; oxygen, 0·04; and carbon dioxide, 1·79. The partial pressure of each gas is proportional to the relative amount of that gas present in a given volume of air. If the pressure of air be just one atmosphere, the partial pressure of the nitrogen will be proportional to 0·79 × 1; of oxygen, 0·21 × 1; and of carbon dioxide, 0·0004 × 1. Hence the relative amounts of these gases absorbed by the water will be: nitrogen, 0·79 × 0·02 = 0·0158; oxygen, 0·21 × 0·04 = 0·0082; and carbon dioxide,

$0·0004 \times 1·79 = 0·00072$. Hence 1 c.c. of water dissolves 0·0158 c.c. of nitrogen; 0·0082 c.c. of oxygen; and 0·00072 c.c. of carbon dioxide. The composition of the dissolved gases, if removed from the solution by boiling, or exposure to a vacuum, will be: nitrogen, 63·9 per cent.; oxygen, 33·2 per cent.; carbon dioxide, 2·9 per cent. The relatively large solubility of the carbon dioxide of the atmosphere is counterbalanced by its low partial pressure, otherwise we might expect a heavy rainstorm to remove a great part of the carbon dioxide from the surrounding air.

J. T. A. Mallet (1869) [3] has a proposal to separate oxygen from atmospheric air freed from carbon dioxide, which is based on the different solubilities of the oxygen and nitrogen. If the carbon dioxide be removed by passing the air through an aqueous solution of sodium hydroxide, the oxygen and nitrogen in the remaining gases after the first absorption will be nearly in the proportion: nitrogen 65·7 per cent., and oxygen 34·3 per cent. If this mixture be driven from the water by boiling, and the mixture again treated with air-free water, a gaseous mixture containing 49 per cent. of oxygen is obtained; and after the eighth absorption, a gas containing 97 per cent. of oxygen results. The relative proportions of oxygen and nitrogen in air obtained from water after successive absorptions is

TABLE V.—EFFECT OF SUCCESSIVE ABSORPTIONS BY WATER ON THE COMPOSITION OF AIR.

	Number of absorptions.								
	0	1	2	3	4	5	6	7	8
Nitrogen	79	66·7	52·5	37·5	25·0	25·0	9·0	5·0	2·7
Oxygen	21	33·3	47·5	62·5	75·0	85·0	91·0	95·0	97·3

The method is not practicable though it is an interesting application of Henry's and Dalton's laws.

EXAMPLES.—(1) The solubility of hydrogen is 0·02 and of oxygen 0·04. Show that 13·3 c.c. of each of these gases is dissolved by 1000 c.c. of water from an electrolytic mixture of hydrogen and oxygen.

(2) If 10 c.c. of an aqueous solution of carbon dioxide saturated at 0° is introduced into a vessel already containing 10 c.c. of carbon dioxide all at atmospheric pressure, show that 8·69 c.c. of carbon dioxide will remain in solution. D. I. Mendeléeff (1868) found 10 c.c. of a saturated solution at 0° contain 18 c.c. of carbon dioxide, and if x denotes the number of c.c. which remain in solution, $18-x$ will represent the number of c.c. expelled and $28-x$ will be present in the atmosphere. Hence, the partial pressure of the dissolved carbon dioxide is $(18-x)/(28-x)$. When the solution is at atmospheric pressure it contains 18 c.c. of carbon dioxide, and when the partial pressure is $(18-x)/(28-x)$, it contains $18(18-x)/(28-x)=x$ c.c. of carbon dioxide, when $x=8·69$ c.c.

The effect of saline solutions on the solubility of gases.—The behaviour of gases towards salt solutions first attracted the attention of physiologists owing to its bearing on the absorption of gases by the blood. Thus J. S. F. Pagenstecher,[4] R. F. Marchand (1846), J. von Liebig (1851), L. Meyer (1857), and E. Fernet (1858), examined the solubility of carbon dioxide in solutions of sodium phosphate. The solubility of a gas is lowered by the dissolution of a salt which does not act chemically on the gas. Thus, F. M. Raoult (1873) [5] found that the solubility of ammonia in aqueous solutions of potassium hydroxide decreased as the proportion of alkali increased from 72 with solution containing 11¼ per cent. K_2O, to 49·5, with solutions containing 25¼ per cent. of K_2O. J. Setschenoff (1889) found that the relation between the quantity of salt x and the absorption coefficient is given very nearly by the formula:

$$\text{Absorption coefficient} = \beta e^{-\frac{k}{x}}$$

where β represents the absorption coefficient of the gas for water, k is a specific constant dependent upon the nature of the dissolved salt, and e is the base of natural logarithms. Equivalent solutions of similar salts of the same acid absorb nearly the same quantities of gas. For instance, J. Setschenoff (1875) found that with calcium, strontium, and barium nitrates the absorption coefficients were respectively 0·923, 0·916, and 0·922. The effect of mixing another liquid with the water resembles that obtained by the dissolution of a salt; thus J. S. Setschenoff (1875) found the absorption coefficients of mixtures of water and sulphuric acid to be less than for either water or sulphuric acid alone, as illustrated in Fig. 13. Other physical properties of mixtures—viscosity, electrical conductivity, etc.—change in a similar manner. O. Müller (1889) obtained similar results with mixtures of alcohol and water. If the salt is acted on chemically by the gas, as is the case when carbon dioxide is dissolved in aqueous solutions of borax, sodium carbonate, or sodium phosphate, the portions of gas held chemically by the salt is almost independent of pressure, while the other portion follows Henry's law. The decrease is supposed to be due to the fixation of some of the solvent by the molecules or the ions, or both molecules and ions of the dissolved salt. On this assumption, J. C. Philip [6] calculated the degree of hydration of the salt from the decrease in the solubility of the gas from the formula :

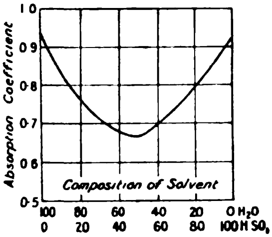

FIG. 13.—Solubility of Carbon Dioxide in Mixtures of Sulphuric Acid and Water.

$$\text{Degree of hydration} = \frac{a-b}{a}\,\frac{100-c}{c}\,\frac{M_1}{M}$$

where M_1 and M respectively denote the molecular weights of salt and water; c the per cent. of salt in solution ; a denotes the number of c.c. of oxygen dissolved by a litre of water; b the number of c.c. of oxygen in 1000 grams of water in the solution calculated from $b=a/(D-C)$, where D denotes the density of the solution, and C the number of grams of water per c.c. of solution. For example, with potassium chloride, bromide, and iodide, C. G. McArthur finds :

	KCl		KBr		KI	
Concentration	$\frac{1}{4}N-$	$2N-$	$\frac{1}{4}N-$	$2N-$	$\frac{1}{4}N-$	$2N-$
Specific gravity . . .	1·0086	1·086	1·017	1·150	1·027	1·230
Oxygen c.c. per litre . .	5·30	3·21	5·52	3·37	5·49	3·77
Degree of hydration . .	16·0	10·4	7·8	8·9	8·9	6·4

The hydration data with salts whose ionization is small were found to give results consistent with the degree of hydration calculated by other methods.

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§ 6. Diffusion in Gases and in Liquids

> If a very small quantity of a salt be dissolved in a great quantity of water, the particles of the salt will not sink to the bottom though they be heavier in specific gravity than the water, but they will evenly diffuse themselves into all the water so as to make it as saline at the top as at the bottom. Does not this imply that the parts of the salt recede from one another, and endeavour to expand themselves and get as far asunder as the quantity of water in which they float will allow ? And does not this endeavour imply that they have a repulsive force by which they fly from one another, or at least, that they attract the water more strongly than they do one another ?—ISAAC NEWTON (1675).

Let a large crystal of a coloured salt—say copper sulphate or potassium dichromate—be placed at the bottom of a tall glass cylinder, and the remainder of the jar be filled with water. A coloured salt is chosen because the movements of the resulting solution can be readily seen. Let the jar stand where it will not be disturbed by evaporation, agitation, etc. The surface of separation between the solid and solvent will be gradually obliterated ; in time, the coloured salt will diffuse uniformly throughout the whole body of liquid. Similarly, if a solution of one concentration be in contact with a solution of another concentration, the dissolved substance passes from the region of greater to the region of lesser concentration, until the concentration is uniform throughout the whole mass of liquid provided the temperature is everywhere the same.[1]

The phenomenon of diffusion was known to Isaac Newton (1695), to C. Berthollet (1803), and to F. Parrot (1815). The last-named attributed the action to a special force which he called *Affinität erster Art, eine neu aufgedeckte Naturkraft*—affinity of the first degree, a newly discovered natural force—which M. L. Frankenheim (1835) styled diffusion. F. Parrot said : All miscible liquids show a tendency to wander one into the other when they are brought into contact, and this process continues until the liquids are perfectly evenly distributed. W. Nernst attributed the driving force to osmotic pressure, a phenomenon about to be described. T. Graham first obtained quantitative data about the speed of diffusion of different salts, and A. Fick then developed a theory of the process based on the hypothesis that *the quantity of a salt which diffuses through a given area in a given time is proportional to the difference between the concentration of two vertical and parallel planes indefinitely close to one another* ; or, the amount of solute dm which will pass in a given time dt between two parallel planes unit distance apart and of unit sectional area, is proportional to the difference in concentration, C_1-C_2, on the two sides of that section—**Fick's law of diffusion** —or $dm=k(C_1-C_2)dt$, where k is the coefficient or constant of diffusion. The hypothesis was tested by many investigators—F. Beilstein (1856), T. Simmler and H. Wild (1857), F. Hoppe-Seyler (1867), E. Voit (1867), and A. Johannisjanz (1877), but the results, as J. Stefan (1878) showed, were not of a sufficient degree of accuracy. Then followed the work of H. F. Weber, W. Seitz (1898), J. Schuhmeister (1879), J. H. Long (1880), R. Lenz (1882), J. D. R. Scheffer (1881), and P. de Heen (1884). The general results have established the validity of A. Fick's law based on the theory of the conduction of heat, and that just as the magnitude of the heat conduction decreases slowly with rise of temperature, so does the diffusion decrease as the concentration increases. The mathematical theory has been discussed by W. Seitz, F. Niemöller, E. Voit, T. Simmler and H. Wild, J. Stefan, O. Wiedeburg, O. Wiener, P. G. Tait, H. F. Weber, F. Neimbrodt, J. Trovert, etc. The speeds of diffusion of many salts have been investigated by T. Graham, J. D. R. Scheffer, L. W. Oeholm, J. Trovert, F. Heimbrodt, W. Scitz, O. Wiedeburg, W. Kawali, etc. T. Graham observed great differences in the rates of diffusion of two classes of substances—what he called crystalloids diffused rapidly, colloids slowly.

	HCl	NaCl	Cane sugar.	$MgSO_4$	Albumen.	Caramel.
Velocity of diffusion . .	1	2·3	7	7	49	98 units

J. H. Long noted a parallelism between the velocity of diffusion and the electrical conductivity. The diffusion of mixtures of salts has been investigated by T. Graham,

J. C. G. de Marignac, and F. Rüdorff. Each salt seems to diffuse independently of other accompanying salts. T. Graham, P. de Heen, H. F. Weber, W. Seitz, L. W. Oeholm, and others have investigated the influence of temperature on the speed diffusion, and found it to increase rapidly with a rise of temperature. W. Nernst found that with dilute solutions of neutral salts, the coefficient of diffusion k at θ° is $k_{18}\{1+0{\cdot}026(\theta-18)\}$, and for acids and bases $k_{18}\{1+0{\cdot}024(\theta-18)\}$.

T. Graham, E. Detlefsen, H. de Vries, L. Chabry, P. Nell, H. Bechhold and J. Liegler, J. Hausmann, S. Leduc, N. Pringsheim, and F. Voigtlander studied the rate of diffusion in agar-agar jelly and found the process similar to that which occurs with water. R. E. Liesegang found that the diffusion of silver nitrate in a tube of gelatine containing ammonium chromate furnishes a series of rings or laminæ—**Liesegang's rings**—at right angles to the axis of the tube. W. Ostwald suggested that it is a supersaturation phenomenon. F. Köhler found that if the ammonium chromate be too concentrated or too dilute the rings are not well developed; and if the gelatine contains the silver salt, *rhythmic precipitation* does not occur. H. W. Morse and G. W. Pierce obtained a similar result with lead nitrate diffusing into gelatine and sodium sulphate.

There seems to be some force at work driving the molecules of the solute upwards against the force of gravity. From the kinetic theory, it is inferred that the molecules of the liquid are in perpetual motion in all directions; and that the protracted time occupied by the diffusion of the molecules of the dissolved salt in the liquid is due to the close packing of the molecules of the liquid, such that the free progress of the molecules of the dissolved salt in the solvent is greatly impeded. It can be shown from the kinetic theory that the potential energy of the molecules of a mixture of gases is diminished by diffusion, and in consequence the phenomenon is due to the tendency of the molecules of the mixing gases to follow the dynamical principle: the position of stable equilibrium is the position of minimum potential energy; diffusion is motion towards a state of stable equilibrium.

The analogy between the dissolution of a substance in a solvent, and vaporization, has been emphasized by R. Hooke (1664), by J. L. Gay Lussac (1839),[2] by B. Bizio (1845), and by A. Rosenstiehl (1870). A substance in solution was regarded as an elastic vapour, and the difference between the dissolved substance and a gas was said to arise from the circumstance that "a gas does not need the presence of the molecules of a solvent, and of their affinity to sustain it in the occupied space." In 1873 A. Horstmann developed a thermodynamic theory of equilibrium between gaseous substances, and showed that the same laws applied for substances in solution. The idea gradually grew into chemistry, and proved singularly fruitful in the work of J. H. van't Hoff (1886), who widely extended the analogy between the physical and chemical behaviour of substances in dilute solution, and in the gaseous state.

Just as the molecules of a gas in a closed vessel are disseminated in a relatively large space, so are the molecules of a solid in solution scattered in a relatively large volume of solvent. It is true that the molecules of the salt in solution could not occupy the space if the solvent were absent, otherwise the analogy between a substance dissolved in a solvent and a gas scattered in space would be very close. Arguments from analogy are notoriously treacherous; and whatever conclusions might be inferred from a closer study of the analogy between the process of solution and gaseous diffusion, the fact that the molecules of the dissolved substance are comingled with the solvent, and that the molecules of the gas are not associated with such an agent, must be constantly borne in mind. As G. F. Fitzgerald[3] has said: "The dynamical condition of molecules in solution is essentially and utterly different from that of the molecules of a gas."

The **rate of solution** of a solid in a solvent depends on the surface area, and on the amount of the solid already present in solution. This latter was suspected by C. L. Berthollet[4] in 1803, and established by the experiments of A. A. Noyes and W. R. Whitney. They showed that the rate of solution of a solid is proportional to the difference between the concentration of the film in immediate contact with the solid and with the more dilute layers. Consequently, it follows that the solution of a solid involves two processes : (i) The reaction between the solvent and solid ; (ii) The rate of diffusion of the solute away from the solid. If the speed of the latter process predominates, the observed rate of solution will not depend merely on the amount of solid already on solution ; whereas if the speed of the former predominates, the observed rate of solution will be proportional to the concentration of the solution in conformity with the observations of A. A. Noyes and W. R. Whitney—see crystals.

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§ 7. Solution Pressure—Osmotic Pressure

Just as a small quantity of water is able to dissolve a quantity of salt which can diffuse itself through a large quantity of water, so a quantity of air which can expand and diffuse itself through a large space may be contained within a small compass.—R. HOOKE (1664).

It has been shown that if the diffusion of gases be resisted by placing a permeable partition between two gases, a pressure will be exerted upon the partition. It is easy to show that the particles of a dissolved substance exert a similar pressure when a partition is placed between the solution and solvent so that the partition offers no obstacle to the free circulation of the molecules of the solvent, but resists the free passage of the molecules of the dissolved substance.

A piece of wet bladder is stretched and wired over the head of a wide thistle-headed funnel with a stem about 10 cm. long. When nearly dry, the bladder is removed and the hot funnel is smeared about the rim with marine glue. The bladder is immediately wired securely in position. The thistle-headed funnel is nearly filled with a concentrated solution of cane sugar and joined by means of pressure tubing or a rubber stopper with a piece of capillary tubing of ½ mm. bore bent S-shaped as indicated in Fig. 14. The funnel is immersed in a jar of water. The level of the index of coloured water in the capillary tube is marked with gummed paper, and the apparatus is allowed to stand over night. In the morning the liquid in the capillary will have risen about 10 cm. Water has obviously passed from the beaker through the membrane into the sugar solution.

The passage of water through a membrane in this manner is called **osmosis**—from the Greek ὠσμός, a push. If the osmosis be inwards, towards the solution, H. Dutrochet's term **endosmosis** can be used; if outwards, **exosmosis**. The membrane permeable to the solvent, impermeable to the dissolved substance, is called a **semipermeable membrane.** The extra hydrostatic pressure exerted upon the membrane by the sugar solution was styled, by W. F. P. Pfeffer (1877), "the **osmotic pressure** of the sugar solution." Solutions with the same osmotic pressure are said to be *iso-osmotic* or **isotonic.**

Experiments on osmosis were made by Abbé Nollet (1748).[1] He showed that if the opening of a glass vessel containing alcohol be tightly covered with a bladder and inverted in water, the contents of the vessel increase so that the bladder sometimes bursts. F. Parrot next studied the phenomenon in 1803, and N. W. Fischer in 1822. F. Parrot saw the important bearing of this subject on phenomena or processes which occur in the living organism. Then R. J. H. Dutrochet took up the subject in 1826 and subsequent years. The greatest interest centred about the changes of level which occurred when two different liquids separated by an animal membrane were kept in contact. G. Magnus (1827), E. B. Jerichau (1825), E. Brücke (1842) tried to develop a theory of the process; K. Vierordt (1845–8), P. Jolly (1849), J. von Liebig (1848), C. Ludwig (1849), A. Fick (1854), and T. Graham (1861) investigated the subject of osmosis through animal membranes.

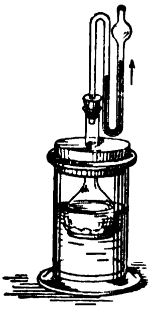

Fig. 14.—Illustration of Osmotic Pressure.

The action is curious. In the ordinary nature of things the sugar would diffuse into the solvent until the whole system had one uniform concentration. The membrane retards this. If the sugar cannot get to the solvent, the solvent goes to the sugar—a case of Mahomet and the mountain. Molecules of sugar and molecules of water attempt to pass through the membrane; the way is open for the molecules of water, but not for the molecules of sugar. Water can pass freely both ways. The extra pressure on the solution side of the membrane—the **solution pressure**—is supposed to be due to the bombarding of the membrane by the molecules of sugar. Equilibrium occurs when the number of molecules of water passing downwards through the membrane is equal to the number passing in the opposite direction. The resulting pressure is the solution pressure or the osmotic pressure of the solution.

Let us be perfectly clear about this or we may be led into error. The *fact* observed is that **the osmotic pressure is the excess of the hydrostatic pressure on the solution side of a semipermeable membrane over the pressure on the solvent side.** The *hypothesis* here suggested—often styled J. H. van't Hoff's kinetic theory of solutions (1886)—is that this pressure is due to the bombarding of the semipermeable membrane by the dissolved molecules trying to diffuse into the solvent and make solvent and solution one uniform concentration. The hypothesis was developed in a very important memoir: *The rôle of osmotic pressure in the analogy between solutions and gases* (1887).[2] The hypothesis has served as a stimulus to much valuable work; there are, however, other possible explanations of the phenomenon. The merits of rival hypotheses cannot be settled by symposia although discussion may bring fundamental issues into relief. Harsh experience alone can shatter or establish this interesting analogy—for *comparaison n'est pas raison.*

Imagine the experiment arranged a little differently. Suppose the aqueous solution of sugar in the lower part of a cylinder, Fig. 15, to be separated from the pure solvent in the upper part of the cylinder by a semipermeable membrane *A*, so fitted that it can slide freely up and down the cylinder. The upward osmotic pressure of the solution will naturally force the piston upwards, and a weight, *P*, equivalent to the osmotic pressure of the solution, will be required to keep the semipermeable membrane in one fixed position.

Many hypotheses have been suggested to explain the function of the membrane in osmotic phenomenon, ranging between the purely physical conception which refers the effect to the passage of the liquid through capillary pores, and the purely chemical conception of a combination between the membrane and the liquid passing through. M. Traube (1867), S. U. Pickering (1891), and W. Sutherland (1907) considered the semipermeable membrane acted as a kind of sieve which allowed the passage of the molecules of the solvent, but obstructed the passage of the supposed larger molecules of the solute. This hypothesis is now abandoned, for no attempt to distinguish between true pore diffusion occurring through capillary openings and the so-called true endosmosis occurring through smaller molecular interstices, has proved successful; and even in the case where collodion membranes and porcelain plates serve as partitions, S. L. Bigelow (1907) found that the same laws described the passage of liquids through both; there is no experimental evidence clearly distinguishing between the passage of a liquid through capillaries and through molecular interstices.

According to the solution hypothesis, a substance will pass through a membrane only if it is soluble therein. According to this hypothesis, if two miscible liquids, A and B, are separated by a membrane, and the membrane has the power to absorb or dissolve only one of them, say A, this liquid will be dissolved on one side of the membrane and given up on the other, and if the liquid B is in a closed cell, an hydrostatic pressure will be there developed. The magnitude of this pressure will depend on the relative attractions or solubility of A and B in the membrane. If A is soluble and B insoluble or sparingly soluble, the membrane will be saturated with A on one side and supersaturated on the other, and there will be a transfer of solvent through the membrane until hydrostatic pressure is developed sufficient to check the flow. Hints of this hypothesis were given by T. Graham, but M. l'Hermite (1855) published the first clear statement of a possible development of osmotic pressure by a selective action of the membrane, and he gave the three-liquid experiment—with chloroform, water, and ether—with the express idea of demonstrating that a substance which passes through the membrane dissolves in that membrane. Accordingly, argued M. l'Hermite, there must be a relation between solution and chemical union; osmotic phenomena are not the result of a special force, but rather the effect of forces of affinity similar to those acting in solutions. L. Kahlenberg (1906) also has sought for evidence in support of the solution theory of osmosis.

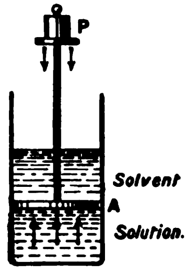

Fig. 15.—Osmotic Pressure.

The following is A. C. Brown's modification of M. l'Hermite's three-liquid layers to illustrate the development of osmotic pressure by the solvent action of the membrane. A concentrated solution of calcium nitrate is saturated with phenol and the mixture poured into a tall narrow cylinder. The excess of phenol rises and floats upon the surface of the calcium nitrate solution. The phenol should not be in larger excess than is required to give a layer a few millimetres thick. Distilled water saturated with phenol is carefully poured above the two layers of liquid in the cylinder. The water floats on the surface of the phenol. The water on both sides of the phenol can traverse the partition of phenol, but the calcium nitrate cannot pass through. Hence the layer of phenol is a semipermeable membrane. Mark the level of the layer of phenol in the cylinder by means of a piece of gummed paper. If the upward motion of the layer of phenol be marked from day to day, it will be found to rise higher and higher, and finally surmount the rest of the liquid in the cylinder.

Osmotic phenomena can be obtained by continuous and by discontinuous or porous films. With continuous films it is necessary for the solvent but not for the solute to dissolve in the membrane; with porous films it is necessary for the pure solvent to be adsorbed by pores so small that only the solvent not the solute can pass through. Benzene, toluene, and pyridine were found by L. Kahlenberg to pass through a rubber membrane while water does not. Hence rubber probably acts as a semipermeable membrane to the three first-named liquids, because these liquids dissolve in the rubber.

W. Ramsay (1894) illustrates the production of an osmotic pressure in solutions by the following analogy illustrating what has been termed the osmotic pressure of gases.

> A palladium vessel at 250° to 350° is filled, at atmospheric pressure, with nitrogen gas or with some gas not absorbed by the warm palladium. This vessel is immersed in hydrogen at a given pressure; hydrogen gas diffuses through the metal membrane until the increase of pressure inside the vessel is nearly equal to the outside pressure. In one experiment, this increase was equivalent to 733 mm. of mercury, which is "regarded as the osmotic pressure of nitrogen dissolved in hydrogen." The excess pressure is independent of the concentration of the hydrogen molecules, for the pressure of the hydrogen is the same on both sides of the septum. The (osmotic) pressure of the nitrogen is produced by the bombardment of the nitrogen molecules on the walls of the vessel, while the osmosis of the solvent hydrogen is possible in virtue of its faculty of dissolving in the metal membrane under conditions where the solute nitrogen is insoluble.

In ordinary or *positive osmosis* the direction of flow of the solvent, water, is from the less towards the more concentrated solution; in some cases the direction of flow is from the more to the less concentrated solution; the phenomenon is then styled *negative or reversed osmosis.* H. Dutrochet first described osmosis with inorganic membranes, and T. Graham attributed the phenomenon to chemical interaction between the salt and the membrane. F. E. Bertel, P. Girard, and H. Freundlich attribute the anomalous effect to the electrical endosmose; the flow of liquid is brought about by a difference in electrical potential, the two ends of the capillary pores in the membrane becoming oppositely charged. Potential differences of this kind were shown to exist in animal cells by M. Oker-Blom and W. Ostwald; in frog's muscle by A. Brünings; in vegetable skins by M. Loeb and R. Beutner; in lung tissue by R. S. Lillie and P. Girard; in copper ferrocyanide membranes by R. Beutner; and in clay by A. Brünings. According to W. D. Bancroft, the sign of the electric charge on the membrane is dependent on the absorption of anions or cations. J. Perrin ascribed the polarization to contact electrification being dependent on the preponderance of $H^{\cdot}$-ions or OH'-ions. F. E. Bartel also showed that the appearance of negative osmosis is dependent on the pore diameter, for the phenomenon occurs with solutions of magnesium chloride only when the pore diameters are less than $0{\cdot}4\mu$. J. Mathieu found negative adsorption occurs with a number of dilute solutions when adsorbed by porous plates, membranes, or capillary tubes, such that the liquid adsorbed by the capillary tubes from N-solutions was often only $\frac{1}{10}N$; and he suggests that if the capillary were fine enough only pure water would be adsorbed. Summing up the literature on the subject, W. D. Bancroft says: (1) Osmotic phenomena may occur with a porous diaphragm provided we have very marked negative adsorption and provided the diameter of the pores is so small that the adsorbed films fill practically the whole of the pores. (2) A porous diaphragm will act as a semipermeable membrane in case there is no measurable adsorption of the solute and in case the adsorbed films fill the pores completely. (3) In the usual case of a semipermeable diaphragm, we do not have a porous diaphragm and the semipermeability is due to the fact that the solvent dissolves in the diaphragm while the solute does not to any appreciable extent under the conditions of the experiment. (4) A liquid is not to be considered as a porous substance and solubility does not depend on porosity. Again, A. M. C. Chanoz found that when the two sides of the membrane differ, as with a skin, differences in the osmosis are obtained depending on whether a given side of the membrane is in contact with solution A or solution B. These differences disappear, of course, when the two sides of the membrane are alike, as with parchment paper. It seems probable that the behaviour of the membrane depends largely on its greater or less permeability.

Animal membranes are objectionable when exact measurements are required, because to a certain extent the results depend upon the nature of the membrane, which is not strong enough to withstand the great pressures developed by osmosis; and, most serious of all, the membrane is not quite semipermeable, so that an appreciable amount of, say, sugar does actually pass through. It would therefore be as profitable to measure the pressure of a gas in a leaking vessel as to try to measure the osmotic pressure of a solution with a membrane which allows part of the dissolved substance to pass through. We therefore fall back on artificially prepared membranes. No artificial membrane has been so successful as a film of copper ferrocyanide deposited between the inner and outer walls of a porous earthenware pot—prepared by M. Traube,[3] and described in 1867 in his *Experimente zur Theorie der Zellenbildung und Endosmose*. The film is made by steeping a clean porous pot in an aqueous solution of potassium ferrocyanide, rinsing in water, and then submerging the pot in an aqueous solution of copper sulphate, and subsequently washing out the soluble salts. The deposition of the copper is symbolized by the equation: $2CuSO_4+K_4FeCy_6=Cu_2FeCy_6+2K_2SO_4$. The porous pot with its semipermeable membrane is fitted with a suitable manometer to indicate the pressure. In 1877, W. F. P. Pfeffer made some measurements with cells prepared in this manner. The apparatus was immersed in a large bath of water to maintain the temperature constant during the experiment. Analogous experiments were made by H. de Vries (1878), G. Tammann (1888), P. Walden (1892), etc. Earl of Berkeley and E. G. J. Hartley (1904) placed a solution of sugar in a porous earthenware pot with a semipermeable membrane of cupric ferrocyanide, and surrounded the pot with water. The pressure on the solution was increased until it was just sufficient to prevent the passage of water into or out of the cell through the septum of the ferrocyanide. H. N. Morse (1901–9) employed an apparatus similar to that of W. F. P. Pfeffer, but he improved the quality of the membrane by depositing the cupric ferrocyanide in the pot electrolytically; and also improved the joints between the cell and the manometer; and the manometer itself.

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§ 8. The Osmotic Pressure of Dilute Solutions and the Gas Laws

> Every formula obtained by the application of thermodynamical considerations alone to a mixture or solution remains the same, no matter what assumptions be made regarding the molecular condition of the substances. Consequently, thermodynamics alone cannot decide whether solution is attended by a chemical change in the molecular state of the dissolved substance or otherwise.—P. DUHEM (1894).

J. H. van't Hoff's kinetic theory of osmotic pressure (1887)[1] emphasizes the analogy between the process of vaporization and the process of solution. In a solution the dissolved substance is distributed throughout the whole bulk of the solvent, and the solvent plays the part of so much space. The vapour pressure of a liquid in space will thus be represented by the osmotic pressure of a solution. In the words of A. Rosenstiehl, the osmotic pressure is analogous to the elastic force of vapours. Just as the closed space above a liquid becomes saturated with vapour, so does a solvent in contact with the solute form a saturated solution. An increase of temperature augments the vapour pressure of a liquid, and also the osmotic pressure of a solution.

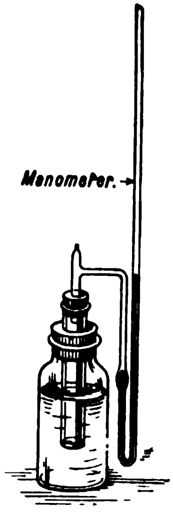

FIG. 16.—Measurement of Osmotic Pressure.

I. The relation between osmotic pressure and the concentration of the solution—Boyle's law.—W. Pfeffer in his *Osmotische Untersuchungen* (Leipzig, 1877) obtained some data with the apparatus which J. H. van't Hoff (1887) utilized, with remarkable cleverness, in developing what he called "the *rôle* of osmotic pressure in the analogy between solutions and gases." The experimental data showed that the osmotic pressure is very nearly proportional to the concentration of the solution; otherwise expressed, the osmotic pressure appears to depend upon the degree of crowding of the molecules of the dissolved substance. Instead of repeating Pfeffer's measurements, a selection from some later determinations with solutions of glucose (sugar) by H. N. Morse (1907) can be quoted (temperature nearly 0°, rounding off the decimals to the nearest tenth of a unit):

Concentration	0·1	0·2	0·3	0·4	0·5	0·6	1·0
Osmotic pressure	2·4	4·7	7·0	9·3	11·7	14·1	23·7 atm.
Equivalent gas pressure . .	2·2	4·5	6·7	8·9	11·1	13·4	22·3 atm.

In dealing with the concentration of solutions, it will be well to adopt the same unit of comparison as that employed in dealing with gases, *i.e.* the molecular weight of the solute expressed in grams per 22·3 litres of solution at normal temperature and pressure. H. N. Morse found that his direct measurements of osmotic pressure came out best when referred to a constant volume of the solvent, not to the volume of the solution.

Assume that a gram-molecule of glucose (180) were it a gas would occupy 22·3 litres. Hence, 0·1 gram-molecule will occupy 2·23 litres. By choosing the concentration so that in Boyle's relation, $PV=\text{constant}$, a solution containing a molecular weight expressed in grams, per 22·3 litres, has a concentration of 22·3 units when $P=1$, we get from Boyle's law $P\div C=22{\cdot}3$. The concentration, it will be remembered, is inversely proportional to the volume. Hence for a concentration 0·1, we get $P=2{\cdot}23$, for $C=0{\cdot}2$, $p=4{\cdot}46$, etc.

The "equivalent gas pressure" is here calculated on the assumption that a "sugar gas" obeying Boyle's law really exists. The results are plotted in Fig. 17. The deviation of the osmotic pressure curve from the dotted curve emphasizes the fact that the deviations of the osmotic from the equivalent "gas pressures" grow larger with increasing concentrations, and hence **exact proportionality occurs only when the solutions are very dilute.** For dilute solutions, the osmotic pressure is nearly proportional to the concentration, or, as W. Ostwald puts it, "the osmotic pressure of a sugar solution has the same value as the pressure the sugar would exert if it were contained, *as a gas*, in the volume occupied by the solution—of course assuming Avogadro's rule." This is another way of saying that the relation between the osmotic pressure of a solution and its concentration has the same form as Boyle's law for gases.

The analogy does not work out so well for concentrated solutions as with dilute solutions—possibly owing to the disturbing effects of overcrowding produced by: (1) molecular attraction between the molecules of the dissolved substance; (2) the volumes of the molecules themselves. The two effects for gases were discussed when dealing with Boyle's law for gases. J. D. van der Waals' corrections for the gas equation $pv=RT$, involves the introduction of terms for the mutual attraction of like molecules and for the space occupied by the molecules, and the corrected equation takes the form $(p+a/v^2)(v-b)=RT$, and by regarding v in the equation $pv=RT$ as the volume of the solvent not of the solution, H. N. Morse really corrected the equation for the space occupied by the molecules of the solute as J. D. van der Waals' did for gases. And (3) the mutual attraction between the molecules of the solute and solvent. On account of the enormous number of molecules of the solvent which are present, each molecule of the solute is probably completely surrounded by molecules of the solvent, and the resultant of all the forces due to the solvent, acting upon each molecule of the solute, is zero. The velocity of the solute molecules impinging on the semipermeable membrane is not affected provided the solution is so dilute that the difference in the concentration of the molecules of the solvent on the two sides of the membrane is negligibly small. O. Stern diminishes the factor a of J. D. van der Waals' equation by a factor $a_{12}(x_0-x)$, expressing the attraction between the molecules of solvent and solute which, so far as osmotic pressure is concerned, acts in the opposite direction to the attraction a_1 between the molecules of the solute itself, for this attraction pulls the molecules of the solute away from the solvent. The term x_0-x represents the difference between the concentration of the solvent outside the membrane and in the solution itself. The term b of J. D. van der Waals' equation is also increased by a factor $b_{12}(x_0-x)$, because the repulsive force b_{12} between the molecules of solvent and solute which makes the solute behave as if the molecular volume b_1 of the solute is smaller than it really is. O. Stern's equation is then:

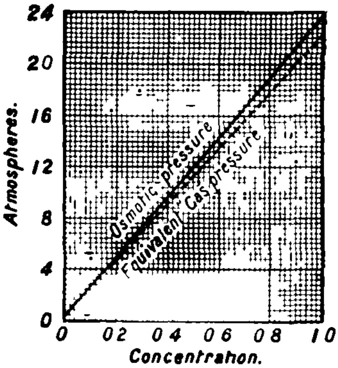

Fig. 17.—Osmotic Pressure and Concentration.

$$\left(P+\frac{a_1-a_{12}(x_0-x)}{v^2}\right)\{V-b_1+b_{12}(x_0-x)\}=RT$$

There are thus four constants in the equation, and since the new constants have to be evaluated from the experimental data, better agreement is to be expected than with an equation including two constants. If two miscible liquids with critical states not very far removed from one another be under investigation, a_{12} and b_{12} are of the same order of magnitude as a_1 and b_1. The difference between the concentrations of the pure solvent and that which it has in solution is nearly identical with the concentration of the solute, then $(x_0-x)/v$ will be nearly $1/v$, the concentration of the solute; the term x_0-x then cancels out, so also do the terms involving a and b, and the gas in solution will then obey the ideal gas law more nearly than it does in the gaseous state, as O. Stern found to be the case with solutions of carbon dioxide in methyl and ethyl alcohols.

2. The relation between osmotic pressure and temperature.—Charles' law.—W. F. P. Pfeffer's measurements on the influence of temperature also showed that the osmotic pressure is proportional to the absolute temperature, which means that the relation between the osmotic pressure and temperature of a given solution has a formal analogy with Charles' law for gases. In illustration, some results by H. N. Morse (1911) for unit concentration may be quoted:

Temperature . . .	0°	5°	10°	15°	20°	25°
Osmotic pressure . .	24·8	25·3	25·7	26·2	26·6	27·0 atm.
Equivalent gas pressure .	22·2	23·0	23·4	23·8	24·2	24·5 ,,

The "equivalent gas pressure" is here calculated on the assumption that a "sugar gas" obeying Charles' law really exists. These numbers are plotted in Fig. 18, and the graphs show the proportionality between osmotic pressure, P, and temperature; P/T=constant. The space between the two curves represents the deviation of the observed osmotic pressure, from the pressure calculated on the assumption that the dissolved substance behaves as if it were a gas. W. F. Magie has also studied the relation between osmotic pressure and temperature.

An experiment due to C. Ludwig (1856) and investigated by C. Soret (1881)[2] —Soret's phenomenon—may be cited in illustration of the applicability of the gas laws to dilute solutions. If a solution be kept at one uniform temperature, it will in time become homogeneous; on the contrary, C. Soret showed that if the two ends of a tube containing a homogeneous solution be kept at different temperatures, the concentration of the solution at the cooler end will increase, and decrease at the warmer end. The warmer solution becomes more dilute because the osmotic pressure of the warm solution is greater than that of a cold solution; and conversely. Equilibrium will be established when the osmotic pressure in all parts of the solution is the same. If the warm end of the tube be 50° hotter than the cold end, then, if Charles' law applies to solutions, the cold solution should increase in concentration $\frac{1}{273}$rd more than the warm solution per degree difference of temperature, and hence the colder solution should be $\frac{50}{273}$rd more concentrated than the warm one. N. M. Hopkins (1905) claims to have observed a difference of 14·03 per cent. in the density of a dilute solution of copper sulphate in a tube 80° at the one end and 20° at the other when the theoretical difference by Charles' law was 14·3 per cent. The phenomenon also appears to be connected with an observation made in 1799, by N. Leblanc, to the effect that if crystals of a salt are placed some at the upper and some at the lower part of a cylinder containing a saturated solution of the same salt, the lower crystals grow larger at the expense of the upper; and likewise also the upper portion of the crystals at the bottom of a liquid decreases while the lower portion increases.

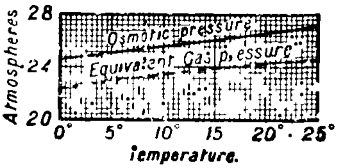

FIG. 18.—Osmotic Pressure and Temperature.

3. Avogadro's hypothesis applied to solutions.—If P denotes the osmotic pressure of a solution, and V the volume containing one gram-molecule of the solute, $PV=RT$ (where R is a constant), and for a solution of volume V containing n gram-molecules of the solute $PV=nRT$. The volume V is to be regarded as the molecular volume of the solution only when, as J. H. van't Hoff (1887) said: "the volume occupied by the molecules of the solute is negligible in comparison with the volume of the solution." Hence, at constant temperature, n molecules of a solute in unit volume of a dilute solution (for which $V=1$) have the same osmotic pressure; otherwise expressed, **equal volumes of solutions containing the same number of solute molecules have the same osmotic pressure;** and conversely, solutions, at the same temperature and the same osmotic pressure contain the same number of molecules of the dissolved substance per unit volume. There is a striking resemblance between this assumption and Avogadro's hypothesis for gases, and it harmonizes with a number of facts. The principle can be applied to measure the molecular weight of substances in solution, for the term "number of molecules" is used in the same sense as the term is used in stating Avogadro's hypothesis for gases: Equal volumes of all gases at the same temperature and pressure contain the same number of molecules; or, conversely, at any assigned temperature the pressure of a gas depends on the *number* of molecules and not on their kind. Hence van't Hoff's hypothesis assumes that *the osmotic pressure and related properties—vapour pressure, freezing point, and boiling point—of dilute solutions* (1) *depend upon the number of molecules of solute dissolved in unit volume of the solution, and are independent of* (2) *the chemical nature of the solvent and solute, and* (3) *of the relations between solvent and solute.* In contradistinction to additive properties like the specific gravity of mixtures, *colligative properties* depend merely on the relative number of molecules present and not on the kind of molecules—*e.g.* the osmotic pressure, freezing and boiling points of solutions.

Examples.—(1) An aqueous solution of 1·0047 grams of orthoboric acid per litre at 0° has an osmotic pressure of 27·3 cm. of mercury. What is the molecular weight of the acid? Since one gram-molecule of a substance in the gaseous state occupies 22·3 litres at 0° and 760 mm., we have here to find what weight of substance will occupy 22·3 litres at 0° and 760 mm., given 1·0047 gram occupy 1 litre at 0° and 273 mm. pressure. Obviously, 1·0047 gram will occupy 0·361 litre at 0° and 760 mm.; and if 0·361 litre weighs 1·0047 gram, 22·3 litres will weigh 62 grams at the same temperature and pressure. Hence the molecular weight of the given acid is 62; this agrees with the formula $B(OH)_3$ for orthoboric acid.

(2) A two per cent. solution of cane sugar has an osmotic pressure of 1016 mm. at 15°; what is the molecular weight of cane sugar? 100 c.c. at 1016 mm. pressure becomes 0·126 litres at 760 mm. pressure and 0°, and 0·126 litre corresponds with 2 grams of cane sugar. Hence 22·3 litres will have 355 grams at the same temperature and pressure. The molecular weight of cane sugar therefore approximates 355. The true number is 342 for $C_{12}H_{22}O_{11}$.

In place of using the equation $PV=RT$, K. Jellinck[3] used J. D. van der Waals' equation in his study of osmotic pressure from the kinetic point of view, and F. Tinker used C. Dieterici's equation.

There are so many experimental difficulties involved in the direct measurement of osmotic pressure that the method is rarely, if ever, employed directly for molecular weight determinations. As in the kinetic theory of gases, it can be shown, with the above assumptions, that the kinetic energy of the solute in dilute solutions is equal to that of a gas at the same temperature and pressure; and that with the same average kinetic energy, the number of impacts depends only on the concentration, and is independent of the presence of the solvent. As a corollary, too, it follows that the mutual exchange of energy at each collision, when equilibrium is established between the solvent and solute, will make the average molecular kinetic energy of solvent and solute the same. Hence, said W. Ostwald (1890),[4] the kinetic energy of the molecules of a liquid is the same as that of the molecules of a gas at the same temperature and pressure.

E. W. Washburn (1915)[5] has drawn attention to the fact that the term osmotic pressure is loosely employed to designate three quite different ideas: (1) The *osmotic pressure* of a solution is really a physical quantity and not a real pressure, and is the difference in the pressure which must be established upon solution and pure solvent in order to make the tendency of the solvent to escape as vapour the same for both; it is the difference of pressure necessary to prevent osmosis through a perfect semipermeable membrane. For dilute solutions, the osmotic pressure at the limit is equal to CRT, where C denotes the concentration of the solute. As the concentration increases, the osmotic pressure increase towards infinity, as illustrated in Fig. 19. (2) In virtue of unordered heat motions, the molecules of a solute in a solution may be considered as exerting a certain pressure, called the *thermal pressure*. For dilute solutions the thermal pressure will be equal to CRT, but as the concentration C increases, the thermal pressure increases towards a large but finite limit, as illustrated in Fig. 19. (3) The partial pressure exerted by the molecules of the solute in a solution against a membrane permeable only to the solvent is called the *diffusion pressure*. For dilute solutions the diffusion pressure is equal to CRT, and as the concentration C increases, the diffusion pressure increases to a finite definite limit whose value depends upon the temperature, pressure, and the attractive forces extended on the molecules of the solute, in the interior of the liquid. See Fig. 19.

The effect of the heat of dilution on osmotic pressure.—Describing osmosis in the language of free energy, the osmosis is attributed to the difference which exists between the free energy of the solvent and solution; and diffusion is an effect of the free energy driving the solvent from the region where the free energy is greatest to the solution where the free energy is least. The process of diffusion continues until the free energy has fallen to the value characteristic of a solution with one uniform composition. When solution and solvent are separated by a semipermeable membrane, the solvent will travel into the solution until the free energy of both is the same. The solute cannot travel through the membrane to the solvent, and therefore the system can never have one uniform composition; for equilibrium, however, the free energy of solution and solvent must be the same.

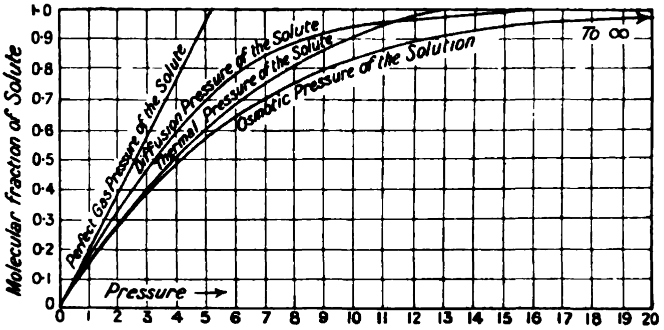

FIG. 19.—Washburn's Illustration of Solution Pressure.

The free energy of the solvent is the greater, and the free energy of the solution can be augmented only by increasing the pressure on the solution; consequently, solvent will diffuse through the membrane to the solution until the hydrostatic pressure—osmotic pressure—required to make the free energy of solvent and solution the same, is attained. The change in the free energy of an isothermal reversible process is given by the expression $W=Q+T(dW/dT)$, where Q is the heat evolved when the solution is diluted. The diminution in the free energy which occurs when a gram-molecule of the solvent passes reversibly and isothermally into a large volume of solution through a semipermeable membrane is therefore

$$PV=Q+T\frac{d(PV)}{dT}$$

where P is the osmotic pressure and V is the increase in volume. This relation represents the temperature coefficient of the osmotic pressure. If Q, the heat of dilution, is zero, the preceding expression reduces, on integration, to $PV/T=$constant, and hence $PV=RT$ is true only when the heat of dilution is zero. For all but extremely dilute solutions, Q is not constant, and the osmotic pressure cannot be calculated from $PV=RT$, but rather from $PV=RT+Q$. Before the above equation can be integrated, it is necessary to know how Q varies with temperature (say, $Q=A+BT+\ldots$). When molecular weights are calculated from the osmotic pressure or related phenomena, neglect of this factor—heat of dilution—may give quite erroneous results.

In his work on the thermodynamics of osmotic pressure, J. H. van't Hoff assumed that the solutions were so dilute that no thermal change occurred on further dilution. W. D. Bancroft (1905)[6] has shown that the osmotic pressure is abnormally high when heat is evolved on dilution, and similarly the lowering of the freezing point of such a solution will not be so great as when the heat of dilution is zero. In the case of the metals of the alkalies and alkaline earths dissolved in mercury, molecular weights equal to half the atomic weights are obtained by formulæ in which the heat of dilution is assumed to be zero; and with sulphuric acid, values ranging from 57·7 to 11·7 when the concentration of the solution ranges from 5·6 to 68·5 per cent. respectively—the anomaly of a decreasing molecular weight with increasing concentration disappears if the heats of dilution are included in the computation.

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§ 9. The Relation between the Vapour Pressure of a Solution and the Molecular Weight of the Solute

> The mutual action of two liquids is observable when a mixture of say alcohol and ether is subject to experiment in the vacuum of a barometer column, for the mixture depresses the column less than either component alone.—C. L. BERTHOLLET (1803).

M. Faraday[1] knew, in 1822, that the vapour pressure of a solution is lower than the vapour pressure of the pure solvent; and C. L. Berthollet's experiment in 1803 shows that at a given temperature the vapour pressure of a solution of ether in alcohol is less than that of either ether or alcohol alone. A. Wüllner discovered the important fact experimentally, in 1858, that **the lowering of the vapour pressure of a solution is proportional to the quantity of substance in solution provided that the dissolved substance is non-volatile.** This is sometimes called **Wüllner's law.** A. Wüllner worked with aqueous solutions, but the abnormal behaviour of such solutions as a result of the extraordinary properties of water prevented him decisively demonstrating the generalization. F. M. Raoult (1887) worked with non-aqueous solutions and succeeded better than his predecessors. The phenomenon can be illustrated by introducing about 2 c.c. of water, 2 c.c. of a 2 per cent. solution of potassium iodide, and 2 c.c. of a 4 per cent. solution of the same salt into the Torricellian vacuum of each of three barometer tubes mounted within a hot jacket. The more concentrated solutions will depress the mercury most, the less concentrated solution will depress the mercury more than water alone, but less than the more concentrated solution. Some observed values[2] of the difference between the vapour pressures of water and of solutions containing *w* grams of potassium iodide, KI, in 100 grams of water are:

	10·33	30·71	54·75	71·54	111·14	134·93	169·14	200·25
w . .	15·6	47·6	91·0	21·7	191·3	231·6	283·4	321·3

W. W. Reed (1913) has an experiment to show the lowering of the vapour pressure of a solution. Three similar thermometers are arranged like the two in a wet-and-dry bulb hygrometer. The wick of one bulb dips in the given solution. The thermometer with the wick dipping in the pure solvent reads lower than the one with its wick dipping in the solution, and both read lower than the dry-bulb thermometer.

Suppose a solution *A*, Fig. 20, confined in a long-stemmed tube, as illustrated in the diagram, be separated by a semipermeable membrane *M* from the pure solvent. Let all be confined in a closed vessel. Osmotic pressure will force the solution to rise in the narrow tube to a height *h*, until the whole system is in equilibrium. Let p_s denote the vapour pressure of the solution in the narrow tube, and *p* the vapour pressure of the pure solvent in the outer vessel. The vapour pressure of the solution at the surface in the narrow tube must be equal to the vapour pressure of the solvent at the same level, otherwise distillation would take place either to or from the surface of the liquid in the narrow tube. In either case, there would be a constant flow of liquid respectively to or from the vessel *A* through the semipermeable membrane in order that *h* may have a constant value. Otherwise expressed, perpetual motion would occur. By the law of excluded perpetual motion this is not possible, hence the vapour pressure of solution and solvent at the upper level of the solution in the narrow tube must be the same. The vapour pressure of the solvent at the level *a* will be equal to the vapour pressure of the solvent at the lower level *b*, less the pressure of a column of vapour of height *h* per unit area. Hence, the hydrostatic pressure of the *liquid* column *h* measures the osmotic pressure; and the hydrostatic pressure of the *vapour* column *h*, measures the difference in the vapour pressure of solution and solvent. Since the height *h* is determined by the osmotic pressure, which, in turn, is determined by the concentration of the solution, there must be **a simple proportionality between the osmotic pressure or concentration of the solution and the lowering of the vapour pressure** $(p-p_s)$, for the vapour of the solution will be in equilibrium with the vapour of the solvent at such a height *h* above the surface of the solvent, that the hydrostatic (osmotic) pressure of the column of liquid will make the vapour pressure of the solution equal to that of the solvent, so that the height *h* measures the lowering of the vapour pressure, $p-p_s$, and also the osmotic pressure, *P*.

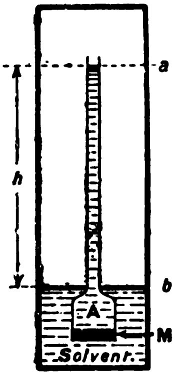

FIG. 20. — Diagrammatic.

If the tube *h* has unit sectional area, $p-p_s : P =$ Weight of column of vapour : Weight of equal column of liquid; or, if *w* and *W* respectively denote the weights of columns of solution and vapour of height *h*, and unit sectional area, then, $p-p_s : P = W : w$. Let one gram-molecule *M* of vapour occupy a volume *v*, and let *V* denote the volume of the solution also containing a gram-molecule of the solute, then $pv = PV$ for dilute solutions, and hence, $v = VP/p$, or the volume occupied by a gram-molecule of the vapour is P/p times the volume of the solution containing a gram-molecule of the solute. A volume *v* of the vapour containing a gram-molecule of the solvent will weigh *M* grams, or $W = M$. If *n* gram-molecules of the solute are dissolved in *N* gram-molecules of the solvent, a volume *V* of the solution containing one gram-molecule of the solute will weigh MN/n grams, and a volume v or VP/p of the solution will weigh $w=PMN/np$ grams. Substituting these values of w and W in the above proportion, and reducing the resulting expression to its simplest terms, there remains :

$$\frac{p-p_s}{p}=\frac{n}{N}$$

In concentrated solutions when n, the number of molecules of the solute, is equal to N, the number of molecules of the solvent, $n=N$, and p_s/p is zero, which is impossible, because the vapour pressure of a concentrated solution will always have some numerical value. F. M. Raoult therefore changed the preceding expression to

$$\frac{p-p_s}{p}=\frac{n}{N+n} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n denotes the number of gram-molecules of the solute, and N the total number of gram-molecules of solvent. In words, the relative lowering of the vapour pressure of a dilute solution is proportional to the relative number of molecules of the solute and solvent. F. M. Raoult[3] found this rule valid for dilute solutions—**Raoult's vapour pressure law**—and for more concentrated solutions $(p-p_s)/p=kn/(N+n)$ represented the results more exactly.

Instead of starting from J. H. van't Hoff's rule applicable to dilute solutions, G. N. Lewis[4] argues that the results are incompatible with solutions of finite concentration, and he prefers to start from Raoult's law, which is the only law of dilute solutions which ever holds in concentrated solutions. He therefore defines a perfect solution as one which follows this rule : At a constant temperature the vapour pressure of the solvent is proportional to its molecular fraction $n/(N+n)$. Thus, a solution which contains $n=0{\cdot}1$ gram-molecule of the solute and $N=0{\cdot}9$ gram-molecule of solvent, $n/(N+n)=0{\cdot}9$; and the vapour pressure of the solvent p should be nine-tenths of the vapour pressure in the pure state. It is assumed that concentrated solutions which deviate very much from this rule are those in which solvent and solute form complex compounds either with themselves or with one another. From this relation it is then possible to deduce expressions for the osmotic pressure and related properties of solutions by the regular methods of thermodynamics. It will be observed that Raoult's rule reduces to Henry's law when applied to gases when the concentration is expressed as a molecular fraction $n/(N+n)$. Henry's law is symbolized $p=Kn/(N+n)$, where the constant K is the vapour pressure of the pure gas, for $p=K$, if the amount N of the solvent is zero.

The relation between the relative lowering of the vapour pressure and the osmotic pressure.—A relation between the osmotic pressure and the vapour pressure was deduced by J. H. van't Hoff in 1886, and the demonstration was improved in 1889 by S. Arrhenius.[5] Many other modifications have been suggested. Let p denote the vapour pressure of water, and p_s that of the solution. S. Arrhenius found the osmotic pressure, P, to be

$$P=\frac{sp}{u}\log\frac{p}{p_s}$$

where u is the specific volume of the solution, s the specific volume of the vapour of the solvent at the pressure p. W. Spens obtained a somewhat similar expression with u representing the increment in volume of a large mass of solution when unit mass of solvent is added ; and Earl of Berkeley and E. G. J. Hartley with u representing the specific volume of the solvent. A. W. Porter, J. E. Trevor, J. J. van Laar, H. Boldingh, G. N. Lewis, E. W. Washburn, and H. L. Callendar have also deduced expressions for the relation between the vapour pressure and osmotic pressure of solutions.

In the demonstration that $(p-p_s)/p=n/N$, the molecular weight of the solvent is assumed to be the same in vapour and in solution. If n represents the number of molecules of the solute of molecular weight m, then $n=w/m$, where w denotes the weight of the n molecules; similarly, $N=W/M$, where W denotes the weight of N molecules of the solvent. Substitute these values of n and N in $(p-p_s)/p=n/N$, and solve for m; there remains $m=wMp/W(p-p_s)$. Let $W=100$ grams, then for any given solvent the constant Mp/W can be represented by k. Consequently, if w denotes the weight of substance in grams dissolved in 100 grams of solvent, and if p' denotes the resultant lowering in the vapour pressure of the solvent $p-p_s=p'$, the molecular weight of the solute in dilute solution is:

$$\text{Molecular weight}=k\frac{w}{p'}, \quad . \quad . \quad . \quad . \quad (2)$$

where k is the so-called **vapour pressure constant** whose numerical value depends upon the particular solvent used; k therefore represents the diminution in the vapour pressure which occurs on dissolving one gram-molecule of the solute in 100 grams of the solvent.

EXAMPLES.—(1) A solution of iodine in ether showed a difference of $p'=7{\cdot}4$ cm. at 15° in the levels of the mercury in the two legs of the differential manometer. The solution contained $w=7{\cdot}139$ grms. of iodine per 100 grms. of ether. The value of k—the reduction in the vapour pressure produced by one gram of the solute in 100 grms. of solvent—for ether at 15° is 260. Hence, from formula (1), $260\times7{\cdot}139\div7{\cdot}4=250$. Theory gives $I_2=254$.

(2) A solution containing the equivalent of 7·435 grms. of sulphur per 100 grms. of carbon disulphide lowered the vapour pressure 4·9 cm. The constant for carbon disulphide at 15° is 171·5. Hence, the molecular weight of sulphur under the conditions of the experiment is 260·2. Theory for $S_8=256$.

The method for determining the molecular weight of a substance from direct measurements of the lowering of the vapour pressure is of great theoretical interest, but in practice it is seldom employed, because some of the related properties of solutions are more amenable to measurement—freezing point, boiling point, etc.

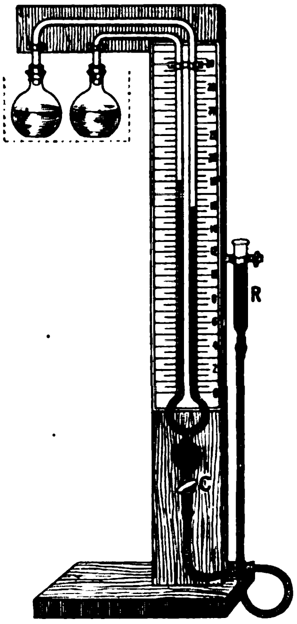

FIG. 21. — Vapour Pressure Method of estimating Molecular Weights.

The practical methods for determining the lowering of the vapour pressure of a solvent are classed as: (i) dynamical, or (ii) statical.[6] W. Ostwald's dynamical process (1891) consists in determining the lowering of the vapour pressure from the ratio of the loss of weight of the solvent to the gain in weight of an absorption bulb when a slow current of air is passed in order through solution, solvent, and absorption bulb. The barometric vacuum process—Fig. 21—is a statical process.

The following modification is one of the most convenient forms of the statical process: Two small c.c. flasks are fitted to a differential manometer, as illustrated in Fig. 21. One flask contains the pure solvent, and the other a known weight of the solute—say from 2 to 4 grms.—and three-fourths filled with solvent. Each flask is heated by placing it in a beaker containing warm water so that the vapour of the solvent can sweep air out of the system *viâ* the three-way cock C. When all the air is expelled, the stopcock is put in communication with the flask and both flasks allowed to cool to any desired temperature by placing them in a suitable bath. The difference in the levels of the mercury in the two tubes is measured. The reservoir of mercury is again adjusted until the level of the mercury in the bulb is below the stopcock; and the flask containing the solution is weighed. Other manipulation details should be obvious. The subsequent procedure can best be illustrated by example.

The methods used in hydrometry to determine the pressure of aqueous vapour in the air, and the relation between this pressure and that of saturated water vapour at the same temperature can be employed to measure the vapour pressures of solutions and solvent (G. Guglielmo, 1901); vapour pressures can also be determined from the rate of evaporation of solutions (H Kronberg, 1893).[7]

The osmotic pressure of solutions of any concentration.—Just as the attempts to adapt the relation $pv=RT$ to gases has led to about fifty more or less unsatisfactory modifications of the formula, so the attempt to adapt the gas equation $pv=RT$ to concentrated solutions has led to quite a number of tentative equations some of which are modelled after J. D. van der Waals' well-known gas equation. While the law holds good for very dilute solutions in which there is no polymerization, dissociation, or formation of complexes, yet it can be regarded only as a limiting law which is approached as the solution becomes more and more dilute, and it results from an unknown general equation by omitting certain terms which become negligibly small as dilution increases. Accordingly E. W. Washburn (1910)[8] has attempted to reconstruct this equation in the following manner. For dilute solutions, $PV_s=nRT$, where V_s denotes the volume of the solution. If N gram-molecules of the solvent have n gram-molecules of the solute in solution and the molecular volume of the solvent is V, $V_s=NV$; consequently, $NPV=nRT$. If the composition of the solution be expressed as a gram-molecular fraction of the solute such that n' represents the molecular fraction of the solute and N' that of the solvent, $n'+N'=1$; $n=n'/(N'+n')$; and $N=N'/(N'+n')$; hence, it follows that

$$P=\frac{RT}{V}\cdot\frac{n'}{N'}$$

This relation is true only at the limit to which the osmotic pressure approaches when the concentration of the solution approaches zero. Hence, by differentiation, $dn'+dN'=0$, and $dn'=-dN'$; accordingly

$$dP=\left(\frac{RT}{V}\right)\left(\frac{-dN'}{N'}\right)$$

which means that the addition of dN' molecules of a solute to a solvent raises the osmotic pressure dP. If the molecular volume of the pure solvent be V_0, under a standard pressure, and if a is the coefficient of the compressibility, $V=V_0(1+aP)$, and integration of the above equation furnishes

$$P+\left(\frac{aP^2}{2}\right)=-\frac{RT}{V_0}\log(1-N')$$

which resembles J. J. von Laar's equation, and represents the osmotic pressure of solutions for all concentrations. The relations between osmotic pressure and vapour pressure, boiling point, and freezing point can be derived from this equation in the usual way. For dilute solutions, if a be very small, the solution can be assumed to be incompressible, without committing sensible error; and if N' be small log $(1-N')$ will be virtually equivalent to N'; and consequently, $P=-N'RT/V$. A deduction from this equation has been tested, with satisfactory results, by J. von Zawidzky (1900) for concentrations ranging from zero to infinity for over a dozen different binary mixtures.

G. F. Fitzgerald (1896)[9] has pointed out that the kinetic theory of evaporation describes the lowering of the vapour pressure of a solution in this manner: The presence of non-volatile molecules of the solute at the surface of the solution hinders the egress, but does not prevent, or possibly facilitates, the return of the volatile molecules. The gas-analogy hypothesis of osmotic pressure assumes that the presence of a body in solution produces no effect or the same effect on the ingress or egress of the molecules of the solute, for the surface of a liquid with a non-volatile solute is a perfect semipermeable membrane—water molecules can pass through the surface freely, but the molecules of the solute cannot. It is a remarkable coincidence that with dilute solutions the osmotic pressure is roughly the same as that which would be produced by the molecules of the solute if it were in the gaseous state, but, as previously indicated, the dynamical theory of the two must be intrinsically different.

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§ 10. Distillation

It is rather curious that the solvent can usually be evaporated from a solution of a non-volatile solid without any of the latter passing away. If the molecules of the solute are moving freely among the molecules of the solvent, it is difficult to understand clearly why the former do not escape from the surface of the solution at a rate which is comparable with the escape of the molecules of the solvent. According to the hydrate theory, the molecules of the solute are loaded with the molecules of the solvent, and this prevents the former from moving fast enough to escape from the attraction of the molecules of the liquid. Of course, most solids are not volatile at the temperature the solutions are evaporated, and the act of solution implies that the attraction of the molecules of the solute for one another is less than the attraction of the molecules of the solvent for those of the solute. It has been argued that the non-volatility of the original solid implies that its molecules are retained by the attraction of the molecules of the solvent so as to prevent the vaporization of the solute along with the free solvent. When a mixture of two liquids is boiling in a retort, their joint vapour pressure will be equal to the barometric pressure, and the boiling point of each liquid will be lower than its boiling point under atmospheric pressure because the partial pressure of each liquid must be lower than the total pressure. Consequently, each substance will behave as if it were being distilled under a reduced pressure, and will volatilize at a lower temperature than its boiling point under atmospheric pressure. In illustration, ammonium chloride or boric acid volatilizes much more rapidly in a current of steam than when alone, and hence these substances are carried off the rising vapour when aqueous solutions are evaporated. J. L. Gay Lussac (1832) [1] showed that if p_1 and d_1 respectively denote the partial pressure and vapour density of the liquid, and p_2 and d_2 the corresponding constants for the other component of the mixture to be distilled, then the relative quantities of the two liquids which distil over are related as

$$\frac{\text{Quantity of substance 2 in distillate}}{\text{Quantity of substance 1 in distillate}}=\frac{p_2d_2}{p_1d_1}$$

If this ratio be large, the distillation of the required substance will be rapid, and conversely, if this ratio be small.

EXAMPLE.—A. Naumann (1877–79) applied Gay Lussac's law to mixtures of immiscible liquids. He showed that a mixture of water and nitrobenzene boils at 99° under atmospheric pressure. The vapour pressure of water at this temperature is 733 mm. and its vapour density is 18; while the vapour density of nitrobenzene is 123. Hence, the vapour pressure of nitrobenzene at 99° is $760-733=27$ mm. Here $p_1=733$; $d_1=18$; $p_2=27$; and $d_2=123$, and the proportion of water to nitrobenzene in the distillate is as 13194 : 3328, or nearly as 4 : 1.

The composition of the vapour formed by the evaporation of the mixture of two liquids depends on the proportion in which the two components are contained in the mixture, and on the vapour pressures of these components at the temperature at which the evaporation occurs. The total vapour pressure of a mixture of completely miscible liquids depends upon (1) The relative solubilities of the vapours in the unlike components of the liquid mixtures; (2) on the relative attraction between like and unlike molecules; and consequently also on (3) the relative proportions of the components of the mixture. If the attraction of the unlike molecules of solvent and solute for one another be negligibly small, the two substances will appear to be insoluble in one another; consequently, the vapour of the one liquid will not dissolve in the other liquid. The greater the attraction of the unlike molecules for one another, the greater will be the solubility of the one in the other. In the case of two immiscible liquids, each exerts its own characteristic vapour pressure independently of the other, although, if one liquid be covered by a deep layer of the other, the lower liquid may take some time to develop its equilibrium pressure—unless the mixture is agitated so as to bring the heavy liquid to the surface and thus facilitate vaporization. In the case of consolute liquids—*i.e.* liquids which can be mixed in all proportions—if the mutual attraction of the unlike molecules be not much in excess of that needed to produce complete miscibility, the vapour pressure may be less than the sum of that of the components, but greater than either one taken singly; while if this attraction be relatively large, the vapour pressure may be less than that of either component. When the mutual attractions of the like and unlike molecules of two consolute liquids are nearly the same the relation between the vapour pressure of the mixture and its composition is comparatively simple, and can be represented by a straight line.

C. L. Speyers (1900) [2] supposed that the total pressure P of a mixture of two liquids, 1 and 2, is related to m, the percentage molecular composition, by $100P=mp_1+(100-m)p_2$, where p_1 and p_2 respectively denote the vapour pressures of the two liquids. This expression resembles one previously obtained by F. Guthrie (1884) when the percentage weights were employed in place of molecular proportions. This is probably the case with closely related compounds—*e.g.*, chloro- and bromo-benzene—where admixture is attended neither by any measurable change in volume, nor by any evolution or absorption of heat. Let a_{12} represent the attraction of unlike molecules, and a_1 and a_2 the mutual attractions of like molecules of the liquid 1 and 2. B. Galitzine (1890) assumed that the relation $a_{12}=\sqrt{a_1a_2}$ will probably obtain when there is no appreciable alteration of temperature or volume when the liquids are mixed in equimolecular proportions. C. L. Speyers' rule does not apply to many mixtures of normal liquids—*e.g.* carbon tetrachloride and benzene—but, according to J. D. van der Waals (1900), it should hold good for liquids whose critical pressures are equal, and whose molecular attractions agree with Galitzine's relation $a_{12}=\sqrt{a_1a_2}$. S. Young (1902) tested this hypothesis for mixtures of chloro- and bromo-benzene, and found that the differences between the observed and calculated pressures were within the limits of experimental error.

EXAMPLE.—The molecular proportion of a mixture of bromo-benzene mixed with chloro-benzene is 50 per cent., while the vapour pressure, p_1, of the former is 526·25 mm., and of the latter, p_2, 992·30 mm. Hence, $P=\{50\times326{\cdot}25+(100-50)992{\cdot}30\}\div100=759{\cdot}4$ mm.; the observed value was 760 mm.

P. Duhem (1887),[3] M. Margules (1895), and others have shown that the relation between the composition and the vapour pressures of the components of a mixture of two liquids, 1 and 2, can be represented by an expression equivalent to

$$\frac{d(\log p_1)}{1-x}+\frac{d(\log p_2)}{x}=0$$

where x and $1-x$ represent the respective molecular proportions of the components of the mixture, such that if n_1 and n_2 respectively denote the number of gram-molecules of the liquids 1 and 2, in the mixture, $x=n_1$ divided by n_1+n_2, and $1-x=n_2$ divided by n_1+n_2. It is assumed that the molecular weights of each liquid is the same in the gaseous and liquid state of aggregation, and that the vapours obey the ideal gas laws. The above equation—sometimes called **Duhem and Margules' equation**—can be translated into a number of different though equivalent forms, *e.g.*

$$\frac{dp_1}{dx}\left(\frac{x}{p_1}\right)=-\frac{dp_2}{dx}\left(\frac{1-x}{p_2}\right)$$

When one liquid, say 2, is present in large excess, the partial pressure p_1 of the other liquid will follow Henry's law approximately, so that $p_1/x=\text{constant}=dp_1/dx$, or $(dp_1/dx)(x/p_1)=1$, and graphically, the variations of x and p_1 will be represented by a straight line; it also follows that the partial pressure curve of the other substance will be represented by a curve of the same type. The value of p_1/x may be expected to increase or decrease continuously as x changes in value from zero to unity when it becomes equal to the vapour pressure of the pure liquid. Thus, for binary mixtures of consolute liquids the vapour pressure curve of the one component will be represented by a straight line—Type II, Fig. 22—or by a curve showing a minimum—Type I—or a maximum—Type III—value. There are no sharp lines of demarcation between the three types; representatives with every degree of curvature between the two extreme maximal and minimal curves are known, with the straight line as a special case. If the two substances are not miscible in all proportions, the partial pressure curve assumes the form Type IV shown in Fig. 22, and in the region of immiscibility, when the solution separates into two layers corresponding in composition and vapour pressure with the points a and b, each of the two layers has the same partial pressure. More complicated variations of each of these types of curve are known.

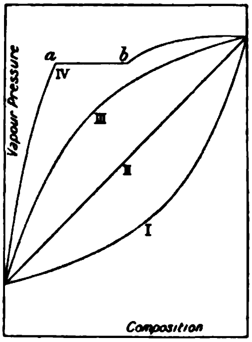

FIG. 22. — Diagrammatic Relations between the Vapour Pressure and Composition of Binary Mixtures.

The total vapour pressure P of a binary mixture is, according to Dalton's partial pressure law, $P=p_1+p_2$, and hence, by differentiation $dp_1/dx=dP/dx-dp_2/dx$. Substituting this value of dp_1/dx in equation (2), it follows that the variation of the total pressure with composition will be represented by

$$\frac{dP}{dx}=-\frac{dp_2}{dx}\left(1-\frac{p_1}{p_2}\frac{1-x}{x}\right)$$

and the vapour pressure P will be a maximum or a minimum when $dP/dx=0$, as is the case in the region between a and b, Fig. 22, or else when $p_1/p_2=x/(1-x)$. The last condition is satisfied by mixtures with a constant boiling point; and for consolute liquids it also follows that there can be one and only one maximum or minimum.

The vapour pressure curves of consolute liquids shown in Fig. 22, are related with the general phenomena of distillation. The vapour pressure curve III with a maximum vapour pressure corresponds with a curve with a minimum boiling point, while the vapour pressure curve I with a minimum corresponds with a mixture showing a maximum boiling point. In general, the distillation of a binary mixture furnishes a distillate which is richer in the more volatile constituent, and a residue in the retort which is richer in the less volatile constituent. There are, however, three cases:

During distillation, the boiling point of the liquid steadily rises. This corresponds with the curve II, Fig. 22, and is illustrated by mixtures of methyl alcohol and water, or of liquid oxygen and nitrogen. The vapour pressure of such mixtures steadily falls during the progress of the distillation, and the vapour pressures and boiling points of all possible mixtures lie between those of the two single constituents. The vapour must, therefore, be always richer than the liquid in the more volatile constituent. By repeated distillation of the distillate, an almost perfect separation of the two liquids can be effected into distillate (more volatile) and residuum (less volatile constituent)—provided, of course, that their boiling points be not too close together.

During distillation, the boiling point of the liquid rises to a maximum corresponding with the minimum vapour pressure. This is typified by curve I, Fig. 22. H. E. Roscoe (1861–2) showed that with aqueous solutions of hydrochloric, hydrobromic, hydriodic, sulphuric, nitric, or perchloric acid, there is a certain mixture which has a higher boiling point than any other mixture. The case of hydrochloric acid was studied by A. Bineau much earlier—1838. He found that if hydrochloric acid with less than about 20·24 per cent. of hydrogen chloride be distilled, water will accumulate in the distillate until the liquid in the retort has 20·24 per cent. hydrogen chloride. Such a mixture will distil over unchanged. If the concentration of the liquid being distilled be greater than about 20·24 per cent. hydrogen chloride, acid will accumulate in the distillate until the residue has 20·24 per cent. hydrogen chloride, and after that an acid of this composition will distil over unchanged. The boiling-point curves of aqueous solutions of formic acid and of hydrazine also show maxima corresponding with distillates of constant composition. The residue in the retort will always have a composition corresponding with a minimum vapour pressure, that is, with the least volatile mixture.

During distillation the boiling point of the liquid falls to a minimum corresponding with the maximum vapour pressure. This corresponds with curve III, Fig. 22. Examples occur with mixtures of propyl alcohol and water. A. A. Noyes and R. R. Warfel (1901)[4] also found a mixture of 4·43 per cent. of water with ethyl alcohol boils at 78·15°, while ethyl alcohol alone boils at 78·3° and water at 100°. The particular liquid with a maximum vapour pressure has a minimum boiling point. Whatever the concentration of the original liquid there is a tendency for the more volatile mixture with the minimum boiling point to distil first.

In neither of these two latter cases can one component be made to accumulate in distillate or in the residue in the retort so that a separation is as complete as in the first case—*e.g.* aqueous solutions of ethyl alcohol can be obtained with no more than about 96 per cent. of alcohol.

W. Ostwald (1904)[5] used the term **hylotropic mixture** (ὕλη, matter; τροπῶς, form) for a body which retains the same composition and the same properties when it changes from one phase to another—*e.g.* when a substance changes its state of aggregation. J. Wade and R. W. Merriman (1911) proposed the term **azeotropic mixtures** (α, not; ζέω, to boil; τροπῶς, form) instead of the phrase "mixture of maximum or minimum boiling point." An azeotrope resembles a chemical individual in boiling without undergoing a change in composition, but differs from it in losing this character when the pressure is altered. If the composition is independent of the pressure and therefore of the temperature, the hylotrope is a *chemical individual.* Hence, a chemical individual is a body which can form hylotropic phases within finite ranges of temperature or pressure. When these limits are exceeded, and the substance begins to dissociate, it is a chemical compound; and if there are no known limits to the range of existence, the body is an *element*.

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§ 11. Other Hypotheses explaining Osmosis

The substitution of analogy for fact is the bane of chemical philosophy; the legitimate use of analogy is to connect facts together and to guide to new experiments.—H. DAVY.

Vague similarities on certain properties are never sufficient to determine a person who earnestly seeks for truth, and is not shackled by hypotheses.—T. BERGMANN (1767).

After J. H. van't Hoff[1] had established the striking analogy between the osmotic pressure of solutions of cane sugar in water, and the elastic pressure of gases, he attacked the problem on the theoretical side, and proved that if the solution be so dilute that the mutual attractions of the molecules of the solute, and the space they occupy can be neglected, and with a perfectly semipermeable membrane, the numerical value of the osmotic pressure must be equal to the elastic pressure the solute would exert if it were in the gaseous conditions at the same temperature and pressure. The method of proof depends on a reversible cycle of operations and the second law of thermodynamics. Both J. H. van't Hoff (1890) and Lord Rayleigh (1897) based their proofs on the applicability of Henry's law, and this was considered by Lord Kelvin (1897) to be an objection. Accordingly, J. Larmor (1897) devised a proof in which the laws of the solubility of gases or possible changes in the state of molecular aggregation during solution are not involved. The thermodynamic explanation of osmotic phenomena makes no assumption as to the cause of osmosis, or how the membrane does its work, and the validity of its deductions is quite independent of all hypotheses as to the cause of the phenomena it seeks to investigate. Consequently, it throws little or no light on the mechanism of the process, and the quest for an explanation of osmotic phenomena proceeds independently of thermodynamics. There are a number of explanatory hypotheses—both physical and chemical—*sur le tapis*. The chemical hypotheses will be considered later.

The gas-analogy hypothesis of osmotic pressure.—The laws associated with the names of Boyle, Charles, Dalton, and Graham, and the hypothesis of Avogadro, are but a few of the many striking analogies subsisting between the behaviour of gases confined in a given space and substances in dilute solution. We know enough about nature to believe that if two things are exactly alike, they will behave alike under the same circumstances; but when the things compared are not quite similar, we must be prepared for discrepancies. Analogy is not proof. Had Isaac Newton measured the refractory power of native cadmium sulphide—greenockite—he would no doubt have said: "greenockite is probably an unctuous substance coagulated," and he would have been wrong. As it happened, this prognostication turned out all right with the diamond. The hypothesis that the osmotic pressure of a dilute solution is produced by the bombardment of the semi-permeable membrane by the dissolved molecules gives a very plausible interpretation of the analogy between the behaviour of dissolved molecules, and the molecules of a gas brought out by J. H. van't Hoff in 1887, but the analogy appears to break down so completely with more concentrated solutions that a number of rival hypotheses have been advanced to explain the phenomena. The principle of exhaustion compels us to investigate other hypotheses.

Solvent pressure hypothesis.—According to F. Tinker,[2] osmotic pressure is primarily a solution pressure and is not a pressure produced by the solute or dissolved substance. He says: The tendency of a liquid to diffuse is measured by its diffusion pressure, which may be defined as the bombardment pressure exerted by the liquid molecules on either side of a plane of unit area placed anywhere within the liquid. Since the absolute concentration of a solvent is reduced by the introduction of a solute, it follows, therefore, that the diffusion pressure of the solvent in a solution is always less than that in the pure solvent itself, and the osmotic pressure of the solution will be proportional to the difference between the absolute concentration of the solvent on the two sides of the membrane. It is also approximately proportional to the concentration of the solute because the latter is itself approximately equal to the difference in solvent concentration on the two sides. If now there be removed from the solution side all the solvent molecules and an equal number from the pure solvent side, the residue of solvent molecules will diffuse across the membrane as before while the solute molecules will bombard the membrane. Moreover, the pressure of the solvent residue on the one side will be equal to the pressure of the solute on the other, and both will be equal to the corresponding gas pressure since the molecules are now at distances from one another comparable to gas distances. Hence to prevent the residue of solvent from flowing across the membrane, a hydrostatic pressure equal to the gas pressure will have to be applied. The phenomenon of osmotic flow is therefore due to the residue or excess of solvent molecules on the pure solvent side. The solute molecules play an indirect part only, but they do cause a strain to be placed on the membrane which tends to rupture it. The fundamental difference between osmotic phenomena in the gaseous and solution states is that whereas the active molecules have a vacuum for a medium in the case of gases they have a liquid for a medium in the case of solutions.

Vapour pressure hypothesis.—H. L. Callendar's hypothesis [3] (1908) is one of the most satisfactory of the purely physical explanations of osmotic pressure, and it is superior, in many respects, to the gas-analogy hypothesis. H. L. Callendar's hypothesis has been tested with somewhat concentrated solutions, and wherever data are available it has been eminently successful. Experiment shows that the maximum vapour pressure of a solution can be altered in three ways: (1) by altering the temperature; (2) by varying the concentration of the solution; and (3) by altering the pressure under which the liquid itself is confined. The effect of pressure on the freezing point of water (*ON*, Fig. 9, Chapter IX) is an application of the third principle. An objection might very properly be raised to the third method of altering the vapour pressure of a liquid; it has been shown to be impossible to raise the pressure on a saturated vapour, without causing some of it to liquefy. If a vertical cylinder, provided with a piston, contains nothing but water—liquid and vapour, it is quite true that the descent of the piston will result in the condensation of water vapour until all the vapour is liquefied, and as long as water vapour is present the vapour pressure remains constant. On the contrary, if air as well as water vapour be present, it is easy to see that the volume of the air decreases, or *the pressure of the air on the surface of the liquid increases* during the descent of the piston. The water vapour still supports its own share of the total pressure up to its maximum vapour pressure, and not quite so much water vapour as before will condense, consequently the liquid under a considerable external pressure can exert a greater vapour pressure than the maximum vapour pressure under atmospheric pressure.

It has been proved experimentally that **the maximum vapour pressure of a solution under very great pressures is rather greater than the maximum**

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vapour pressure of the same solution under atmospheric pressures (see the curve *ON*, Fig. 9, Cap. IX). Again, the vapour pressure of a solution is *less* than the vapour pressure of the pure solvent, Fig. 21. Consequently, if the pressure on a solution be sufficiently augmented, the pressure of its vapour can be made equal to the vapour pressure of the pure solvent under atmospheric pressure. This is the condition necessary in order that solution and solvent can exist side by side in equilibrium. If the vapour pressure of the solution were less than that of the pure solvent, the system would not be in equilibrium, because vapour would distil from the solvent into the solution until the vapour pressure of both were the same. Conversely, when a solution under its own osmotic pressure and the pure solvent are in equilibrium, it follows that their vapour pressures must be equal. Hence, according to H. L. Callendar: **The osmotic pressure of a solution represents the external pressure which must be applied in order to make its vapour pressure equal to that of the pure solvent.** With this hypothesis, H. L. Callendar has calculated the osmotic pressures of sugar solutions of different concentration from published vapour pressure data, and the results are in close agreement with observation:

Concentration (grams per litre)	180	300	420	540
Observed osmotic pressure (atmospheres)	14·6	26·8	44·0	67·5
Calculated osmotic pressure (atmospheres)	14·1	26·8	43·7	67·6

Hence it is inferred that **osmotic equilibrium depends upon the equality of the vapour pressure of the solution and of the pure solvent.**

The semipermeable membrane has been styled a *vapour sieve*, and likened to a partition pierced by a large number of minute capillary tubes. Suppose that the capillary tubes are not wetted by either the solvent or solution, then neither the liquid solvent nor the solution can enter the capillaries—unless the pressure on one of the liquids exceeds 100 atmospheres—although vapour can diffuse through the capillary tubes. But the vapour pressure of the solution on one side of one of the capillary tubes is less than the vapour pressure of the solvent on the other side; consequently, vapour will pass through the capillary and distil from the solvent to the solution. Hence the volume of the solution will increase, and if the solution be confined in a closed vessel, the pressure must rise and continue rising until the vapour pressure of the solvent and solute are the same. This increase is the so-called osmotic pressure of the solution.

The agreement of this expression for dilute solutions with observation does not necessarily mean that the molecules of the solute can move independently of the solvent. It is difficult to believe that the molecules of solute and solvent are independent of one another, and J. Larmor (1897) assumed that each molecule of the solute forms for itself a nidus in the solvent; that is, it sensibly influences the molecules around it up to a certain minute distance so as to form a loosely connected complex in the sense, not of chemical union, but of *physical* influence; and, if the solution be dilute, each such complex is very much the greater part of its time out of the range of influence of other complexes, an application of the principles of thermodynamics then necessitating the osmotic laws. J. H. Poynting (1896)[4] has shown that the very same expression can actually be obtained by the assumption that the molecules of the solute enter into some sort of chemical combination with the solvent. Evaporation occurs when the molecules pass through the surface of the solution with a sufficient velocity to overcome the attractions of the neighbouring molecules, and if the molecules of the non-volatile solute are each loaded with molecules of the solvent, the complexes will not pass out of the solution, and the surface of the solution may be likened to a semipermeable membrane as regards solute and solvent; accordingly, the evaporation of a solution must proceed more slowly than with the pure solvent. The complex hydrates, however, are supposed to be always as effective as the solvent molecules in entangling the particles which impinge on the surface, and accordingly condensation proceeds more rapidly than evaporation until equilibrium is established. Hence, both evaporation and condensation proceed more slowly with the solution than with the solvent. A similar state of things is supposed to prevail at the surface of a semipermeable membrane, but owing to the rigidity of the latter, the excess of " condensation " over " evaporation " gives rise to a hydrostatic pressure on the solution side which is a measure of the osmotic pressure. T. M. Lowry (1897) has shown that it is not necessary to assume, with J. H. Poynting, that the molecules of the solute are hydrated, and he shows that in virtue of the mere presence of the molecules of the solute in the surface layer of the solution, evaporation must be retarded; a molecule of the solvent rising from the interior of the solution may strike a molecule of the solute in the surface layer and rebound back into the liquid without passing through the surface into the region of the vapour; condensation is more rapid because it will proceed as if no solute were present. While T. M. Lowry's hypothesis gives a similar relation between vapour pressure as that previously obtained, J. H. Poynting's hypothesis requires that if the molecules of the solute are mono-hydrated the osmotic pressure will be doubled; etc.

Surface tension hypotheses.—M. l'Hermite (1855), S. L. Bigelow (1907), I. Traube (1904), G. Jäger (1891), and B. Moore (1894)[5] tried to explain osmotic phenomena as a result of the different surface tensions of the two liquids—solution and solvent. Let T and T_s denote the respective surface tensions of the two liquids A and B contained in vessels connected by a capillary tube of radius r so that the liquids meet in the capillary. If T be greater than T_s the skin of liquid at the surface of contact with the wall of the capillary tube will move in the direction of A with a force equivalent to $(T-T_s)2\pi r$. If the radius of the capillary be small enough to bring all the contained liquid within the range of the capillary force—as is probably the case with ordinary osmotic membranes—the whole body of liquid in the tube will be driven in the direction of A. Hence, osmosis should proceed from the region of the less to that of the greater surface tension. Hence, (1) the surface tensions of solutions obeying the other solution laws should be greater than those of the pure solvents; and (2) the surface tensions of solutions of a given substance in a given solvent should be proportional to the concentrations. I. Traube (1904) compared hundreds of measurements of surface and osmotic effects, and found one and all in agreement with the hypothesis that the motive force of osmotic phenomena is determined by a difference in the surface tensions of solution and solvent. A. Battelli and A. Stefanini (1906) showed that aqueous solutions of salicine (or of ethyl alcohol) have a less surface tension than water, and yet osmosis takes place in the direction of the solution. Hence, they, like I. Traube, ascribe osmotic phenomena to differences in the surface tensions of the liquids on the two sides of the membrane; but, unlike B. Moore and I. Traube, they consider that osmosis proceeds in the direction which lends itself best to an equalization of surface tensions. If the membrane be permeable to but one liquid, it alone will pass through; but if permeable to both, osmosis will proceed in both directions until the surface tensions are equalized. If the passage of n molecules of water will increase the surface tension of a given mass of alcohol less than the passage of n molecules of alcohol would decrease the surface tension of water, water will flow to the alcohol more rapidly than alcohol will flow to the water. Solutions with the same surface tensions have the same osmotic pressure independent of their concentration. For instance, a 1·78 per cent. solution of magnesium sulphate, and a 1·11 per cent. solution of sodium sulphate have the same surface tension, and they produce no difference in osmotic pressure when placed on each side of an osmotic cell. In conclusion, no one has yet succeeded in giving an adequate account of osmotic pressure, but that facts seem to indicate that osmotic pressure and surface tension are related in some way so that the two phenomena exhibit in many cases an interesting parallelism.

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§ 12. The Relation between the Boiling Point of a Solution and the Molecular Weight of the Solute

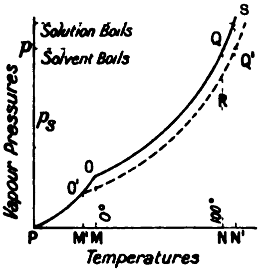

FIG. 23.—Diagrammatic.

In Fig. 23 the curve *PO* represents the vapour pressure of the solid, and *OQ* the vapour pressure of the pure liquid. The two curves intersect at the freezing point *O*. Let *Q*, Fig. 23, represent the boiling point of the solvent at 760 mm. pressure, then since the vapour pressure of a solution is less than the vapour pressure of the pure solvent, let *O'Q'* represent the vapour pressure curve of a given solution. Then *PM* will represent the freezing point of the solvent, and *PM'* the freezing point of the solution. Since *PM'* is less than *PM*, the freezing point of the solution will be less than the freezing point of the solvent ; and since *PN'* represents the boiling point of the solution and *PN* the boiling point of the solvent, the boiling point of the solution must be greater than the boiling point of the pure solvent. This agrees with experiment. For instance, with solutions of potassium iodide in 100 grams of water, G. T. Gerlach (1887)[1] found :

Boiling point . .	100°	101°	102°	103°	104°	105°
Potassium iodide .	0	15	30	45	60	74 grams.

If the solutions are very strong the relation is not quite the same, but **the raising of the boiling point of a dilute solution is directly proportional to the weight of the dissolved substance in a given weight of solvent.** Double the concentration of the solution, and the elevation of the boiling point will be doubled. An equal number of molecules of the dissolved substance in the same quantity of a solvent give the same elevation of the boiling point—F. M. Raoult (1886).[2] Hence **the rise in the boiling point of a solvent is proportional to the number of**

molecules of the dissolved substance in solution, and inversely proportional to the molecular weight of the solute.

In Fig. 23, QN and RN represent the respective vapour pressures of solvent and solution at the boiling point PN of the pure solvent; QS and RQ' represent the vapour pressure curves as the temperature rises; QQ' is parallel to the temperature axis, and represents the rise in the boiling point $NN'dT$. The solution is supposed to be dilute, and therefore there will be no sensible error if the curves be taken close together and parallel. Then $QQ'=QQ'.QS/Q'S$; or $dT=QR(Q'S/QQ')$; but $Q'R=p-p_s$; and $Q'S/QQ'=dp/dT$. Consequently, $dT=(p-p_s)dp/dT$. From Clapeyron's equation, neglecting v_2 for small differences of temperature, and putting the vapour density $D=1/v_1$ per unit mass of substance,. it follows that $dp/dT=\lambda D/T$; and from $p-p_s=PD/s$, where s denotes the specific gravity of dilute solution or solvent, and P denotes the osmotic pressure of the solution. Hence, $dT=PT/\lambda s$, where λ represents the latent heat of vaporization of the solvent. This expression shows that *the osmotic pressure is directly proportional to the rise of the boiling point.* Since P denotes the osmotic pressure of the solution containing one gram-molecule of solute in a volume V, it follows that $PV=RT$, and if the same volume of solution has n gram-molecules of the solute $PV=nRT$, or $P=nRT/V$; if the solution, of specific gravity s, contains N gram-molecules each of molecular weight M, it follows that $V=NM/s$. Remembering that R is nearly equivalent to 2 cals., substituting in $dT=PT/\lambda s$ for the values of P and V just determined; and reducing to its lowest terms, $dT=2nT^2/NM\lambda$; or, $dT=(n/N)(2T^2/M\lambda)$. As previously indicated, if $n=w/m$, and $N=100/M$, it follows that $dT=(w/m)(0{\cdot}02T^2/\lambda)$.

Let the symbol k stand for the so-called boiling constant; then, since, for any given solvent, T and λ are physical constants, the

$$\text{Boiling constant, } k=\frac{0{\cdot}02T^2}{\lambda}$$

and m, the molecular weight of the vapour of the solute, becomes $m=kw/b$, where b, the raising of the boiling point, has been put in place of dT. The meaning of k is obtained by assuming that one gram-molecule (w/m) of the solute—say 342 grams of cane sugar, $C_{12}H_{22}O_{11}$—is dissolved in 100 grams of the solvent, then $k=b$, and therefore k represents the elevation of the boiling point produced by dissolving one gram-molecule of a substance in 100 grams of solvent; k is called the **boiling constant**, or *the molecular elevation of the boiling point.* E. Beckmann and O. Liesche [3] have shown a number of other ways of computing the boiling constant; thus $100k=mp(dT/dp)$; $k=0{\cdot}0096MT$; $k=0{\cdot}0011089T^2/a^2$; $k=0{\cdot}004343MT(1-T/T_c)\div\log(P_c/p)$, when dT/dp represent the rise dT in the boiling point for a change dp in the vapour pressure; a^2 denotes P. Walden's specific cohesion of the solvent at the boiling point; and T_c and p_c respectively denote the critical temperature and pressure of the solvent.

EXAMPLE.—What is the molecular elevation of the boiling point of water boiling at 100°, when its latent heat of vaporization is 537 cals? Here $T=100+273$; and $k=0{\cdot}02\times(373)^2\div537=5{\cdot}18$, which is very near the observed value 5·2.

Each solvent has its own specific boiling constant: *e.g.* acetone, 16·7; benzene, 26·7; ether, 21·6; carbon disulphide, 23·5; ethyl alcohol, 11·5; chloroform. 35·6; pyridine, 30·1; etc. The boiling constant is determined by finding the boiling point of, say, water and of aqueous solutions containing 0·02, 0·06, 0·10 gram-molecules of cane sugar, and calculating the results per 342 grams of cane sugar. Suppose that w grams of a substance dissolved in 100 grams of water raised the boiling point of the water b°. Then, if M be used to denote the molecular weight of the substance, we have the proportion $w : M=b : 5$, or, for substance dissolved in water:

$$\text{Molecular weight}=5{\cdot}2\frac{w}{b} \quad . \quad . \quad . \quad . \quad (3)$$

This enables the molecular weight of many substances to be determined from their effect on the boiling point of water. The particular solvent to be used depends on the solubility of the substance under investigation. If ether is used in place of water, 5·2 must be altered to 21·6, etc. In no case must a solvent be employed which reacts chemically with the substance under examination.

EXAMPLES.—(1) E. Beckmann (1890) found that 2·0579 grams of iodine dissolved in 30·14 grams of ether raised the boiling point of the ether 0·566°. What is the molecular weight of iodine? Here, 2·0579 grams of iodine in 30·14 grams of ether correspond with $100 \times 2{\cdot}0579 \div 30{\cdot}14 = w = 6{\cdot}8278$ grams of iodine in 100 grams of the solvent. Hence, $M = 21{\cdot}6 \times 6{\cdot}8278 \div 0{\cdot}566 = 254{\cdot}6$. This corresponds with the formula I_2 when iodine has a molecular weight of 253·84. The numbers seldom, if ever, coincide, but there can be no mistake in the significance of the figures.

(2) E. Beckmann (1890) found that a solution of 1·4475 gram of phosphorus in 54·65 grams of carbon disulphide raised the boiling point 0·486°. What is the molecular weight of the phosphorus? Answer: Molecular weight, 129·16. The atomic weight of phosphorus is 31, hence the molecule of phosphorus is represented: P_4.

(3) A. Helff (1893) found that 0·2096 gram of sulphur in 17·79 grams of carbon disulphide raised the boiling point 0·107°. Hence show that the molecular weight of sulphur is probably S_8. Here $w = 1{\cdot}17$; and the molecular weight is 259. This is close to the theoretical value 256 for S_8.

(4) A solution of 3·164 grams of cupric chloride in 100 grams of alcohol raised the boiling point 0·308°. The boiling constant of alcohol is 11·5, what is the molecular weight of the solute? Answer: 134·5.

(5) L. Marchlewsky and J. Sachs (1892) analyzed Roussin's salt and found it to contain 38·29 per cent. of iron; 16·54 of sulphur; 16·70 of nitrogen; and 6·54 per cent. of water. When 0·1826 gram of the salt was dissolved in ether, the boiling point was raised 0·012°. Show that this agrees with the recognized formula of the salt: $Fe_4(NO)_7S_3K.H_2O$.

E. Beckmann's process for the determination of boiling points (1888–96).—This method of determining molecular weights has been much employed by F. M. Raoult, E. Beckmann, H. C. Jones, and many others.[4] The process is applicable only to solutes which do not give off an appreciable amount of vapour at the boiling point of the solution. The so-called Beckmann's thermometer has contributed largely to the successful application of the method. The modern forms of this instrument are sensitive to 0·001°. Great precautions must be taken to measure the temperatures accurately since a small error in the temperature readings has a large influence on the computed result.

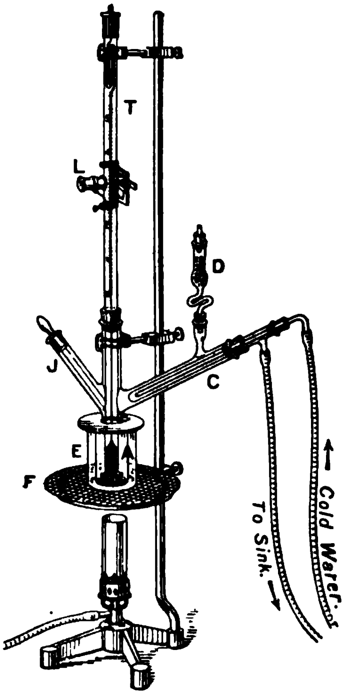

FIG. 24.—Beckmann's Apparatus for Boiling-point Determinations.

The apparatus consists of a glass boiling tube *A*, Fig. 24, with a piece of platinum wire sealed in the bottom, and packed with beads to prevent irregular boiling. A side tube with a condenser, *C*, liquefies the vapour given off during the boiling; and the exposed end of the condenser is closed with a calcium chloride tube, *D*. The boiling tube is surrounded by a jacket of some non-conducting material, *E*, to prevent the radiation of heat. The boiling tube is fitted with Beckmann's thermometer, *T*, which can be read to $\frac{1}{1000}$ of a degree, and set so that the mercury is about halfway up the stem when the solvent is boiling. Beckmann's thermometer has a reservoir of mercury at the top so that it can be set for use at any desired temperature. As indicated in text-books of laboratory processes, this avoids an inconveniently long, or an inconveniently large number of thermometers. The thermometer is always tapped before a reading to make sure the mercury is not lagging behind. The lens *L* facilitates the reading of the thermometer. The barometer should be read to make sure no appreciable change occurs during a determination.

The boiling tube has a stoppered side tube, *J*, for introducing the solutions under investigation. The whole is clamped to a stand and rests on an asbestos tray, *F*. The boiling point of the solvent is first determined. The boiling tube is weighed. The solvent is introduced and its boiling point determined when the boiling is brisk and vigorous. A known weight of the substance is then introduced, and the boiling point of the solution determined. A correction is made by subtracting 0·2 to 0·4 gram from the weight of the solvent in order to allow for the solvent condensed on to the walls of the apparatus and the condenser. The actual correction depends upon the nature of the solvent and the particular form of the apparatus used. The difficulty with this apparatus is to avoid fluctuations of temperature in the boiling tube due to the radiation of heat; dripping of the cold liquid from the condenser into the boiling solution, etc. Many other forms of apparatus for this determination have been devised.

W. Landsberger's method for the determination of boiling points (1898).—When the solution of a non-volatile solute boils, the vapour of the solvent and solution are in equilibrium, and this condition can be established by leading the vapour of the boiling solvent into the solution. When the solution is boiling, the vapour will pass through the system without condensation; if the solution is below this temperature some vapour will condense, and the latent heat of condensation will continue heating the solution until the boiling point is reached. There is virtually no danger of superheating the solution. This method of determining the boiling point of a solution has been employed with some success in molecular weight determinations.[5]

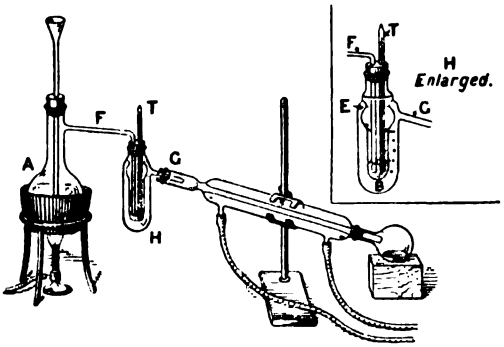

FIG. 25.—Landsberger's Apparatus for Boiling Determinations.

In W. Landsberger's apparatus, a modification of which is shown in Fig. 25, the solvent is boiled in the flask *A*, and the vapour passed into the solution *viâ* the tube *F*. The temperature of the solution is raised to its boiling point by the latent heat of condensation of the vapour of the solvent. The vapour of the solvent passes to the condenser *G* through *E* around the boiling tube, and thus the inner tube is jacketed with the vapour of the boiling solvent. This reduces radiation losses. The boiling point of the solvent is first determined, and a weighed amount of the solute is introduced into the inner tube *B*, which is graduated so that the boiling can be interrupted for a moment before more solute is added, and the volume of the solution read at a glance.

With this apparatus, **the boiling constant** for water is nearly 5·4; allowing for this, and using the preceding notation, with water as a solvent,

$$\text{Molecular weight} = 5{\cdot}4\,\frac{w}{b} \quad . \quad . \quad . \quad . \quad (4)$$

where *w* denotes the weight of the substance per 100 c.c. of the solvent, and *b* represents the elevation of the boiling point. If other solvents be used 5·4 is altered thus: for acetone (sp. gr. 1·827), 22·2; benzene (sp. gr. 0·879), 32·8; ether (sp. gr. 0·736), 30·3; carbon disulphide (sp. gr. 2·63), 26; ethyl alcohol (sp. gr. 0·80), 15·6; chloroform (sp. gr. 1·526), 26·0; aniline (sp. gr. 1·022), 38·2. If the boiling tube be weighed so that the amount of solvent is determined by weight, and not by volume, the original formula is used.

EXAMPLES.—(1) 0·8686 grm. of boric acid with 7·73 c.c. of water raised the boiling point 0·917°. What is the molecular weight of boric acid? Ansr.: 63·7. Theory for $B(OH)_3$ is 62. Show that this result is concordant with an elevation of the boiling point of 0·262° when 33·4 c.c. of water contains 1·015 grms. of the acid in question.

(2) W. Landsberger (1898) found that 0·4929 grm. of cadmium iodide with 7·30 grms. of ethyl alcohol gave a rise of 0·218° in the boiling point of the solvent. Show that this is in harmony with the theoretical molecular weight of 366 for CdI_2. The value computed from the observed data is 356.

Correction for the volatility of the solute.—The formula (3), for calculating the molecular weight of a solute from its effect on the boiling point of the solvent, is valid only when the solute does not volatilize. If the solute volatilizes along with the solvent, this formula must be replaced by

$$\text{Molecular weight}=5{\cdot}4\frac{w-w_1}{b}\text{ ; or, Molecular weight}=k(1-a)\frac{w}{b} \quad . \quad (5)$$

where w represents the number of grams of the solute in 100 grms. of the solvent, and w_1 the number of grams of the solute per 100 grms. of the vapour, and its value is obtained from the mean value of the concentration of the solute in 100 grms. of the distillate when the solution is distilled; and a represents the ratio of the concentrations of the volatile solute in the vapour and in the solution; k is the boiling constant—for water, $k=5{\cdot}4$.

EXAMPLE.—Compare the molecular weights of iodine in carbon tetrachloride and in benzene when it is found that 8·498 grms. of the distillate from iodine in carbon tetrachloride contained 0·168 grm. of iodine per 8·330 grms. of the solvent; the initial and end concentrations of the boiling solutions were 4·507 and 6·592 respectively; 0·722 grm. of iodine in 30·2 grms. of the same solvent raised the boiling point 0·315°; and the boiling constant for this solvent is 48·8. Similarly, for the solvent benzene, $a=0{\cdot}144$; boiling constant $k=25{\cdot}7$; and 1·195 grms. of iodine in 22·3 grms. of the solvent raised the boiling point 0·467°. For carbon tetrachloride, w is the mean value of 4·507, 6·592, and 5·550; w_1 is $100\times0{\cdot}168\div8{\cdot}330=2{\cdot}107$; and a is $2{\cdot}107\div5{\cdot}550=0{\cdot}36$. Again, the solution used for measuring the effect of iodine on the rise of the boiling point of carbon tetrachloride, $w=0{\cdot}722\times100\div30{\cdot}2=2{\cdot}391$, and $w/b\times48{\cdot}8=2{\cdot}391\times49{\cdot}8\div0{\cdot}315=370$. The uncorrected molecular weight of the iodine in boiling carbon tetrachloride is 370, and when corrected for the volatility of the iodine it is $370(1-a)=370\times0{\cdot}66=244$. Similarly, the uncorrected molecular weight of iodine in boiling benzene is 294, and the corrected value 252.

In the laboratory, advantage is taken of the fact that the boiling point of a solution is higher than the boiling point of the solvent to get liquids for baths, etc., boiling a few degrees higher than water, by using salt solutions in place of water. For example, a saturated solution of sodium nitrate boils at 120°, and a saturated solution of sodium chloride at about 108°.

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§ 13. The Relation between the Freezing Point of a Solution and the Molecular Weight of the Solute

F. M. Raoult's method for determining the molecular weight of a substance is the most significant contribution to the list of physical processes applicable to chemical investigations since the discovery of the law of Dulong and Petit.—V. MEYER (1888).

Similar remarks apply *mutatis mutandis* to the freezing point of solutions as were made with reference to the boiling point. A study of Fig. 23 will show that if the vapour pressure of a solution is less than that of the pure solvent, the vapour pressure curve will cut the ice curve at a temperature below the freezing point of the pure solvent. This means that the freezing point of a given solution will be lower than the freezing point of the pure solvent, and experiment shows that the lowering of the freezing point will be proportional to the weight of the substance dissolved in a given weight of the solvent. This reminds us of C. Blagden's discovery (1788) that the depression in the freezing point of a solvent produced by the addition of a salt is directly proportional to the concentration of the solution; in 1861 F. Rüdorff rediscovered the law and explained certain deviations he observed by assuming that hydrates were formed; and in 1871, L. C. de Coppet found that if the quantity of salts dissolved is proportional to the molecular weight, salts of analogous constitution produced the same depression. Experiments show that an equal number of gram-molecules of different substances in the same solvent depress the freezing point to the same extent—F. M. Raoult's law (1883–84).[1] **The depression in the freezing point is proportional to the weight of the dissolved substance in a given weight of the solvent; and inversely proportional to the molecular weight of the dissolved substance.** The same law was deduced from thermodynamics by J. H. van't Hoff in 1886.[2] Solutions of sugar (342 grms.), methyl alcohol (32·03 grms.), etc., in 100 grms. of water depress the freezing point 18·5°. This is the **freezing constant** for water; Raoult called it the molecular depression of the freezing point per 100 grms. of solvent, and its numerical value for each solvent can be derived precisely like the boiling constant by substituting the latent heat of fusion for λ in place of latent heat of vaporization.

$$\text{Freezing constant } (k)=\frac{0{\cdot}02T^2}{\lambda}$$

EXAMPLES.—(1) The latent heat of fusion of water is 79 cals; hence $T=273$, and $\lambda=79$, and k is 18·9; the observed value is 18·5 (F. M. Raoult).

(2) The observed value for the freezing constant of acetic acid is 39; show that this deviates from the theoretical value by about 2 per cent. when the latent heat of fusion is 43·66 cals. The computed value is 38·2.

(3) The freezing constant or molecular lowering of the freezing point of sulphur which freezes at 119·25°, and has a latent heat of fusion 9·368, is $0{\cdot}02\times(392{\cdot}25)^2\div9{\cdot}368=328$.

Each solvent has its own specific freezing constant; *e.g.* acetic acid, 38·88°; benzene, 49°; mercury, 425°; naphthalene, 69°; phenol, 74°; etc. If *w* grms. of a substance, molecular weight *M*, dissolved in 100 grms. of solvent, lowers the freezing point $f°$, we have the proportion $w:M=f:18{\cdot}5$ for water; or, for substances dissolved in water,

$$\text{Molecular weight}=18{\cdot}5\frac{w}{f} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This enables the molecular weight of a substance to be computed from its effect on the freezing point of water. The particular solvent to be selected is of course determined by the solubility of the substance under investigation, and the number 18·5 must be replaced by another if a different solvent be used. In no case must a solvent be chosen which can enter into chemical union with the substance to be examined.

EXAMPLES.—(1) W. Tammann (1889) found that a solution of 0·022 grm. of sodium in 100 grms. of mercury lowered the freezing point of mercury 0·39°. What is the molecular weight of sodium? Here, $M=425\times0{\cdot}022\div0{\cdot}39=23{\cdot}8$. Hence the atomic and molecular weights are the same.

(2) W. R. Orndorff and J. White (1893) found that a solution of 0·2735 grm. of hydrogen peroxide in 19·86 grms. of water lowered the freezing point of water 0·746°. What is the molecular weight of hydrogen peroxide? Here $w=100\times0{\cdot}2735\div19{\cdot}86=1{\cdot}3773$; $f=0{\cdot}746$; hence, $M=34{\cdot}2$. This corresponds with the molecule H_2O_2. An earlier determination by W. Tammann (1899) gave H_4O_4, but this was afterwards found to be due to the use of an impure sample.

(3) J. Hertz (1890) found that 2·423 grms. of sulphur in 100 grms. of naphthalene lowered the freezing point of naphthalene 0·641°; hence show that the molecular weight

of sulphur under these conditions corresponds with the formula : S_8. Ansr. : The molecular weight by experiment is 262, and by calculation for S_8, 256.

(4) G. Buchbock (1897) found that a solution of 21·740 grms. of ethyl ferrocyanide in a litre of water lowered the freezing point 0·1270°; show that this corresponds with the formula $(C_2H_5)_4FeCy_6$. The theoretical molecular weight is 328, observed 323.

(5) J. L. R. Morgan and H. K. Benson (1907) find that 0·292 grm. of potassium chloride dissolved in 100 grms. of molten calcium chloride, $CaCl_2.6H_2O$, as solvent depressed the freezing point 0·181°. The freezing constant of $CaCl_2.6H_2O$ is 45·0. Hence show that these observations agree with the formula KCl.

(6) G. Marchetti (1899) found that an aqueous solution of 1·703 grms. of a hydrated molybdenum oxide in 100 grms. of water lowered the freezing point 0·072°. An analysis of the compound gave 56·9 per cent. of molybdenum. Show that these results agree with the formula $Mo_3O_8.5H_2O$.

E. Beckmann's process for the determination of freezing points.—Applications of the freezing process for the determination of molecular weights present no particular difficulty. Several different forms of apparatus have been devised by investigators who have followed Raoult, but no apparatus has proved so useful as the later forms of E. Beckmann's. Precautions have to be taken against undercooling. Satisfactory results too are only obtained with those solvents which do not separate out with the solute in form of solid solutions.

Freezing-point determinations are usually made in Beckmann's apparatus.[3] The tube *A*, Fig. 26, with a side neck, *B*, is weighed, and about 15 c.c. of the solvent are added, and the tube is weighed again. Beckmann's thermometer, reading to the 0·01° of a degree. It is set so that the mercury is near the top of the scale at the freezing point of the solvent, and it is provided with a reading lens. The thermometer *T* and a stirrer *S* are placed in the solvent, and the whole arrangement is placed in a glass tube *A*, which serves as an air jacket. This is surrounded by a vessel *D* of water or some liquid at a temperature about 5° below the freezing point of the solvent. This vessel is fitted with a thermometer T_1 and stirrer S_1. The temperature recorded by the thermometer slowly falls until the solvent begins to freeze ; it usually falls from 0·2° to 0·3° below the freezing point of the solvent, and then begins to rise to the freezing point proper. The thermometer should always be tapped before a reading is taken to make sure the mercury is not lagging behind. The highest point reached by the mercury in the thermometer is taken to be the freezing point of the solvent. Owing to undercooling, it is sometimes difficult to start the freezing of the solution. In that case, a few pieces of platinum foil, or a minute fragment of the frozen solvent, will start the freezing. It is sometimes necessary to introduce a correction for undercooling as indicated in text-books for the laboratory. Each determination should be repeated two or three times and the successive observations should agree within 0·002° to 0·003°. When the freezing point of the solvent has been determined, add a sufficient amount of the substance under investigation to give a depression of 0·3 to 0·5°. After the freezing point has been determined again, find the freezing point after adding a second and then a third portion of the substance under investigation.

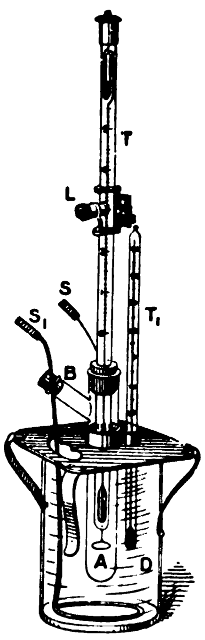

Fig. 26. — Beckmann's Apparatus for Freezing-point Determinations.

The molecular weights of volatile substances relative to the weights of the hydrogen molecule have been determined from the vapour density determinations and Avogadro's hypothesis. The osmotic pressure and related properties of solutions enable the molecular weights of *liquids* and *solids* in solution to be determined. There is an extensive choice of solvents, and it is possible to utilize such widely different substances as stearic acid, mercury, ether, fused metals, etc. Molten salts containing water of crystallization may be used—*e.g.* sodium sulphate, $Na_2SO_4.10H_2O$; calcium chloride, $CaCl_2.6H_2O$; lithium nitrate, $LiNO_3.3H_2O$; sodium chromate, $Na_4CrO_4.10H_2O$; etc.—the results agree with those obtained with other solvents. The molecular weights of a great many substances in solution are in agreement with those furnished by the vapour density method, yet there are some irregularities. F. M. Raoult found that the molecular weights of substances in solutions are sometimes greater and sometimes less than what we should expect. Organic substances, like cane sugar and alcohol in aqueous solution, gave normal values for their molecular weights, while inorganic salts like potassium and sodium chlorides gave about half the values which correspond with their normal formulæ. The results are then said to be abnormal. F. M. Raoult first assumed that organic substances must form double molecules in solution, while inorganic salts are normal. He then tried if extreme dilution would break down the supposed doubled molecules, but the experiments returned a negative answer.

The **relation between the osmotic pressure and the rise in the boiling point or depression of the freezing point.**—From the Clapeyron-Clausius equation, $\log p - \log p_s = (M\lambda/R)(dT/TT_s)$, where dT is put in place of $T_s - T$; and T denotes the temperature at which the vapour pressure is p, and T_s a slightly higher temperature where the vapour pressure is p_s. Since it has been shown that $(p-p_s)/p$ is an approximation for $\log p - \log p_s$, and $(M\lambda/R)(dT/TT_s)$ can be substituted for $(p-p_s)/p$ in equation (1), the result reduces to the relation $P = s\lambda dT/T$, which shows the relation between the osmotic pressure P and the rise dT in the boiling point. A similar relation between the depression dT of the freezing point and the osmotic pressure obtains if λ denotes the heat of fusion of the solvent in place of the heat of vaporization. The simpler form obtained by G. M. Lewis (1908),[4] $P = 12{\cdot}06f - 0{\cdot}21f^2$ atm., gives the osmotic pressure of a solution which lowers the freezing point f°.

EXAMPLE.—If an aqueous solution contains enough solute to raise the boiling point 1°, show that the osmotic pressure is nearly 47 atmospheres, $dT = 1$; $T = 373$; $s = 0{\cdot}96$; and $\lambda = 537$ cals.

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§ 14. The Relation between the Solvent Power of a Solvent and the Molecular Weight of the Solute

The capacity of a pure solvent A to dissolve another liquid B is reduced when another substance C is dissolved in B. For instance, an ethereal solution of naphthalene (C) dissolves less water (B) than does pure ether (A). In following out the analogy between vaporization and solution, W. Nernst (1890)[1] argued that whatever depresses the vapour pressure of A should also depress the solubility of A. The relative lowering of the vapour pressure of A is proportional to the number of gram-molecules of non-volatile solute C in A, so the relative lowering of the solubility of B and A should also be proportional to the number of gram-molecules of the solute C in A when the solute C is not soluble in B. Let S denote the solubility of the liquid B in the pure solvent A; and S_s the solubility of the liquid B in the solution of C in A; the lowering of the solvent power of A is $S - S_s$, then, by analogy with the vapour pressure formula:

$$\frac{p-p_s}{p}=\frac{n}{N}, \quad \frac{S-S_s}{S}=\frac{n}{N}$$

where n denotes the number of gram-molecules of the solute C in N gram-molecules of the solvent A. If w grms. of C are dissolved in A, $n = w/m$, where m denotes the molecular weight of C. Then, $(S-S_s)m/w=S/N$; and since S/N is a constant, say k, whose numerical value can be determined experimentally for a particular temperature and amount of solvent, then, if S' denotes the lowering of the solubility $S-S_s$,

$$\text{Molecular weight}=k\frac{m}{S'} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Experimental details for the application of the principle were worked out by S. Tollaczko (1895) for substances soluble in ether, and insoluble in water. The accuracy of the process does not appear to be very great even though the temperature be maintained constant for all the readings.

Example.—The constant k was found to be 536, and 0·1266 grm. of naphthalene depressed the solubility of water in ether about 0·55; accordingly, the molecular weight of naphthalene is $536 \times 0{\cdot}1266 \div 0{\cdot}55 = 123$—the theoretical value for $C_{10}H_8$ is 128.

If there is an appreciable change in the volume of the solvent on addition of the solute, a correction factor v/v_s is required—v represents the initial volume of the solvent and v_s its volume after the addition of the solute.

The **relation between osmotic pressure and the lowering of the solvent power of a solvent.**—By analogy with formula (3), above, the osmotic pressure P is related with the relative lowering of the solvent power of the solvent by

$$P=\frac{S-S_s}{S}\cdot\frac{sRT}{M}$$

The connection between the osmotic pressure and the colligative properties of a solution—the lowering of the vapour pressure, of the freezing point, and of the solvent power of a solvent, and the raising of the boiling point—has thus been established. Consequently, results obtained by these different methods cannot be regarded as independent evidence supporting any particular hypothesis, for the different processes are simply different ways of measuring one quantity, and they must necessarily lead to similar conclusions. The different methods are distinguished from one another by the degree of accuracy which can be obtained in the application of a particular process ; by convenience in the theoretical (mathematical) treatment ; and by the range of temperature over which they are applicable.

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§ 15. Anomalous or Abnormal Results for the Molecular Weights of Substances in Solution

We never profit more than by those unexpected results of experiments which contradict our theories and analogies.—Guyton de Morveau.

I thank God that I was not made a dexterous manipulator, for the most important of my discoveries have been suggested to me by failures.—Humphry Davy.

The analogy between gases and solutes in dilute solution has been pursued further. If the molecules of a dissolved substance are in a similar state to what they would be if the substance were in the gaseous condition, the relation between the pressure, temperature, and concentration will be represented by the expression, $PV=iRT$; or, since the concentration C is inversely as the volume, by $P/C=iRT$. As before, if i be unity, the molecules of the substance in solution and in the gaseous condition are presumably similar ; if i be greater than unity, the analogy with similar phenomena with gases $pv=iRT$, has led to the assumption that the molecules dissociate when they pass into solution ; and if i be less than unity, the molecules polymerize. If we apply the uncorrected relation, $P/C=RT$, it is now easy to see that if i be greater than unity (dissociation), the osmotic pressure will appear too high; and if i be less than unity (polymerization), the osmotic pressure will appear too low. When we speak of the lowering of the osmotic pressure, we also imply that the vapour pressure is increased, the boiling point is lowered, and the freezing point raised; and conversely, the raising of the osmotic pressure implies that the boiling point is raised, and the vapour pressure and freezing point are lowered.

EXAMPLES.—(1) F. Vogel (1903) found that the lowering of the freezing point of a 2N-solution of barium nitrate, $Ba(NO_2)_2$, was 3·931°, and of a 0·2N-solution, 0·479°. The specific gravity of the former solution at 21° was 1·1604, and of the latter 1·0017. Calculate the value of $i=M$ (theoretical)/M_1 (observed) for each solution. Here 50 c.c. of the 2N-solution contains 11·4740 grms. of barium nitrate and 46·5456 grms. of water; and the 2*N*-solution, 1·1474 grms. of barium nitrate and 48·9358 grms. of water. The computed molecular weights of the salt in the two solutions are respectively 97·4016 and 99·7581, the theoretical value for both solutions is 229·14, hence, $i=2·54$ for the 2N-solution, and 2·48 for the 0·2N-solution.

(2) Which is the more probable equation for the action of a potassium hydroxide solution on aluminium hydroxide: $KOH+Al(OH)_3=Al(OH)_2OK+H_2O$, or $2KOH+Al_2(OH)_6=Al_2(OH)_4(OK)_2+2H_2O$, when the freezing point of solutions of potassium hydroxide are not changed by the addition of aluminium hydroxide? C. L. Speyers (1898). The former, because one molecule of aluminate is produced per molecule of potassium hydroxide, etc.

Again, from the argument based upon Fig. 23, it follows that the osmotic pressure P is to the lowering of the vapour pressure $p-p_s$ of the solvent and solution as the density s of the solution is to the density D of the vapour; or $P:p-p_s=s:D$; and since $p-p_s=pn/N$, and $p=DRT/M$, where M represents the molecular weight of the vapour, the osmotic pressure,

$$P=\frac{n}{N}\cdot\frac{s}{M}RT$$

According to J. H. van't Hoff's relation, $P=nRT$, unit volume of all solutions, with n molecules of the solute, have the same osmotic pressure. If unit volume of a solution of specific gravity s has N molecules of the solvent of molecular weight M', then $NM'/s=1$, or $N=s/M'$; and hence,

$$P=nRT\times\frac{\text{Molecular weight of solvent}}{\text{Molecular weight of solute}};\text{ or, }P=\frac{M'}{M}nRT$$

which shows that van't Hoff's relation—$P=nRT$—is valid only when the molecular weight M' or the solvent is the same as that of the vapour, M.

Abnormally high osmotic pressures—dissociation of solute, or polymerization of the solvent.—The molecules of the liquid may be more complex than the molecules of the vapour, so that the molecular weight of the liquid molecules is $M'=aM$, where a, the so-called association factor, represents the number of normal molecules of molecular weight M which combine to form one molecule of the associated liquid. The observed osmotic pressure P_1 of a solution containing n gram-molecules of the solute in unit volume of the solvent, whose molecular weight is a times that of the vapour, will be a times the osmotic pressure P of a solution in which the solvent is not so associated, or $P_1=aP$. A very considerable number of aqueous solutions of acid, bases, and salts furnishes a much greater osmotic pressure than we should naturally expect. The deviation of a gas from Avogadro's law is usually explained by assuming that the molecules of the gas are dissociated into simpler forms. Iodine molecules, I_2, at high temperatures appear to behave as symbolized: $I_2=I+I$. S. Arrhenius (1887) sought to explain deviations of the molecular weights of salts, acids, and bases in aqueous solutions by assuming that the molecules are dissociated into simpler parts. The molecules of sodium chloride, for instance, are supposed to be dissociated in aqueous solutions into two parts—Na and Cl. The idea came as a surprise, and much opposition has been raised against this interpretation of the results, because there are no signs of chemical action which might be expected if the molecule of sodium chloride were dissociated into electrically charged Na+ and Cl— atoms on solution in water. Accordingly, other hypotheses have been invented to make the first hypothesis fit the facts. In spite of this, Arrhenius' hypothesis at once explains in a seductive and plausible manner the abnormally high osmotic pressures obtained for these substances. There is a strange coincidence. Arrhenius determined the value of *i*—the number of molecules in the above equations—for ninety different substances. He noticed at once that these substances could be roughly divided into two classes: those which gave values of *i* nearly unity were either non-conductors or poor conductors of electricity; whereas those which gave values of *i* materially greater than unity were fair or good conductors of electricity. In the following table is taken to represent, within the limits of experimental error, the relative number of molecules formed when one molecule of the substance is dissolved:—

TABLE VI.—NORMAL AND ABNORMAL OSMOTIC PRESSURES.

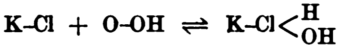
Non-conductors.		Conductors.	
Substances in solution.	*i*	Substances in solution.	*i*
Methyl alcohol	0·94	Calcium nitrate	2·48
Mannite	0·97	Magnesium sulphate	1·25
Cane sugar	1·00	Strontium chloride	2·69
Ethyl acetate	0·96	Potassium chloride	1·81
Acetamide	0·96	Lithium chloride	1·92

We naturally inquire: What connection, if any, subsists between the alleged dissociation of the molecules of a substance in a solution and the conduction of electricity? How can one molecule of sodium chloride, one molecule of lithium chloride, each furnish what appears to be two molecules when dissolved in water? Is this dissociation hypothesis the only possible explanation which covers all the facts?

Chemical theory of osmotic pressure.—The circumstantial evidence adduced to show that in liquid water at any given temperature, it is highly probable (i) that definite relation subsisting between polymerized and simple molecules; and that (ii) the presence of salts in solution displaces the equilibrium in favour of the simpler molecules. Hence, with some differences, J. J. van der Laar (1906)[1] and H. E. Armstrong (1902–6) argue that the osmotic pressure is not a result of a pressure produced by the molecules of the dissolved substance, but rather a secondary effect of the reduction in the concentration of the more complex water molecules by the dissolved substance which causes the pure solvent, say, water, to travel towards the water of the solution. Here, osmotic pressure is a consequence of the impulse of diffusion which continues until the concentration of the complex water molecules is the same on both sides of the separating membrane. A certain proportion of the complex molecules are supposed to be continuously resolvèd into simpler molecules as the pure solvent diffuses through the partition, and conversely, a certain proportion of the simple water molecules which diffuse from the solution side of the partition are polymerized on the pure solvent side. The addition of a non-electrolyte disturbs the equilibrium $(H_2O)_n \rightleftharpoons nH_2O$ in the direction $(H_2O)_n \rightarrow nH_2O$, and the resulting molecules of hydrone, H_2O, exert an attraction on similar molecules in the region of the pure solvent or more dilute solution, so that the solvent passes through the membrane to the solution until equilibrium is re-established. Osmotic pressure is then a measure of the disturbance of the equilibrium, $(H_2O)_n = nH_2O$, produced by the continuous depolymerization of the water molecules on the solution side of the partition, and a continuous polymerization of water molecules on the pure solvent side. The greater the difference in the concentration of the more complex water molecules on the two sides of the partition, the greater is the impulse of diffusion, and the greater the osmotic pressure. Electrolytes exert an attractive influence on the solvent, which is superposed on the effect produced by dissociated water complexes, so that solutions of electrolytes exert a greater osmotic pressure than solutions of non-electrolytes of equivalent molecular concentrations. H. E. Armstrong (1909) explains the selective action of the membrane in the following manner:

> The compounds which penetrate the membrane are all substances which attract water presumably only to a minor extent and which exist to some extent in solution in an unhydrated condition; those which cannot penetrate it, on the other hand, probably all form hydrates of considerable stability in solution. I picture surfaces generally, colloidal surfaces in particular, as not merely wetted by water, but as more or less hydronated and hydrolated, that is to say, they are not merely wetted by water complexes, but associated with hydrone, the simple fundamental molecule of which water is composed. The intra-molecular passages in a colloidal membrane, if thus hydrolated, would be guarded by the attracted hydrone molecules; and the hydrolated molecules in a solution which attempted to effect an entry through such passages, would be seized upon and held back in virtue of the attraction which two hydrolated surfaces—that of the membrane and that of the solute—would exercise upon one another. The hydrolated passages. however, would be indifferent to molecules which were not hydrolated—consequently such a substance as acetic acid, of which probably only a small proportion is present in solution in the hydrolated state, would gradually pass through them.

H. E. Armstrong further assumes that the reason non-electrolytes in equivalent concentration all exert the same osmotic pressure, while, in contradistinction, electrolytes exert an excessive pressure, turns on the assumed fact that non-electrolytes dissolve in water in the form of their fundamental molecules, which exerts no appreciable attractive action (affinity) on the water molecules; and that electrolytes have the power to attract water molecules in proportion to their efficiency as electrolytes. It is inferred that the process of solution implies a strong affinity of a chemical or quasi-chemical nature in order to break up the cohesion of the crystal. The molecules of a compound like mercuric chloride which dissolves in water with difficulty probably differ from the molecules of, say, calcium chloride in exerting but a slight attractive force on molecules of water, while the so-called ionized molecules are assumed to form complex reversible systems of solvent and solute, say:



$$\text{K-Cl} + \text{O-OH} \rightleftharpoons \text{K-Cl}<^{\text{H}}_{\text{OH}}$$

The observed osmotic effects are thus assumed to be an effect of two distinct forces: (1) the *depolymerization* of the complex water molecules; and (2) the *hydration* of the solute whereby the solvent is attracted towards the solute by the same forces which cause it to dissolve in the water. The function of the electric current is to break down such systems by drawing certain groups of atoms apart. As these systems are broken down by the current new ones spontaneously form in the solution. Molecules which exhibit no tendency to form such systems are virtually non-electrolytes. Thus, in the words of M. Faraday, "the inability of a system to suffer decomposition by electricity . . . may be dependent upon the absence of that mutual relation of the particles which is the cause of aggregation." J. Larmor has also shown that the osmotic laws deduced for dilute solutions by thermodynamics are the same, even supposing that a complex between solvent and solute is formed, provided that the solution is so dilute that each such complex is for very much the greater part of the time out of the sphere of influence of other complexes.

V. A. Vilde and A. J. Bogorodsky (1915)[2] explain the abnormal depression of the freezing point of aqueous solutions by assuming with A. Hantzsch (1907) that just as ammonia may attach itself to a hydrogen atom forming ammonium, NH_4, so can a molecule of water similarly form *hydroxonium*, called for brevity *hydronium*, OH_3. When a little water is dissolved in absolute sulphuric acid, H_2SO_4, *hydronium sulphate*, $OH_3.HSO_4$, is formed: $HSO_4H+H_2O=OH_3.HSO_4$; just as ammonia under similar conditions reacts: $HSO_4H+NH_3=NH_4.HSO_4$. Assuming, however, that water is polymerized and contains, say, trihydrol molecules, $(H_2O)_3$, then, when a little acid, HR, is dissolved therein, $(H_2O)_3+HR=H_3O.R+H_3O.OH$; with a base, M.OH, the action is represented: $(H_2O)_3+M.OH=H_3O.OH+H_2MO.OH$; and with a salt, MR, similarly: $(H_2O)_3+MR=H_3O.R+H_2MO.OH$. In dilute solution, with the molecules $(H_2O)_3$ in large excess, the effect of such changes would make the solution behave as if each molecule of the solute formed two molecules on passing into solution. *The number of molecules is increased owing to the reaction between solvent and solute.* An analogous case occurs when various salts or oxides are dissolved in fused alkali hydroxides: $n\mathrm{KOH}+\mathrm{PbO}=\mathrm{Pb(OK)_2}+\mathrm{H_2O}+(n-2)\mathrm{KOH}$.

There are available at least three explanations of an abnormally high osmotic pressure: (i) Dissociation of the solute; (ii) Polymerization of the solvent; and (iii) Reaction between polymerized solvent and solute. Observations on osmotic pressures and the related phenomena—raising of the vapour pressure, raising of the boiling point, lowering of the freezing point, etc.—do not discriminate between these three explanations unless it be to decide against the hypothesis that the molecules of the electrolytes are dissociated, both on account of its revolutionary nature, and *a priori* improbability. It is therefore necessary to seek evidence from other sources. The solvent water is undoubtedly associated, and it has been shown that the degree of association is diminished by the dissolution of salts in the liquid. It has not yet been shown that the degree of association of different solutions varies concomitantly with the changes in their osmotic pressure (or related phenomena); it has, however, been shown that solutions of salts in non-associated solvents—*e.g.* hydrocarbons and their halogen derivatives, ethers, esters, most aldehydes and ketones—do not usually show abnormally high osmotic pressures; while solutions of salts in associated solvents—*e.g.* water, compounds containing hydroxyl groups like the alcohols, organic acids, oximes, some nitro-compounds, and compounds containing amidogen groups—do show phenomena corresponding with abnormally high osmotic pressures. It will probably be found in later years that the abnormal behaviour of water retarded the development of the generalizations concerning the effect of solutes on the depression of the freezing points, the elevation of the boiling points, and the lowering of the vapour pressures of solutions. F. M. Raoult's success followed as a result of his experiments with non-associated solvents where the main phenomenon was not obscured by secondary effects. If it turns out that electrolytes are salts which are in the normal or unassociated condition when dissolved in associated solvents, the so-called ionization hypothesis which has been elaborated on the assumption that electrolytes have molecules which are dissociated into electrically charged units when in solution, will be unnecessary. It is also remarkable how tenaciously the ionization hypothesis is held when it is remembered how very many properties of electrolytes, supposed to be uniquely and adequately explained by the hypothetical *dissociation of the solute* can be satisfactorily explained by the observed *association of the solvent.*

Abnormally low osmotic pressures—polymerization of solute.—If the liquid solvent and its vapour have the same molecular weight, and the solute is so associated that it has an association factor, i, then, in place of n molecules of the solute, there are in reality n/i molecules, and the observed osmotic pressure P_2 will be i times smaller than the osmotic pressure P would be if the solute were not associated, or, $P=iP_2$. F. M. Raoult (1886) noticed that the depression of the freezing point of a solution of alcohol in benzene, naphthalene, nitrobenzene, ethylene dibromide, etc.—is just about half what we should expect if the molecules of alcohol were represented by the regular formula: C_2H_5OH. This means that the molecules of alcohol—C_2H_5OH—in benzene solutions are doubled, and may be represented by $C_4H_{10}(OH)_2$ in benzene solution. This phenomenon is common with molecules possessing hydroxyl, OH, groups—*e.g.* alcohols and acids. Formic—H.CO.OH—and acetic—CH_3.CO.OH—acids, and indeed water, behave in a similar manner, and we know that if these substances be vaporized, they appear to have twice the molecular weight they would have if their molecules could be really represented by the ordinary formulæ. Otherwise expressed, the molecules are polymerized. Increasing dilution usually reduces the abnormality indicating that the association becomes smaller and smaller; W. Ramsay and J. Shields also noticed that the dilution of associated molecules has a similar effect to an increase of temperature. It is also necessary to remember that the dissolved substance may freeze out along with the solvent so as to form a kind of solid solution—for example, the ice which separates from a dilute solution of ether or alcohol in water contains appreciable quantities of the solute. The observed reduction of the freezing point of the solution may be less than that calculated from the regular molecular formula of the dissolved substance. J. H. van't Hoff (1890) demonstrated the elevation of the freezing point from this cause. In 1889, W. Ramsay[3] determined the lowering of the vapour pressure of mercury by the solution of a number of metals—lithium, sodium, barium, magnesium, zinc, aluminium, tin, lead, antimony, manganese, silver, gold, etc.—and found the results agreed with the assumption that the metals are in the atomic condition in mercurial solution. C. T. Heycock and F. H. Neville examined solutions of several metals in molten tin and sodium. There is abundant evidence of the existence of definite compounds of mercury with the metals, the alkalies, or the alkaline earths, and there is no reason to assume that these compounds break up when in mercurial solution. If there is no evidence of the formation of chemical compounds, it might be assumed that the lowering of the freezing point is an indication of the molecular state of the metals—*e.g.* zinc, cadmium. bismuth, lead, and tin, dissolved in mercury.

If both liquid solvent and solute are associated, it follows from the above discussion that the osmotic pressure P_s, will be equal to $P\alpha/\beta$; and if $\alpha=\beta$, the osmotic pressure will appear to be normal, but both solvent and solute would have polymerized. It also follows by analogous reasoning that J. H. van't Hoff's relation, $k=0{\cdot}02T^2/\lambda$ applies only to the unassociated solvent and solute; if the solvent be alone associated, this relation becomes $0{\cdot}02T^2\alpha/\lambda$; and if the solute is alone associated, $0{\cdot}02T^2/\beta\lambda$.

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§ 16. The Cause of Solution

There is probably no sharp line of demarcation between chemical union and the process of solution.—S. L. BIGELOW (1907).

Clear answers to the questions: What determines the solubility of a substance? Why is cæsium chloride, CsCl, so very soluble and silver chloride so very sparingly soluble in water? are not forthcoming. The alchemists considered solution to be produced by the penetration of the particles of the solute between the particles of the solvent, or to the result of some kind of union of the two. P. Gassend,[1] following the old atomic theory, taught in 1647 that the atoms of one substance could enter the interstices between the atoms of another substance. The cubic particles of common salt, for example, filled up the water molecules, and when all such pores were filled, the water could dissolve no more salt; similarly the octohedral alum. Hence, it was supposed that water also contained octahedral pores which the alum but not the salt could enter. The ideas of solution prevailing in the seventeenth century may be gathered from R. Boyle's essay: *Of the producibleness of chymical principles* (Oxford, 1663). He says:

Dissolution depends not so much on the pretended cognation between the solvent and

> the body it is to work upon as upon the congruity, as to size and figure, between the pores of the latter and the corpuscles of the former.

A similar view of solution was advocated about the same time by N. Lemery in his *Cours de chymie* (Paris, 1675). Near the beginning of the eighteenth century Isaac Newton naturally extended the idea of attraction to the particles or atoms composing a substance; and, reasoning from the fact that the particles of a salt dissolving in water, in spite of their greater density, diffuse themselves uniformly throughout the solvent so that the particles of the salt recede from one another and endeavour to get as far asunder as the solvent will allow, Isaac Newton asked: Does not this endeavour imply that the particles of the dissolved substance exert a repulsive force on one another, or else attract the particles of the solvent more strongly than they do one another? Otherwise expressed: Does not the solute dissolve because it exerts an attraction on the solvent? H. Boerhaave (1772) took a somewhat similar view, and added:

> The particles of the solvent and those of the dissolved substance unite, after solution, to form a new homogeneous substance. . . . The cause of this must be sought for in both the solvent and the dissolved substance. It is common to them both. *Particulæ solventes et solutæ se affinitate suæ naturæ colligant in corpora homogenea.*

About this time, J. K. Wallerius (1772),[2] M. H. Klaproth (1806), and many others also regarded solution as the result of the action of chemical affinity between solvent and solute which must be stronger than the cohesion of the particles of the dissolved substance each to each.

In 1789, A. L. Lavoisier distinguished between *dissolution, a chemical process*, typified by the dissolution of zinc in dilute acid; and *solution, a physical process*, typified by the solution of salt in water. In the latter process, said A. L. Lavoisier, the salt molecules are simply torn apart from one another, but neither the solvent nor solute suffers any other change, because both can be recovered in the same quantity as before the operation. These views were adopted by A. F. de Fourcroy (1801), who regarded a solution as a physical or mechanical mixture in which the dissolved substance is in a state of fine subdivision in the solvent. With reference to purely physical hypotheses of this kind, W. A. Tilden adds:

> Such a theory, however, serves to account only for the initial stage in the process of solution, and does not explain the selective power of solvent, nor the limitation of the solvent power of a given liquid, etc.

The father of the chemical school, C. L. Berthollet (1803),[3] took the contrary view. A solution, said he, is a true chemical compound which is not very stable, and which shows the characteristics of the dissolved body. Solution must be due to a force which is great enough to overcome the cohesion of the dissolved substance. The difference between a solution and a chemical compound is to be found in the firmness of the union of the parts. In solutions the parts are the less firmly united, and the characteristic properties of the dissolved substance have not been lost. J. P. Cooke[4] expressed similar views in 1881. C. L. Berthollet, it will be remembered, did not accept the laws of definite and multiple combination; hence he could say: Chemical union and solution must therefore follow the same laws.

After the laws of combination had been generally accepted, it became necessary for those who regarded solution as a chemical process to explain the reason why chemical combination takes place in certain definite proportions, while solution occurs in any proportion up to a certain limit. This was done by J. L. Gay Lussac,[5] who assumed that the force which leads to chemical combination is more powerful than that which produces solution. He compared the process of solution with that of vaporization—both are dependent on temperature and obey its variations. The essential difference between the two processes consists in this: Gaseous molecules do not need a solvent to maintain them in a given space, their own repulsive force suffices for this purpose. On the other hand, in a solution, the particles of the dissolved substance cannot maintain themselves in the space if they are not united by affinity to the molecules of the solvent.[6]

These ideas were fairly general during the greater part of the nineteenth century, and they are typified by the views of L. Dossios,[7] who referred solution to the molecular attraction between unlike molecules exceeding the attraction between molecules of the same kind. Consider the case of two fluids A and B in contact with one another. Molecules of the one fluid A will enter among the molecules of the other B if the molecules of the latter attract the former more strongly than the attraction of either the molecules of A or B have for one another. When the number of molecules of A passing into the fluid B is equal to those passing from B in a given time is equal, the liquid B is saturated; similar considerations apply to the fluid A and the molecules of B. Finally, therefore, each liquid will be saturated with the other. The same remarks apply, *mutatis mutandis,* to the solution of a solid in a liquid. The solubility will increase with a rise of temperature, if the temperature diminishes the attraction of like molecules for one another more than it does for unlike molecules. If the solution of a salt in water is a consequence of the attraction of the molecules of water for a molecule of the salt exceeding the attraction of the molecules of a salt for one another, it follows, says W. W. J. Nicol[8]:

> As the number of dissolved salt molecules increases, the attraction of the dissimilar molecules is more and more balanced by the attraction of the similar molecules; when these two forces are in equilibrium, saturation takes place.

D. I. Mendeléeff[9] modified the views of C. L. Berthollet and J. L. Gay Lussac so as to bring the conception in accord with the law of definite proportions and the phenomena of dissociation. He supposed that the solvent and solute formed chemical compounds with so feeble an affinity that the compounds are more or less dissociated at ordinary temperatures. According to the nature of the solute one or more such compounds may be simultaneously in the solution. M. Berthelot (1879)[10] also advocated the view that a solution is a mixture of the free solvent and a compound of solvent and solute—called, in the case of aqueous solutions, a hydrate—united in definite proportions. *Les phénomènes de la dissolution normale sont en quelque sorte intermédiares entre le simple mélange et la combinaison véritable.* Definite hydrates are formed in solution by the union of the solvent water with the anhydrous salt, and they are comparable with the crystalline hydrates of the salt, but with this difference, the hydrates in solution are in *une état de dissociation partielle* which depends on the relative quantities of solute and solvent and the temperature in accord with the law of mass action. In some cases, he added, the whole mass of the solvent takes part in the action as in the case of strong acids; and in other cases, as with salts of the alkalies, only a part of the solute is combined with the solute; and lastly, there may be many hydrates, or equivalent bodies existing in the solution in equilibrium at the same time.

D. I. Mendeléeff could see no way of definitely determining the composition of the supposed hydrates, and his attempt to determine the character of the hydrates was not very successful. He plotted the specific gravities of solutions of sulphuric acid of varying concentrations against the concentrations, and assumed that the maxima in the curves represented definite hydrates. S. U. Pickering[11] also examined the physical properties of numerous aqueous solutions, and when one of these properties is plotted against the concentration he inferred that (i) abrupt changes in the curvature of the resulting curves, and (ii) the supposed points of discontinuity of the first or second differential coefficient of a function connecting the physical property of a solution with concentration, indicated the presence of certain definite hydrates.[12] Some of these discontinuities are possibly due to experimental errors, since a small error may be much magnified in the differential process. Definite breaks do exist in many curves connecting the composition with some physical property—specific heat, specific gravity, viscosity, refractive index, electrical conductivity, compressibility, surface tension, thermal expansion, heat of solution, etc.—but striking irregularities are encountered, when the attempt is made to connect these with specific hydrates. For example, Pickering's hydrates did not always correspond with those deduced by other physical methods—*e.g.* by the freezing points of the solutions.[13]

According to T. M. Lowry, the breaks observed in the density-composition curves of dilute solutions are due to distortions produced by alterations in the character of the solvent water whereby complex water molecules are depolymerized.[14] Apart from the question whether the hydrates actually assumed are those really present, the underlying hypothesis that the cause of solution is dependent on the chemical affinity between solvent and solute is very generally accepted.

In the ionic theory, to be described later, it is assumed that in dilute solutions the molecules of the salt, presumably *after* the salt has dissolved, are more or less dissociated into parts which carry electric charges, and which are called ions; and in the so-called solvate theory, the ions as well as the non-ionized molecules are supposed to be more or less hydrated, so that aqueous solutions of a salt may contain hydrated molecules, and hydrated ions.

The formation of hydrates or of complexes between solute and solvent is evidenced by the so-called abnormal effects produced by the solute upon the freezing point, boiling point, vapour pressure, and solvent power of a solvent; by the distribution of a solute between two solvents, or a solvent and a gas (Henry's law); breaks and irregularities in the solubility curves; by deviations in the physical properties—specific gravity, thermal expansion, heat of solution, specific heat, surface tension, viscosity, conductivity, compressibility, index of refraction, magnetic rotation of the plane of polarization, diffusion, ionic velocities, hydration and colour changes, etc.; effect of salts on the velocities of reactions in aqueous solutions, etc.

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§ 17. The Physical Properties of Solutions

In a sense it is unfortunate that such an enormous number of observations have been made on aqueous solutions, and so few with other solvents, because water is so emphatically exceptional in its physical and chemical properties, and the mechanism of solution will never be clearly demonstrated until these observations have been supplemented by prolonged series of investigations with less complex non-aqueous normal solvents. Nearly every physical property of water is profoundly modified when it is used as a solvent for the various salts, and the evidence as to the formation of hydrates is ambiguous, in that it may be interpreted to imply that the complex molecules of this solvent are more or less depolymerized in the presence of a solute.

According to the law of mixtures, the molecular physical properties X of a mixture are additive if $X=X_1N_1+X_2N_2+\ .\ .\ .$, where X_1, X_2, . . . represent the magnitude of a molecular physical property of the components, and N_1, N_2, . . . denote the molecular fractions of the corresponding components of the mixture. Deviations from this rule are attributed to changes in one or more of the components —*e.g.* polymerization or depolymerization of one or more components of the mixture —or to the chemical union of two or more of the components of the mixture.

The specific gravity of solutions ; the molecular volumes of salts in solution. —The early observers, P. Gassend, A. Nollet, and M. Eller believed that salts dissolve in water without a change in volume, but R. Watson demonstrated that the assumption has no foundation in fact.[1] In 1840, J. Dalton discovered that a contraction occurs when some salts dissolve in water ; and in some cases, the contraction is as large as that of the volume of the anhydrous salt in solution, so that the volume of the solution is not greater than that of the solvent alone. He experimented with hydrated and anhydrous salts and concluded :

> I have tried the carbonates, the sulphates, the nitrates, the muriates or chlorides, the phosphates, the arseniates, the oxalates, the citrates, the tartrates, the acetates, etc., etc., and have been uniformly successful ; only *the water adds to the bulk, and the solid matter adds to the weight.*

J. Dalton said of this observation (1840) : " This fact is new to me and I suppose to others. It is the greatest discovery that I know of next to the atomic theory ; " but, added L. Playfair, " Dalton was here inclined to generalize much further than the observation would bear. There is, indeed, a class of salts which behaves in this manner—magnesium, copper, zinc, and iron sulphates and a few other salts like sodium borate and phosphate." Apparently unknown to J. Dalton, E. Swedenborg (1721), a century earlier, made a similar observation as is indicated in a previous citation. J. Dalton's work was followed up by S. Holker (1844), L. Playfair and J. P. Joule (1845), J. C. G. de Marignac (1846), and others. The degree of contraction varies with different salts, and in some cases—*e.g.* lime water—the volume of the solution is even less than that of the contained solvent. The contraction which occurs during the formation of a concentrated solution continues as the solution is diluted and either approaches a constant value in a dilute solution, or else becomes negative so that the volume of the solution is less than the original volume of the water used as a solvent.[2] In some cases—*e.g.* silver nitrate—the solution occupies almost as great a volume as the sum of the volumes of salt and water, whereas with solutions of sugar and water the solution occupies the same volume as the joint volume of the two components in accord with the law of mixtures. Again, solutions of organic compounds in hydrocarbons, though seldom strictly conformable to the law of mixtures, show but slight deviations.[3] P. A. Favre and C. A. Valson, I. Traube, and J. Y. Buchanan [4] showed that with lithium bromide and nitrate and the ammonium halides and nitrate, the volume of the solutions is greater than the sum of the volumes of the water and dry salt. According to G. P. Baxter and C. C. Wallace, lithium and cæsium halides also produce expansion during solution ; lithium chloride is exceptional, but it too produces an expansion if the concentration is high and the temperature over 25°.

Does the contraction which occurs when a solid is dissolved in water or when water is progressively added to its solution indicate the formation of hydrates ? The answer is in the negative. The curves shown in Fig. 27 represent the differences between observed molecular volumes and those calculated on the assumption that the law of mixtures obtains for sulphuric anhydride with up to ten molecules of water, SO_3+10H_2O ; and for sodium chloride with up to $NaCl+100H_2O$. Hence, there is no point in the curve where we should be justified in setting up a distinction between the effect due to chemical combination, and that due to other causes.[5]

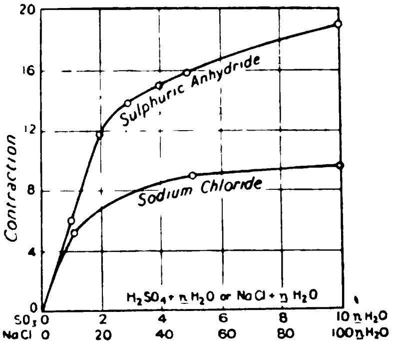

Fig. 27.—Contraction during Solution and Progressive Dilution.

Table VII, by G. P. Baxter and C. C. Wallace, shows the change in volume *a* which occurs during the formation of the solid salt from the solid or liquid elements, and the change in the molecular volume *b* of the salt during the solution of the alkali halides. The change in volume which occurs during the solution of a salt in water is a highly complex phenomenon. According to P. A. Favre and C. A. Valson, the observed change of volume during solution is the joint result of two opposing influences : (i) the contraction of the solvent under the influence of the solute, and (ii) an increase in the volume of the salt *par suite de la dissociation plus ou moins avancée de ses éléments constituents*. The observed contraction which usually occurs is taken to prove that the first effect is usually greater than the second.

Table VII.—Changes in the Molecular Volumes of the Alkali Halides during their Formation from their Elements, and during Solution.

Salt.	Mol. wt.	Sp. gr. fused salt at 25°.	Sum of at. vols. c.c.	Mol. vol. c.c.	Contraction in formation of solid = *a* c.c.	Change in vol. during solution at 25° = *b* c.c.	*a*+*b* c.c.
LiCl . .	42·40	2·068	38·1	20·5	−17·6	−2·03	−19·6
LiBr . .	86·86	4·364	38·7	25·1	−13·6	+0·16	−13·4
LiI . .	133·86	4·061	38·8	33·0	− 5·8	+3·40	− 2·4
NaCl . .	58·46	2·162	48·7	27·0	−21·7	−8·48	−30·2
NaBr .	102·92	3·203	49·3	33·1	−17·2	−6·94	−24·1
NaI . .	149·92	3·665	49·4	40·9	− 8·5	−4·50	−13·0
KCl . .	74·56	1·988	70·4	37·5	−32·9	−8·71	−41·6
KBr . .	119·02	2·749	71·0	43·3	−27·7	−7·72	−35·4
KI . .	166·02	3·123	71·1	53·2	−17·9	−6·31	−24·2
RbCl . .	120·91	2·798	80·8	43·2	−37·6	−9·19	−46·8
RbBr. .	165·37	3·349	81·4	49·4	−32·0	−8·70	−40·7
RbI . .	212·37	3·550	81·5	59·8	−21·3	−7·86	−29·2
CsCl . .	168·27	3·974	96·0	42·4	−53·6	−1·09	−54·7
CsBr . .	212·73	4·433	96·6	47·9	−48·7	0·00	−48·7
CsI . .	259·73	4·509	96·7	57·6	−39·1	+1·77	−37·3

The contraction is usually attributed to hydration. G. Tammann[6] argues that since solutions behave in approximately the same way when subjected to changes of temperature and pressure, as the same volume of water, at a higher pressure, there must be a compression of the water by the solute owing to an increase of internal pressure which he calls the *Binnendruck*. It is not clear whether the *Binnendruck* is exerted throughout all the water or only to the portions in the vicinity of the solute molecules. This, however, is immaterial from the present point of view. G. P. Baxter argues from T. W. Richards' hypothesis of compressible atoms that under the influence of chemical affinity the atoms are more or less compressed—the greater the affinity, the greater the compression. This agrees with the observed thermal values of the reactions. For related elements, the greater the heat of formation the greater the difference between the sum of the atomic volumes and the observed molecular volume of a salt. During solution, the compression due to chemical affinity and molecular cohesion is more or less relieved. In addition to the contraction due to hydration, the expansion due to dissociation (or ionization), and the expansion due to the partial release of the compression (T. W. Richards' hypothesis), profound changes are produced in the degree of polymerization of water during the dissolution of a salt.

C. A. Valson (1874)[7] noticed the curious fact that the differences between the specific gravities of solutions containing one gram-equivalent of various salts per litre of two specific metals with one acid are equal, and therefore independent of the nature of the acid; and conversely the differences between the specific gravities of solutions of various salts of two specified acids with one metal are equal, and therefore independent of the nature of the metal. Hence, the specific gravity of a normal salt solution—that is, a solution containing one gram-equivalent of the salt per litre—is obtained by adding two numbers to the standard value—one is a characteristic or modulus of the metal, and the other is a characteristic or modulus of the acid. C. A. Valson used a solution of ammonium chloride of specific gravity 1·015 as his standard of reference, but water would have been the better standard.

TABLE VIII.—VALSON'S MODULI.

Ammonium	0·000	Manganese	0·037	Chlorine	0·000
Potassium	0·030	Iron	0·037	Bromine	0·034
Sodium	0·025	Zinc	0·041	Iodine	0·064
Calcium	0·026	Copper	0·042	Sulphate	0·020
Magnesium	0·020	Cadmium	0·061	Nitrate	0·015
Strontium	0·055	Lead	0·103	Carbonate	0 014
Barium	0·073	Silver	0·105	Bicarbonate	0·016

Thus the specific gravity of a solution of silver nitrate is 1·015+0·105+0·015=1·135. The rule is valid only for dilute solutions. The observed irregularities depend upon the regular volume changes which accompany the formation of salts in solution. It has been found that at a given concentration, within the limits of observational errors, the physical properties of dilute aqueous solutions of strong electrolytes—*e.g.* volume changes on mixing, the thermal, optical, and other properties—are purely additive functions of the constituent ions. Consequently, it is assumed that in these solutions, the electrolytic solute is completely ionized. For example, if the partial volumes of HCl, HBr, and KBr are known in $\frac{1}{10}N$-solution, the partial volume of KCl in the same concentration can be computed. C. Bender[8] tried to extend the rule to concentrated solutions by showing that the difference between the specific gravities of two substances containing an equal number of gram-equivalents per litre was proportional to the number of equivalents. This extension of C. A. Valson's moduli is made possible on account of the empirical fact that the dilution of equivalent salt solutions is attended by almost the same contraction.

In 1878, W. Ostwald[9] showed that the changes in volume observed by G. T. Gerlach (1859), C. Tissier (1859), and J. Regnauld (1865), to accompany the neutralization of solutions of ammonium and alkali hydroxides by various acids, in solutions containing a gram-equivalent of base or acid per kilogram of solution, are dependent on both the acid and the base, and that the difference in the changes in volume which accompany the neutralization of different bases by one acid is the same whatever acid is used; and conversely, the difference in the volume changes which attend the neutralization of the different acids by one base is independent of the nature of the base. W. Ostwald showed that similar additive relations hold good for many other properties of dilute salt solutions, and used the facts as an argument in support of the ionic hypothesis. These relations do not hold so well for concentrated solutions. It is argued that a negative molecular volume for the solute is impossible, and accordingly a portion of the solvent must be denser than the pure solvent. Consequently, the increase in density which occurs when salts are dissolved in water is attributed to the union of a portion of the solvent water with the solute to form a salt which is hydrated in aqueous solution, and this is supposed to be confirmed by the increased density of the water of crystallization in solid crystalline hydrates. The alternative hypothesis is that the increase in the density of solutions is due to the depolymerization of the solvent water. The attempts made to determine the formulæ of the supposed hydrates from irregularities or discontinuities in the density-composition curves have not been generally successful, for the alleged breaks in the curve have been shown in many cases to be due to experimental errors,[10] and that no reliable conclusions about the formation of hydrates can be drawn from the density-composition curves.

The thermal expansion and compressibility of salt solutions.—Some remarks on these properties have been discussed in dealing with water. Aqueous solutions of salts do not follow the mixture law.[11] In general, the thermal expansion of aqueous solutions of salts is the more uniform the more concentrated the solution; the more dilute the solution the greater the curvature of the line showing the relation between its volume and temperature; and with the more concentrated solutions, the more nearly does the volume-temperature curve approach a straight line. This is attributed to the depolymerization of the so-called ice-molecules when salt is dissolved in water. Similarly with the compressibility of salt solutions. W. C. Röntgen and J. Schneider investigated the compressibilities of 1·5 and 0·7 normal solutions of various salts of the alkalies and ammonium, and the corresponding acids, and concluded:

> The substitution of one constituent of the compound in solution by another, *e.g.* I by NO_3, Br, Cl, OH, SO_4, or CO_3, alters the compressibility of the solution to an extent which is only slightly dependent on the nature of the other constituent of the compound (H, NH_4, Li, K, Na). It appears, then, as if each constituent of a salt exerted a specific effect on the compressibility of the solution of that compound, which effect is only slightly modified by replacing the other constituents by different substances; or, in other words, it seems as if the components of the dissolved body, and not the compound in which these components are contained, had the greatest influence on the compressibility of the solution.

Water and ammonia are exceptions; and each of the exceptional solutions is found to be a relatively poor conductor of electricity.

The viscosity of solutions.—The viscosity curves of binary solutions are of three kinds: those which follow the law of mixtures, and those which exhibit maxima or minima. According to A. E. Dunstan, the minima are produced by the depolymerization of one or both the associated components of the mixture; the maxima are produced by the formation of complexes between solute and solvent. T. Graham attributed the maxima he obtained with aqueous solutions of many common acids and alcohols to the formation of definite compounds, and in this he is supported by A. E. Dunstan, D. E. Tsakalotos, O. Faust, R. B. Denison, and others.[12] As in the case of the specific gravities, the existence of numerous hydrates has been deduced from points of discontinuity in the viscosity curves. Four hydrates of acetone, six of methyl alcohol, and seven of ethyl alcohol have been reported by E. Varenne and L. Godefroy to be formed in aqueous solutions of these compounds. E. W. Washburn takes the view that the deviations of a physical property from the mixture law cannot give conclusive evidence of the existence of hydrates or other complexes; and he states that in the case of aqueous solutions of methyl alcohol, "the points of discontinuity in the viscosity curves are purely imaginary, and due to experimental errors." Probably the larger part of the abnormal effects of salts on the physical properties of water should be ascribed to changes in the complexity of the solvent.

The specific heat of solutions.—The molecular specific heat of mixtures of some organic compounds—*e.g.* carbon disulphide and chloroform—follow the mixture law, but mixtures of alcohol and water, and indeed aqueous solutions generally, do not follow this rule. This was noticed by A. A. B. Bussy and J. L. H. Buignet [13] in 1865. The thermal capacity of mixtures of alcohol and water is always greater than that calculated by the law of mixtures, but in the case of aqueous solutions the thermal capacity is usually less than that calculated by the law of mixtures. The total heat capacity of aqueous solution of salts is frequently less than that of the contained water; in illustration, J. Thomsen found that the difference between the thermal capacity of 100 parts of water and the thermal capacity of a 10 per cent. solution of sodium chloride is 2·01 cals.; a 20 per cent. solution, 0·36 cal.; and a 30 per cent. solution, —2·66 cals. J. Thomsen has also shown that the calculated molecular heat capacity of the solute in solutions of electrolytes is nearly always less than for the solute alone, and it steadily decreases on dilution, passing through zero, and finally assuming a negative value. A negative heat capacity has no physical meaning; consequently, the heat capacity of the water as a whole, or of a certain portion of the water is lowered by the presence of a solute. M. Berthollet believed that the formation of hydrates with a smaller heat capacity than water explains the phenomenon satisfactorily. The depolymerization of the solvent water is the alternative hypothesis.

The heat of solution.—The heat developed or absorbed during the formation of a solution may be expressed in different ways. The magnitude measured in the calorimeter usually refers to the thermal change which occurs when a gram of the substance is dissolved in so large a quantity of the solvent, that any further dilution of the resulting solution is not attended by any thermal change; or when a gram of the substance is dissolved in *w* grams of water; or when a gram of the substance is dissolved in sufficient water to form a saturated solution; or when a small quantity of the substance is added to a saturated solution containing a gram of the substance—this is, the reversible heat of saturated solution; the heat evolved or absorbed when a small quantity of water is added to a saturated solution containing a gram of the solute; etc. These magnitudes can all be represented in terms of the gram-molecule instead of the gram.

In the solution of a solid, work must be performed in the separation of the molecules against intermolecular attraction, *this* is equivalent to the latent heat of sublimation or to the heat of fusion plus the heat of vaporization. This exerts a cooling effect. In the solution of a liquid, work equivalent to the heat of vaporization must be expended against intermolecular attraction. Thermal phenomena of greater or less magnitude may also accompany a reaction between solvent and solute, the formation of complexes, depolymerization of the solvent, etc. The observed heat of solutions is a resultant of these several effects. The heat of solution of gases includes the external work—pv or RT—performed in compressing the gas, and this magnitude must be subtracted from the observed heat of solution. The external work associated with the solution of solids and liquids is negligibly small. All known gases have a positive heat of solution; and this is usually the case with liquids; solids also may have a positive heat of solution, but more usually the heat of solution of solids is negative, for they dissolve with an absorption of heat. If the heat of vaporization of a liquid exceeds the heat of solution, it will dissolve with an evolution of heat, and with an absorption of heat if the heat of vaporization is less than the heat of solution. Similarly with solids, the nature of the thermal change is conditioned by the difference in the heats of solution and sublimation. Consequently, the heat of solution of a gas is usually greater than the heat of vaporization; and the heat of solution of a solid is usually less than the heat of sublimation. As a rule, the heat of solution of a substance is smaller the less its solubility.[14]

Does the evolution of heat which occurs when a solid is dissolved in water, or when a concentrated solution of the salt is diluted indicate the formation of hydrates? J. Thomsen [15] returns a negative answer. The progressive addition of water to sulphuric anhydride, SO_3, gave him the curve indicated in Fig. 28, and it is asked: At what point in such a curve should we be justified in setting up a distinction between the effect due to chemical combination and that due to other causes? The volume of the solution obtained when anhydrous salts are dissolved in water is always less than the sum of the volume of solvent and solute, and the subsequent dilution of the solution is likewise followed by a contraction. P. A. Favre and C. A. Valson[16] calculated the amount of heat required for the contraction which occurs when sulphuric acid, H_2SO_4, is diluted with a gram-molecule of water from the specific heat and coefficient of thermal expansion, and found it to be 179 calories less than that actually observed. Hence, the hypothesis that the observed change in volume is merely due to such a change in the mean distances and motions of the molecules as would be produced by a change of temperature is not tenable. The effect must be complicated either by the formation of hydrates, or to a polymerization or depolymerization of the solvent. Analogous results are obtained with sodium chloride, only that the heats of solution and dilution are negative.

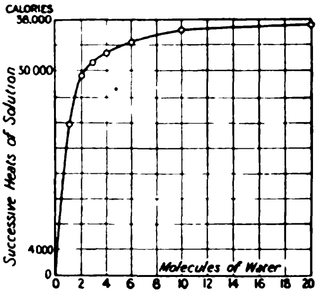

FIG. 28.—Heat of Solution and Dilution of Aqueous Solutions of Sulphuric Anhydride.

There is a parallelism between the heat of solution and the degree of hydration when the process of solution is attended by the formation of one or more hydrates. This is shown when the heats of hydration of salts with a common ion are compared with abnormal freezing points or vapour pressures. The magnitude of the depression corresponds with the order of the hydrates of these salts, which is that indicated in Table IX.

TABLE IX.—HEATS OF SOLUTION (CALORIES).

—	Nitrate NO_3	Thiocyanate SCy	Cyanide Cy	Chloride Cl	Bromide Br	Iodide I
Potassium . .	−8·64	−6·00	−3·12	− 3·12	− 5·04	−5·04
Ammonium . .	−6·24	—	—	− 4·08	− 0·24	−3·60
Sodium . . .	−5 04	—	—	− 1·20	− 0·24	+1·20
Lithium . .	+0·24	—	—	+ 8·40	—	—
Barium . . .	—	—	—	+ 2·16	+ 5·04	—
Strontium . .	—	—	—	+11·04	+16·08	—
Calcium . .	—	—	—	+17·52	+24·48	—
Magnesium . .	—	—	—	+24·00	—	—

J. Thomsen found that of thirty-five salts he examined:

The chlorides of *sodium*, *ammonium*, calcium, magnesium, zinc, nickel, and copper; *potassium bromide*, *potassium cyanide*; the nitrates of *sodium*, *ammonium*, *strontium*, *lead*, magnesium, manganese, zinc, and copper; the acetates of potassium, sodium, ammonium, and zinc; the sulphates of *ammonium*, magnesium, manganese, zinc, and copper; sodium hydrogen sulphate; *ammonium tartrate*, and *bicarbonate*,

eighteen salts which evolve heat when the anhydrous salt dissolves in water also evolve more heat on dilution; and eleven salts (italicized in the list) which absorb heat on solution also absorb still more heat on dilution. All those salts which form definite crystallizable hydrates evolve heat, the other salts do not. The six exceptions included:

Ammonium and potassium bisulphates, sodium sulphate, sodium iodide, and the carbonates of potassium and sodium.

J. Thomsen's opinion is that

> There is no doubt that the salts which dissolve in water with the evolution of much heat, and form crystallizable hydrates, are present also in solution as hydrated compounds; but a determination of the number of water molecules contained in such compounds must be very difficult.

In 1858, G. R. Kirchhoff[18] obtained thermodynamically an expression between the vapour pressure and the heat of solution of a solid or the thermal change which occurs when a gram of the substance is dissolved in sufficient water to form a saturated solution. G. R. Kirchhoff also deduced an equation for the heat of dilution of a saturated solution, and his formulæ have been verified by F. Jüttner (1901) and R. Scholz (1892), and improved by N. N. Schiller. Assuming that the variation in the heat of dilution dl of a solution with change of temperature $d\theta$ is equal to the rate at which the thermal capacity dC of the solution changes with concentration dm—that is, $dl/d\theta=dC/dm$—provided the thermal capacity of the solution does not change with respect to temperature, H. Teudt has shown that the change in the heat capacity of a salt solution with temperature is in general less than that of water; and F. R. Pratt, that the ratio dC/dm or $dl/d\theta$ decreases considerably with an increase of temperature.

It has been shown[19] that the solubility S—gram-molecules per litre—at the absolute temperature T, is related with the heat of solution Q by the expression:

$$\frac{d\log S}{dT}=-\frac{Q}{RT^2};\text{ or }\log\frac{S_2}{S_1}=-\frac{Q}{2}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

when S_1 denotes the solubility of a compound in water at the absolute temperature T_1, and S_2 the solubility at a temperature T_2; and Q denotes the heat of solution on the assumption that the heat of solution Q does not vary with temperature. If the heat of solution does vary with temperature—say $Q=a+bT+cT^2+\ldots$—changes corresponding with those previously indicated must be made. The heat of solution here refers to the solution of a gram-molecule in its own saturated solution. This fictitious quantity may differ considerably from the observed heat of solution in a large quantity of water, and it may even be of opposite sign, as L. T. Reicher and C. M. van Deventer observed with copper chloride, $CuCl_22H_2O$, which evolves heat when dissolved in a large quantity of water, but absorbs heat if "dissolved" in its own saturated solution. With sparingly soluble substances, the difference between the two heats of solution is negligibly small.

EXAMPLE.—Boric acid has a solubility 1·95 at 0°, and 2·92 at 12°. Accordingly, by substituting $T_1=273$, $S_1=1{\cdot}95$; and $S=2{\cdot}92$ and $T=285$ in the preceding expression, and using natural logarithms, $Q=5{\cdot}2$, the observed value is 5·6.

For solutions of substances which dissociate so as to increase the number of molecules in the solution to i per molecule of solute during solution, J. H. van't Hoff introduces the factor i; and J. J. van Laar the factor a, where a denotes the degree of dissociation such that $1+a=i$. The respective equations are:

$$\frac{d\log S}{dT}=-\frac{Q}{2iT^2};\quad\frac{d\log S}{dT}=-\frac{Q}{2T^2}\cdot\frac{2-a}{2}$$

Equations (1) and (2) show that the change of the solubility of a compound with temperature is of opposite sign to the heat of solution—if the solubility increases with a rise of temperature, heat will be absorbed when the substance dissolves in its own saturated solution—this phenomenon occurs with most substances: cupric chloride, $CuCl_2.2H_2O$, etc.; if the solubility decreases with a rise of temperature, heat will be evolved—examples, gases, ether, carbon disulphide, bromine, etc.; and if the solubility is a maximum or a minimum, the solubility does not change appreciably with a small variation of temperature, and the heat of solution will be zero—examples, the solubilities of isobutyl alcohol (W. Alexejeff),[20] calcium sulphate (H. le Chatelier), and of sodium chloride (C. M. van Deventer and H. J. van de Stadt) in water; the heat of solution of two liquids at their critical solution temperature is also zero.

The effect of chemical composition on solubility.—It has been empirically observed[21] that while there is a marked tendency for unlike substances to react chemically, there is a strong disposition for like substances to dissolve in like, for *when there is a close connection in chemical constitution between a liquid and a solid, the solid will usually dissolve readily in the liquid.* In illustration, nearly all salts which contain water of crystallization are soluble in water—calcium sulphate is one of the least soluble, while magnesium phosphate and arsenates, and some natural silicates, are exceptional in being insoluble. Insoluble salts are almost always anhydrous and rarely contain the elements of water. The solubility and capacity for uniting with water of crystallization of a series of salts containing nearly allied metals generally diminishes as the atomic weight increases—*e.g.* the sulphates of magnesium, calcium, strontium, and barium; the chlorides or nitrates of calcium, strontium, barium, and lead. These facts have been taken to imply that the salts which readily crystallize with water of crystallization also dissolve readily in water, because they are likewise readily hydrated in the solvent. Anhydrous copper sulphate is white, and its hydrated crystals as well as its aqueous solutions are blue. It has also been demonstrated by P. Vaillant and by G. N. Lewis[22] that the colour changes produced in aqueous solutions of copper and cobalt salts are due to hydration. Hence, there is here direct evidence of the formation of hydrates in solution. Chemical composition, however, is not a sufficient criterion to determine whether a solid will be soluble or insoluble in a given menstruum.

W. Herz[23] has tried to show that the solubility of a number of organic liquids in water is greater the smaller the diameter of the molecule; but the relationship between molecular diameter and solubility is still largely conditioned by the specific chemical properties of the substance concerned.

The relation between the solubility and the melting point of a solid.—A. L. Lavoisier (1793)[24] expressed the opinion that the solubility of a solid must be related with its fusibility. He stated that the solubility of a salt in cold and hot water is greater the more readily it fuses. T. Carnelley, W. A. Tilden and W. A. Shenstone have shown that there appears to be some connection between the two constants in that the more fusible a substance, the more readily does it dissolve in a given liquid. In illustration, the solubilities and fusibilities of the alkali chlorides may be cited:

	$LiCl$	$NaCl$	KCl	$RbCl$	$CsCl$
Melting point . .	602°	801°	790°	726°	646°
Solubility (15°) . .	80	36	33·4	80	179

Fusibility, however, is not sufficient in itself to determine whether a solid shall be soluble or insoluble in a given menstruum. Silver chloride, $AgCl$, for instance, is more fusible than any of the alkali chlorides—its melting point is 490°—but it is very sparingly soluble—almost insoluble.

According to I. Schröder, if s denotes the molecular fraction of the dissolved molecules to the total number in a given solution, s will be proportional to the osmotic pressure, and J. H. van't Hoff's well-known equation, $dp/p=QdT/RT^2$, becomes $ds/s=QdT/RT^2$, as indicated above. Consequently, the integral $\log s=Q/RT$ plus the constant of integration. This result was obtained independently by H. le Chatelier in 1894. To evaluate the integration constant, it will be observed that when the absolute temperature T rises, the concentration of the solution increases until at the melting point T_m, $s=$unity, and Q is then identical with λ the latent heat of fusion of the solvent. Since $\log 1=0$, the integration constant $=-Q/RT$; and therefore the relation between the melting point

T_m, and the solubility of the solid at a temperature T, can be represented by the expression:

$$\log s=\frac{1}{R}\left(\frac{Q}{T}-\frac{\lambda}{T_m}\right); \quad \text{or, } \log s=\frac{M\lambda}{2}\cdot\frac{T_m-T}{TT_m}$$

if T_m be the melting point of the solution and T that of the pure solvent when $M\lambda$ is the molecular latent heat of fusion of the solvent (a negative quantity). I. Schröder found the approximation $\lambda=Q$ to be applicable for a number of organic compounds.

The above expression contains no term relating to the dissolved substance, so that when the solubility is expressed by the number of molecules of the solvent present in one gram-molecule of the solution, it is found to be independent of the nature of the dissolved substance, and one and the same solubility curve records the behaviour of a given solvent towards all the compounds which it may be capable of dissolving. The term solvent here refers to the substance which crystallizes first from the liquid mixture on cooling, or the substance whose melting point is being lowered—*e.g.* if salt crystallizes out on cooling an aqueous solution, then the salt is here regarded as the solvent. H. Crompton adds that since $M\lambda=1{\cdot}38T\Sigma v$, where Σv denotes the sum of the valency bonds, it follows by substitution for $M\lambda$, and solving for T_m, that $T_m=-0{\cdot}7T\Sigma v/(\log s-0{\cdot}7\Sigma v)$, from which it follows that, knowing nothing more than the chemical constitution and melting point of a given compound, it should be possible to deduce its solubility curve, and its general behaviour as a solvent.

If a mixture of two substances be in question, the preceding expression will apply to the one, and $T_m'=-0{\cdot}7T'\Sigma v/\{\log(1-s)-0{\cdot}7\Sigma v'\}$ will apply to the other. At the eutectic temperature $T_m=T_m'$, and therefore

$$\frac{T\Sigma v}{T'\Sigma v'}=\frac{\log s-0{\cdot}7\Sigma v}{\log(1-s)-0{\cdot}7\Sigma v'}$$

which shows that if T be greater than T', s will be less than $1-s$, or, in a eutectic mixture, the substance with the lower melting point will be present in the greater proportion. A. Miolati was the first to show that *the eutectic point always lies nearest to the melting point of the lower melting constituent of the mixture; and the eutectic mixture always contains the larger proportion of the lower melting constituent.* With a mixture of potassium and sodium nitrates, for instance, $\Sigma v=\Sigma v'$, and since T differs by about 3 per cent. from T', s should be nearly equal to $1-s$; or, more exactly, the eutectic mixture contains 47 gram-molecules of KNO_3, 53 of $NaNO_3$, and melts at 217°. H. Crompton and M. A. Whiteley also showed that the above relations hold for a number of pairs of organic compounds. The observed melting points are higher than the calculated values in cases where the solvent does not crystallize out alone but forms a solid solution with the solute.

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CHAPTER XI

CRYSTALS AND CRYSTALLIZATION

1. The Crystallization of Salts from Solutions

> The world is not a meaningless medley. We do not believe that blind chance reigns supreme. On the contrary, we see order everywhere, and law is the regulating principle in all things and processes.—P. Carus.

If a saturated solution of a salt be allowed to evaporate at a given temperature, crystals of the salt separate when the concentration of the solution becomes greater than that represented by a point on the solubility curve. The phenomenon becomes a little more complex when the solution contains two or more salts which do not act upon one another; and more complex still if the salts react with one another forming double salts or with the solvent forming hydrates.

The solubility of a mixture of sodium and potassium chlorides in water at 25° is represented by the curves shown in Fig. 1. These salts form neither hydrates nor double salts at this temperature. The ordinates represent quantities of sodium chloride, NaCl; the abscissæ, quantities of potassium chloride, KCl. The concentration of a saturated solution of sodium chloride at 25° is represented by a point *A*, and of a saturated solution of potassium chloride by a point *B*. The line *AC* represents the composition of solutions of sodium chloride saturated in presence of the proportions of potassium chloride indicated by the abscissæ of the curve *AC*; and the line *CB*, the composition of solutions of potassium chloride saturated in presence of the proportions of sodium chloride represented by the ordinates of *CB*. The point *C* represents the composition of a solution saturated with both salts. The composition of all possible solutions of these two salts can be represented by a point inside the surface *AQBO*, points outside this area can only represent super-saturated solutions not in a state of equilibrium. Hence, when a solution containing equal molecular proportions of both salts—say 50 gram-molecules per 1000 molecules of water—is evaporated, the relative proportions of the two salts will not alter; water alone is removed and the solution becomes more and more concentrated, so that the abscissa and ordinate, representing the composition of the solution, change from those of the point *P* to those of the point *Q*—when *P* is left of *Q*. At *Q* the solution will be saturated with respect to the less soluble potassium chloride, and this salt will accordingly crystallize from the solution; as evaporation proceeds, potassium chloride continues to separate; the successive states of the solution are represented by points passing from *Q* in the direction *BQ*.

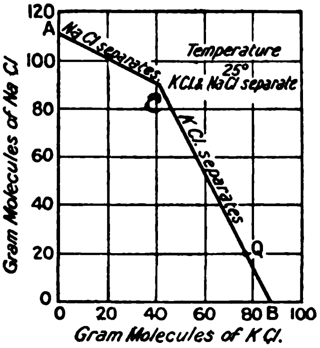

Fig. 1. — Solubility Curves of Mixed Solutions of Sodium and Potassium Chlorides.

The phenomenon is really wonderful. The molecules of both sodium and potassium chlorides are uniformly diffused throughout the original solution; but, as soon as the evaporating liquid has attained a certain concentration, the molecules of the potassium chloride alone commence crystal-building; and ordered cosmos grows out of a chaotic mixture of molecules; the molecules of the solute appear to be dominated by some occult power, for they withdraw from the solution in harmonious order, which is followed as rigorously as the bricklayer, when building a mansion, places brick upon brick, according to the plan predetermined by the architect. The operation continues until the solution has the composition represented by the point of intersection, *C*, of the lines of *A* and *B*. At *C* the solution is saturated with respect to both salts. Any further concentration of the solution will result in the deposition of sodium and potassium chlorides side by side, and at rates which are proportional to the concentration of the solution. A solution which has the composition represented by the point *C* continues to deposit a mixture of crystals of a constant composition until it has been evaporated to dryness. J. H. van't Hoff (1905) calls the point *C* **the end-point of crystallization,** and he draws attention to the fact that when a solution of the two salts is depositing crystals of one of them, the composition of the solution changes further and further away from the composition of a saturated solution of that salt until the end-point of crystallization is reached. Similar remarks would have been applicable for a solution with, say, 90 gram-molecules of sodium chloride and 20 of potassium chloride. Sodium chloride would separate along the curve *AC* until the end-point *C* was attained. Here the molecules of both salts are simultaneously building crystals side by side.

§ 2. Fractional Crystallization

> What chemist who has watched under the microscope the beautiful symmetrical manner in which minute particles of a substance separating in solid form from solution, arrange themselves in geometrical figures obeying well-established mathematical laws, can pretend to explain the cause of the astounding behaviour of inert lifeless matter ?—H. C. Bolton.

The molecules of a substance in solution appear to be distinct individuals before crystallization, while **in a crystallizing solution each molecule appears to exert some specific attraction on its fellow molecules** to enable them to separate from the solution in a definite orderly way so as to form crystals whose architectural symmetry has been called "a miracle of beauty and delight." The alignment of the molecules in a growing crystal can proceed so rapidly that a few seconds of our time must appear a long era in the molecular world. Thus, if concentrated solutions of aluminium and potassium sulphates be mixed, and constantly stirred, a mass of transparent sparkling crystals of alum is immediately precipitated. The molecule of alum is represented in its simplest form by $KAl(SO_4)_2.12H_2O$; and accordingly, in these few seconds, the atoms have had ample time to arrange themselves in molecular groups each containing at least 48 atoms; and the molecules, in turn, have had time to align themselves in a precise methodical way to form an indefinitely large number of regular octahedral crystals. Each tiny crystal contains more molecules than could be enumerated by continuous counting for myriads of years.

G. la Valle noted in 1853 that under suitable conditions crystals grow in directions in which growth is opposed by an external force; this was denied by H. Kopp, but the fact has been abundantly confirmed by O. Lehmann and others. Still further, the force—*crystallizing force*—exerted by a growing crystal as it builds up its structure, molecule by molecule, must be comparatively great. Sodium sulphate or thiosulphate crystallizing in the pores of earthenware will shatter the body into small fragments.[1] G. F. Becker and A. L. Day (1905)[2] placed a plate of glass, supporting a kilogram weight over a growing crystal of alum about one centimetre in diameter, and found that it raised the weight several tenths of a millimetre. The disintegration of rocks, etc., by the growth of ice crystals; the bursting of a test-tube when plaster of Paris is allowed to set therein; and the disintegration of porous bricks and tiles by crystallizing sodium sulphate, are illustrations of a definite and powerful crystallizing force. F. E. Wright and J. C. Hostetter found that when crystals are grown under pressure, the results agree with an hypothesis made by J. Thomson, namely, that during crystallization each particle—atom or radicle—enters into the crystalline state in the condition of the crystal at the point to which it becomes affixed; and that if the crystal be under a state of strain, the freshly deposited particle enters into the same state of strain.

The separation of a mixture of potassium chloride, chlorate, and perchlorate.—When a solution of two (or more) salts is slowly evaporated, if the solubilities of the salts differ appreciably, one salt may pass more or less completely out of solution before the other commences to separate; provided, at the temperature of separation, the solubilities are independent of one another so that the salts exhibit no tendency to unite chemically or physically.

Warm 50 grams of potassium chlorate, just above its melting point, in a new porcelain dish, and keep the mass at that temperature until it becomes viscid and almost solid. This will occupy from ten to fifteen minutes. Let the mass cool. It contains undecomposed potassium chlorate, some potassium chloride, and potassium perchlorate. Add 50 c.c. of hot water, say at 50°, and when all has disintegrated and the solution cooled, the crop of crystals of potassium perchlorate can be filtered off. Evaporate the filtrate until a drop crystallizes when rubbed on a cold surface. The first crop of crystals which separates as the solution cools is mainly potassium perchlorate, because this salt is so very much less soluble than the other two; 100 c.c. of water, at 15°, holds in solution about 36 grams of potassium chloride, 6·6 gram of the chlorate, and 1·5 gram of the perchlorate. The solubility curves of these three salts are shown in Fig. 2. If the evaporation be carried too far, crystals of potassium chlorate will separate. The first crop of crystals is redissolved and again allowed to crystallize by cooling the hot solution; potassium perchlorate can thus be obtained almost free from the other two salts; and by repeated recrystallization it is possible to isolate the salt in a high degree of purity. Recrystallization is needed to get a more pure product, because the crystallizing salt often carries down with it some of the mother liquid, or some of the other salts dissolved in the mother liquid. Indeed, it is perhaps impossible to prepare crystals quite free from the imprisoned solvent. If the evaporation be continued after the separation of the perchlorate, potassium chlorate will eventually separate, and the product must be recrystallized in order to isolate a purer salt. The remaining mother liquid contains potassium chloride contaminated with the chlorate.

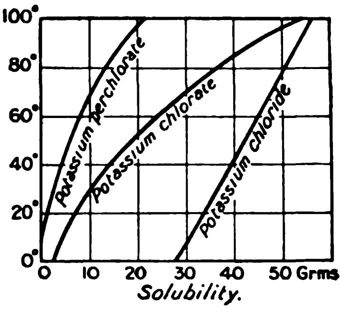

FIG. 2.—Solubility Curves of Potassium Chloride, Chlorate, and Perchlorate.

This operation—**fractional crystallization**—is sometimes a useful method of separating salts which differ appreciably in solubility. In some cases it is the only method of separation available, even though the salts in solution do not differ very much in solubility. The process of fractional crystallization is then very laborious, involving, maybe, scores of crystallizations and recrystallizations. In other cases it is impossible to separate the salts in this way, because double salts separate.

As a rule, the slower the process of crystallization, the larger and more perfect the crystals. The chemist must learn from the mineralogist many facts concerning the slow growth of crystals because some natural phenomena cannot be imitated in the time at man's disposal, for, said J. W. Judd in his work, *The Rejuvenescence of Crystals* [3]:

> Nature is unstinting in the expenditure of time upon her handiwork, and her slow elaboration of crystals during millions of years accounts for the presentation of some natural products of curious phenomena that are not reproducible in test-tubes and crucibles.

Crystals are usually more or less distorted because, owing to local differences in concentration, the crystallizing solution, in the vicinity of some faces of the crystal, may be more concentrated than the others. Perfect crystals are rarely found in nature or in the laboratory.[4]

The purification of salts by recrystallization is a well-known process. The Latin Geber frequently alludes to the purification of salts by recrystallization, and the process was recommended by R. J. Haüy [5] in 1801 for the purification of nitre. The operation, however, was the subject of a controversy in 1814. Thus, F. Clément and J. B. Désormes [6] in their *De l'épuration des corps par la cristallisation,* cited many experiments which demonstrated the fact, and remarked that chemists who did not believe in the process should cease to purify their salts in this manner. The operation of fractional crystallization has been compared with fractional distillation; the former is determined by the solubility of a body at a given temperature, the latter by the temperature of vaporization.

Inclusions in crystals.—Ideal crystals are homogeneous, but crystals are sometimes coloured with pigments—*e.g. smoky quartz*—and they may also have other inclusions discernible under the microscope. There may be cavities in the crystal containing gases of various kinds—*e.g.* air, carbon dioxide, hydrocarbons, sulphur dioxide, etc.—or the cavities may be wholly or partially filled with liquid —*e.g.* water, liquid carbon dioxide, salt solutions, etc. Fig. 3 shows a photograph of quartz (from Cornish granite) with four cavities containing a liquid, each liquid inclusion has a bubble of air or gas. If the liquid be condensed carbon dioxide, the crystal was probably formed under great pressure. Similar cavities are found in natural crystals of rock salt, calcite, fluorspar, topaz, beryl, barytes, etc. A cavity formed at an elevated temperature may be filled with liquid; as the temperature falls the liquid contracts faster than the solid, and a space containing a vapour bubble results. The cavities may also contain crystals which have separated from the solution. Then again, crystals of a totally different substance may be embedded (included) in the larger crystal—*e.g.* in the so-called *sagenitic quartz* (*σαγήνη*, a net)—needle-like crystals of rutile cross one another, giving a reticulated or net-like appearance to the quartz; and in the variety poetically called *veneris crinis* or *Venus' hair*, or *flèches d'amour* (love's darts), the quartz encloses bunches of reddish-yellow rutile needles; this variety of quartz is probably the *chrysothrix* (golden hair) of the Orphic poem. *Aventurine quartz* has imprisoned golden or brassy-yellow spangles of, presumably, mica. H. C. Sorby (1858) [7] has shown that crystals deposited from solutions usually contain cavities enclosing small quantities of the mother liquid, and this the more the quicker the rate of crystallization.

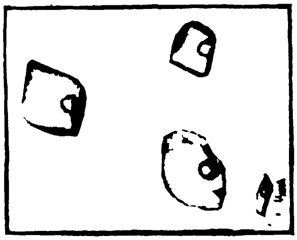

FIG. 3.— Quartz in Cornish Granite showing Four Cavities with Liquid Inclusions and Gas Bubbles (× 1000).

Experiments on this subject can be made conveniently by allowing a solution of potassium chloride to evaporate slowly; the crystals which form are more or less opaque towards the centre, and clear and transparent elsewhere. Under a high magnification (50 to 400 diameters) in a shallow glass cell containing a cold saturated solution of the salt itself, the opacity appears to be produced by vast numbers of minute cavities arranged in bands parallel to the sides of the crystals. The cavities are full of liquid. This is demonstrated by allowing sodium chloride to crystallize from a solution tinted with potassium dichromate, the crystals of sodium chloride appear yellow to the naked eye; and on magnification, this coloration is evidently an effect due to a large number of cavities in the colourless crystals filled with yellow liquid.

The decrepitation of common salt on heating is due to the vaporization of the included water; similarly, the decrepitation of some varieties of quartz just over 1000° is due to the release of imprisoned gases. So important is this imprisoned solvent in the preparation of pure material for exact work that, according to T. W. Richards (1903), many records of painstaking determinations of atomic weights can be safely ignored because the contamination of the materials from this cause has been entirely overlooked, or inadequate means have been taken to counteract the effects.

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§ 3. Crystals

> In whatever manner, or under whatever circumstances, a crystal may have been formed, whether in the laboratory of the chemist or in the workshop of nature, in the bodies of animals or in the tissue of plants, up in the sky or in the depths of the earth, whether so rapidly that we may literally see its growth, or by the slow aggregation of its molecules during perhaps hundreds, perhaps thousands of years, we always find that the arrangement of the faces of the crystal, and therefore its other physical properties, are subject to fixed and definite laws.—H. P. GURNEY.

When homogeneous substances solidify from a state of vapour, fusion, or solution, their particles often cohere so as to form solid figures—**crystals**—with regular symmetrical shapes bounded by plane faces. The solids are then said to be crystallized. M. A. Capellar's *Prodromus crystallographiæ*, published at Lucerne in 1723, was the first book devoted to crystallography; and in an essay on the crystal forms of calcspar, in 1773, T. O. Bergmann[1] made what may be regarded as a first approximation to a definition of crystals. He said: "Crystals are bodies which, though destitute of organic structure, yet externally resemble geometrical figures more or less regular." The term crystal originally referred to the ice-like appearance of rock crystal or quartz, but the angular shape of this substance, as well as that of garnet, beryl, and other minerals, seems to have been regarded by the ancients as an accidental and not an essential characteristic. The alchemists must have studied many salts and noticed that on evaporation of their solutions, definite and regular crystals were obtained which were to some extent characteristic of particular salts. Thus, at the end of the sixteenth century, A. Libavius, in his *Ars probandi mineralia* (Francofurti, 1597), stated that the nature of the saline components of mineral waters could be ascertained by an examination of the crystalline deposit left on evaporating the water to dryness; and in his *Chemical Lectures* (London, 1712), J. Freind said:

> Let these salts be never so divided, and reduced into minute particles, yet when they are formed into crystals, they each of them reassume their proper shape; so that one might as easily divest and deprive them of their saltness, as of their figure. This being an immutable and perpetual Law, by knowing the figure of the crystals, we may understand what the texture of the particles ought to be, which can form those crystals.

The constancy of interfacial angles.—In 1669, N. Steno,[2] in an essay *De solido intra solidum* (Florentiæ, 1669), showed that in spite of numberless variations in the size and shape of crystals of different specimens of rock crystal, he could detect no variation in the angles between the faces. Thus, by cutting a series of specimens at right angles to the faces of the prism, he obtained six-sided sections with sides of varying length, and apparently different figures, but the angles were all equal, each to each—Fig. 4. Soon afterwards, D. Guglielmini, in his *Riflessioni filosofiche dedotte delle figure de' sali* (Bononeæ, 1688), and in his dissertation *De salibus* (Venetiæ, 1688), generalized N. Steno's observation, and asserted that the crystals of every salt have their own peculiar shape which never changes, and that even in imperfect and broken crystals, the interfacial angles are always constant. As a result of an examination of over four hundred crystal forms, J. B. L. Romé de l'Isle confirmed the earlier generalization of D. Guglielmini, and developed the idea further in his *Essai de cristallographie* (Paris, 1772). **Every crystalline substance of definite chemical composition has a specific form characteristic of that substance.** This is sometimes called **Haüy's law,** because R. J. Haüy (1801) may be said to have "erected the science of mineralogy on a crystallographic basis which was in turn founded on this principle." The faces of crystals of the same substance may vary in size and shape; but if the crystals possess the same chemical composition, and are at the same temperature, the interfacial angles have the same numerical value. In other words, **the angles between similar faces of crystals of the same substance are precisely the same, and are characteristic of that substance.** As indicated above, this generalization was first announced by D. Guglielmini (1688). This means that the crystalline form of a substance is not determined by the absolute position nor by the sizes of the faces of the crystal, but rather by the dimensions of the interfacial angles. The primary dominant faces, so to speak, may persist, but the angles and edges of some of the crystals may or may not be truncated and bevelled (*cf.* Fig. 4), giving rise to new facets, or secondary faces. As a general rule, when crystals are formed rapidly the faces are simple, while the faces of crystals which have grown slowly may be more complex. The dominant form of the crystals of a given substance "persists in spite of these variations; although the primitive fundamental form can sometimes be recognized, the crystal can be interpreted only after careful study." The doctrine of the identity of the primitive form of the crystals of a substance was not at first generally accepted; and even so late as 1783, G. L. L. de Buffon, in his *Histoire naturelle des minéraux* (Paris, 1783–88), combated the idea. He said:

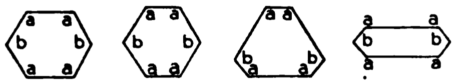

FIG. 4.—N. Steno's Demonstration of the Equality of the Angles of Quartz Crystals of Different Sizes.

> No crystallization will ever afford a specific character, for the variety is infinite; not only are there forms of crystallization common to several substances of a different nature, but, on the contrary, there are few substances of the same nature which do not present different forms on crystallization. It would thus be more than precarious to establish differences or resemblances, real and essential, by means of this variable and almost accidental character. . . . Our crystallographers thus propose . . . to substitute ideal combinations for the real facts of Nature.

This is a remarkable testimony to the difficulties which the contemporaries of D. Guglielmini and R. J. Haüy encountered in seeing order among the diverse forms of the crystals of a substance.

In 1767, C. F. G. H. Westfeld,[3] and in 1773, T. O. Bergmann, stated their opinion that the different forms of crystals could be regarded as variations of a very small number of primitive forms, and J. B. L. Romé de l'Isle (1783) followed up the idea, using the method employed by geometers—*e.g.* W. Janitzer (1568) and J. Kepler (1619). J. B. L. Romé de l'Isle derived all the different forms of crystals from six primitive forms by replacing similar edges and corners by one or more planes. The idea was still further developed by R. J. Haüy (1782) in a remarkable *Essai d'une théorie sur la structure des crystaux* (Paris, 1784); it was extended by F. Mohs (1820) and others;[4] and finally culminated in the seven systems now in general use. Some emendations must be made to the law of the constancy of crystalline form.

Crystal mimicry.—At first sight there appears to be a kind of mimicry among the crystals of some minerals. for a mineral sometimes has the external crystalline form characteristic of a totally different mineral species. Such crystals are said to be **pseudomorphs,** and they appear to have been formed by secondary chemical processes whereby the original mineral has been decomposed, and its place taken by another. As a result of some such process of infiltration, quartz crystals are sometimes found with the external form characteristic of calcite or fluorspar, or barytes ; tin-stone in the form of felspar ; galena (cubic) in the form of pyromorphite (hexagonal) ; etc. The apparent mimicry is confined to the external form of the crystals, the internal structure is that peculiar to the normal crystals. A crystalline substance with its own characteristic outlines is said to be **idiomorphic.**

The twinning of crystals.—It appears as if, during the building of some crystals, the structural units instead of continuing to deposit in layers with units oriented all in the same direction, suddenly commence to deposit in layers turned through an angle—sometimes 180°—about an axis perpendicular to those previously laid down. As a result, two individual crystals appear to be united in a common plane, or to penetrate one another symmetrically. The phenomenon is called *twinning* ; and the double crystal is called a **twin.** Twinned crystals of selenite often have the appearance of an arrow-head, Fig. 5 ; tinstone similarly forms twinned crystals. Sometimes too, after a number of layers of the crystal units have been laid in the new direction, there is an abrupt reversion to the original form. The result is a kind of twinning band which has different texture from the material on either side.[5] Sometimes, too, a series of parallel bands are formed in this way. R. J. Haüy was interested in twinning. He pointed out that the phenomenon is subject to certain laws, so that "instead of precipitating themselves tumultuously on one another, the crystals have in a prearranged manner prearranged their disposition." There is a plane of juncture "so that the two structures follow their regular development, each in its sphere, towards their common plane, which forms their respective limits." Fig. 6 is a photograph of a twinned crystal of pyrite from Minden (Prussia). The twinned crystals may not only be juxtaposed but they may also be interpenetrant. The interpenetration may be so complete as to form a single crystal, which may then appear to have a higher degree of symmetry than it really possesses. Thus a rhombic crystal may be so twinned that externally it cannot be distinguished from a tetragonal crystal. Crystals so twinned are pseudo-symmetric, and this form of mimicry is called **mimetic twinning**—*e.g.* rhombic aragonite may be so twinned as to form a pseudo-hexagonal prism.

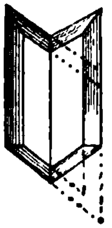

Fig. 5.—Twinned Selenite Crystal.

Fig. 6.—Twinned Crystal of Pyrite.

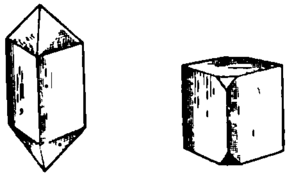

Fig. 7.—Dimorphic Forms of Alkali Diphosphate.

Substances with crystals of more than one form.—Crystals of different substances usually have different forms ; crystals of the same substance developed under the same conditions have the same form ; but crystals of the same substance developed under different conditions may or may not have the same form. For instance, crystals of sulphur formed above and below 94·5° are different ; there are two differently shaped crystals of sodium phosphate—Fig. 7. These are cases of *polymorphism*. The *habit* of crystals of sodium chloride is octahedral, if grown in alkaline solutions; and cubical, in neutral solutions; and conversely, crystals of alum are usually octahedral, but cubical if grown in alkaline solutions. The two phenomena, change of habit and polymorphism, are quite different. Change of habit does not mean a change of phase, while polymorphic modifications represent different phases. There is no change of properties in crystals with a different habit, but the transformation from one polymorphic form to another usually involves a discontinuous change of scalar and vectorial properties, and it takes place within a definite range of temperature, or at a definite temperature, the so-called transition point.

A. G. Werner mistook aragonite from Spain, described by J. B. L. Romé de l'Isle,[6] for apatite, but M. H. Klaproth showed that the composition is the same as that of calcspar, and he said that aragonite must be regarded as ordinary calcspar, which while retaining the same constituents has been altered by a change in the disposition of its constituent parts. If this be the correct interpretation, it was recognized that R. J. Haüy's law required revision. In consequence, a great many new analyses were made by French and German chemists—A. F. de Fourcroy and L. N. Vauquelin, L. J. Thénard and J. B. Biot, L. J. Proust, C. F. Bucholz, J. B. Trommsdorff, etc. A. F. de Fourcroy and L. N. Vauquelin said that their analyses rendered it necessary for mineralogists to inquire if it is not possible for the same substance to assume different forms; and L. J. Thénard and J. B. Biot added that aragonite and calcspar are compounded from the same elements (*principes chimiques*) united in the same proportions; and that the same elements uniting in the same proportions can form compounds with different physical properties, because the molecules of the constituent elements can combine in many different ways. The analyses showed that impurities are present in the native minerals. In 1801, L. N. Vauquelin and M. A. Klaproth showed that anatase and rutile consisted of titanic oxide along with some impurities; while A. Laurent and P. Dejussieu found that marcasite and pyrite were modifications of iron disulphide—*comme l'analogue de l'arragonite*. A. Stromeyer, in his *De arragonite ejusque differentia a spatho calcareo rhomboidali chemica* (Göttingen, 1813), recorded the presence of strontium in aragonite, and that this had been overlooked in previous analyses. This lent support to R. J. Haüy's contention that small quantities of a foreign agent with a great power of crystallization may cause a compound to change its crystalline form. A. Laugier found no difference in strontian-free and strontianiferous aragonite. The question was not decided until E. Mitscherlich's work on polymorphism of sulphur and sodium dihydrogen phosphate, $NaH_2PO_4.H_2O$, had been accepted.

Each kind of crystal is stable only within a limiting range of temperature, so that the amended form of Haüy's law is: **Every crystalline substance of definite chemical composition has one specific stable form within certain definite limits of temperature.** Substances which crystallize in two different forms are said to be **dimorphous.** Fig. 7; and substances which crystallize in three different forms are said to be **trimorphous.** Titanic oxide, TiO_2, for example, is known in three forms—rutile, anatase, and brookite. Two of these forms will probably be found to be in a metastable condition at ordinary temperatures. Magnesium metasilicate, $MgSiO_3$, exists in four different crystal forms, and it is **tetramorphous. Polymorphism** is the general term applied to the phenomenon when a substance crystallizes in more than one form. When the crystals are similar and yet so fashioned that one is the mirror image of the other, the crystals are said to be **enantiomorphic**—*e.g.* *d*- and *l*- quartz, *d*- and *l*- tartaric acid, etc. Enantiomorphic crystals are not usually regarded as polymorphic forms.

One or more faces of a crystal may be abnormally developed or stunted in growth. During the growth of a crystal, the concentration of the mother liquid is rarely so evenly balanced on all sides as to allow the growth to proceed with the same rapidity in all directions. The crystal will grow fastest where the solution is most concentrated. If a crystal grows on the bottom of a liquid at rest, flat plates, almost parallel with the bottom of the vessel, may be formed; while if the solution be agitated during crystallization, a more uniform growth in all directions may prevail. This is not all the story, for a crystal may habitually grow more rapidly in *one* direction so as to form a prismatic crystal—**prismatic habit**—*A*, Fig. 8. This may take the form of needle-like or **acicular crystals**; hair-like or **trichitic crystals**; arborescent, branching, or **dendritic crystals** (δένδρον, a tree); or fibrous masses; or the crystals may grow in *two* directions so as to form a tabular or plate-like crystal—**tabular habit**—*B*, Fig. 8, this may take the form of groups of thin separate plates, fan-like more or less divergent plates, feather or branching aggregates (*e.g.* the six-rayed snow crystals); or again the crystals may grow uniformly in all *three* directions, and the ideal cube—*C*, Fig. 8—will be produced. In the well-known *en tremies* or hopper-shaped crystals of bismuth, quartz, or of sodium chloride—*D*, Fig. 8—growth has been fastest along the edges and corners of the cube, and the crystals assume the form of hollow cubes—*hopper salt*. These crystals can be obtained by the addition of a little alum to the salt. In every case of distorted cubical crystals, the angles between the faces, however, will remain unchanged—90°. Similar remarks apply to the different forms of crystal other than the cubes.

The most suitable condition for uniform growth in all directions occurs when the growing crystal is suspended in the middle of the given solution by means of a thread. The crystal then sometimes approximates more or less closely to the ideal form. If the crystallization of a solution be rapid, the crystals are usually much smaller than if the process be slow. O. Lehmann laid down the empirical rule:

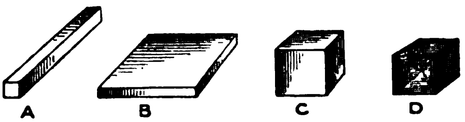

FIG. 8.—Ideal and Distorted Cubic Crystals.

> When a substance crystallizes from a solution owing to the withdrawal of the solvent, the crystals are the more irregular in shape (i) in proportion as the separation occurs with greater rapidity; (ii) in proportion as the solvent is the more viscid; and (iii) in proportion as the substance is less soluble.

The minute crystals precipitated by alcohol from solutions of barium chloride, copper sulphate, lead nitrate, etc., were found by P. Gaubert to be almost perfect in form.[7]

As a rule, needle-shaped (*acicular*), fibrous, hair-like (*trichitic*), or branching fern-like, moss-like, or tree-like forms (*dendritic*) grow in labile solutions where crystallization is rapid, while well-formed characteristic crystals grow in metastable solutions where growth is slow and uniform. The dendritic forms are also common with highly viscous solutions, and with crystals grown in the presence of colloidal suspensions. Ammonium chloride, calcium sulphate (Fig. 10), copper sulphate (Fig. 9), or potassium dichromate (Fig. 11) can be used in illustration. When, say, the last-named salt is deposited slowly from metastable solutions, well-developed crystals are formed, while if crystallized from labile solutions feather-like aggregates are developed. This is illustrated by Fig. 11, which shows that the first crystals deposited have arborescent branches, while the later crystals have the regular crystalline form.

Again, the *habit* of a crystal may change when grown from liquids containing other salts in solution. This fact was noted by Robert Boyle[8] in 1666, in the words: "Notwithstanding the regular and exquisite figures of some salts, they may by the addition of other bodies, be brought to constitute crystals of very differing, yet curious shapes." Again, J. B. L. Romé de l'Isle (1783)[9] showed that the crystals of *sodium chloride* which separate from an aqueous solution containing fresh urine are octahedral, and not cubical. Urea or carbamide can be used provided, as J. W. Retgers emphasizes, not too small a quantity of urea is present. The presence of colloids in a solution usually inhibits or modifies crystallization; thus, sodium chloride crystallizing from a solution containing a trace of gum arabic forms tree-like or dendritic-masses. Again, *ammonium chloride* crystallizing from cold aqueous solutions forms dendritic masses, but if the saturated solution is tinted yellow with ferric chloride, and a few crystals of ammonium acetate are dissolved in the solution, well-formed cubic crystals of ammonium chloride separate out. Further, if a few grains of octahedral alum crystals be added to a supersaturated solution of potash alum, octahedral crystals are formed; whereas, if potassium carbonate be added to a boiling solution, the liquid, on cooling, deposits cubic crystals. Z. Weyberg has studied the effect of hydrochloric acid on the habit of the crystals of alum; and H. Gerhardt the effect of foreign salts on the crystals of barytes. Potassium chlorate gives *prismatic crystals* when grown in aqueous solutions; but if much calcium chloride be present, small needle-like crystals are obtained, and if some potassium iodate be present long plate-like crystals separate from the solution—the crystal angles, however, are the same in each case; or else the different sets of planes which bound the crystals are all derived from the same internal structure by the suppression of certain planes, and the abnormal development of others. Near the beginning of the nineteenth century R. J. Haüy [10] showed that the crystals of axinite which are coloured violet by manganese show additional faces not found on the crystals of axinite coloured green by chlorite, and that the green-tinted crystals are more regularly shaped and do not present the striated surface observed on the violet-tinted crystals. He said:

FIG. 9.—Copper Sulphate grown in a Labile Solution.

FIG. 10.—Calcium Sulphate grown in a Labile Solution.

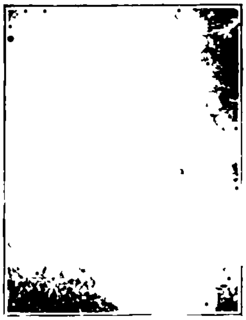

FIG. 11.—Potassium Dichromate grown in a Labile Solution.

> The molecules of a substance in a solution and disposed to unite in the formation of a crystal, are at the same time attracted towards each other and even by the molecules of the solvent itself; and it is because their mutual affinity exceeds that of the solvent that crystallization operates. . . . If there are foreign substances in the solution, they will modify the action of the liquid upon the coalescing molecules.

The general shape of a crystal, or, as it is usually called, the **habit of a crystal,** thus depends upon the character of the distortion it has suffered during growth, and the distortion is often a characteristic feature of the crystals of a given substance. Calcite occurs as rhombohedra, scalenohedra, or hexagonal prisms, but all can be referred to one fundamental form. However much the crystals may be distorted, the angles between like faces have the same value, and in consequence, similar faces can be imagined at the same distance from the centre of the crystal. In this way, the **ideal form of a crystal** can be derived from that of a distorted crystal. The term **distortion,** as distinct from habit, is also applied to certain crystals which appear as if they had been mechanically deformed—*e.g.* twisted crystals of topaz.

If a layer of gelatine containing a solution of salt be allowed to dry slowly at the temperature of the room, the water is lost quickest at the edges, and as the solution approaches a state of supersaturation, crystals of the salt begin to separate.

There are three ways in which the crystals may appear: (i) single crystals irregularly distributed are formed—*e.g.* sodium chloride; (ii) dendritic lines or branches of crystals may extend from the edges towards the middle of the gelatin—*e.g.* potassium chromate; or (iii) a number of strips, concentric lines, or bands of crystals separated by zones free or almost free from crystals may be formed—*e.g.* trisodium phosphate or ferrous sulphate. E. Liesegang's explanation of the phenomenon of **rhythmic or periodic crystallization** is as follows:

> Before the first crystals are formed at the outermost edge there is present at this place a zone of supersaturated salt solution. As the degree of concentration increases a spontaneous deposit of the salt necessarily occurs. These rows of crystals act as a nucleus upon the supersaturated solution in their vicinity, *i.e.* the solute diffuses towards the crystals and increases the size of the latter. In this manner an area poor in salt content is produced. As the loss of water proceeds this area becomes supersaturated in its turn. Accordingly the impoverishment in salt content becomes still more marked through the solute travelling towards the nuclei. Finally, however, the migration in this area ceases entirely because of the fact that the solution is entirely dried up. In the mean time, at a certain distance from the first row of crystals, the salt solution reaches such a degree of supersaturation, that the separating out of the salt begins spontaneously to occur once more. This row of crystals grows just as the first one did, and the process is repeated indefinitely. The more abrupt the precipitation, the closer together the bands of crystals. Since the first spontaneous deposit of crystals occurs very suddenly, while their increase in size through diffusion takes place more slowly, each band may exhibit a very different aspect as regards its inner side respectively, *i.e.* dense aggregates of small crystals on the outer side and larger crystals on the inner side.

The phenomenon of rhythmic crystallization is analogous with that of rhythmic precipitation.[11]

Cleavage.—Crystals can usually be readily split along certain definite planes. Thus, a fragment of calcite when struck sharply and lightly will split into a number of fragments of variable size but similar form—rhombohedrons; a crystal of rock salt similarly treated splits into little cubes; while mica splits into thin plates. Fluorspar, selenite, galena, and hornblende also illustrate the property very well. Orthoclase—normal potash felspar—splits in two directions with an angle of 90° between them, whereas the two cleavages of albite—ordinary soda felspar—are inclined at an angle of about 86°. Galena, like rock salt, splits in three directions, fluorspar in four. This property is termed *cleavage.* The cleavage of calcite into six-faced rhombohedra was noticed by T. O. Bergmann in 1773; and this suggested to R. J. Haüy that the ultimate components of crystals are irreducible formative nuclei, so that J. Herschel could say:

> From the moment that the genius of Haüy discovered the general fact that the crystals could be cloven or split in such directions as to lay bare their peculiar primitive or formative forms, from that moment, mineralogy ceased to be an unmeaning list of names, a mere laborious cataloguing of stones and rubbish.

Fracture is different from cleavage, for it is irregular and has no definite relation with the crystalline form. Cleavage is obviously a structural weakness related to the mode of aggregation of the particles which build up the crystal, and it will be obvious that once a crack is started in a crystal, it will follow the line of least resistance, that is, where the structural units exert least cohesion. If a number of spheres or ellipsoids be packed together in a regular way, the cleavage will naturally follow the direction where the number of contacts per unit area is least. If a layer of spheres be formed so that each sphere touches six others, and a second layer be laid directly over the interstices of the first one; and a third layer over the interstices of the second; a pyramid is eventually obtained representing the half of a cubical crystal. In such a configuration, the number of sphere contacts per unit area parallel to the base is $2\sqrt{3}/d^2$, where d denotes the diameter of each sphere; and $4/d^2$ sphere contacts per unit area parallel to the front face. Hence, such a crystal will break more easily along a direction parallel to one of the cubic faces of the crystal since $2\sqrt{3}$ is less than 4. This corresponds with the fact that the cubic crystals usually have an octahedral cleavage.[12]

Cleavage is an important factor in the identification of some of the commoner minerals in rocks. The possible cleavage forms given by A. J. Moses, *The Characters of Crystals* (New York, 1899), in the cubic system the chief cleavages are *cube*—*e.g.* galena ; *octahedron*—*e.g.* fluorspar, diamond ; *rhombic dodecahedron*—*e.g.* sphalerite. In the hexagonal system, *basal pinacoid*—*e.g.* beryl, pyrosmalite ; *hexagonal prism*—*e.g.* nephelite, apatite ; *rhombohedron*—*e.g.* calcite, siderite ; *hexagonal pyramid* (rare)—*e.g.* pyromorphite. In the tetragonal system, *basal pinacoid*—*e.g.* apophyllite ; *tetragonal prism*—*e.g.* rutile, wernerite ; *tetragonal pyramid* (rare)—*e.g.* scheelite. In the rhombic system, *pinacoid*—*e.g.* topaz, anhydrite ; *prisms or domes*—*e.g.* barytes ; *pyramid*—*e.g.* sulphur. In the monoclinic system, *clinopinacoid*—*e.g.* orthoclase, gypsum ; *basal pinacoid*—*e.g.* muscovite, orthoclase ; *orthopinacoid*—*e.g.* epidote ; *orthodome*—*e.g.* epidote ; *prism*—*e.g.* pyroxene, amphibole ; *pyramid* (rare)—*e.g.* gypsum. *Triclinic crystals* usually admit of equally easy cleavages parallel to any principal plane.

It has been known for a long time that many substances in the act of crystallization in the dark exhibit a bright sparkling light. G. Pickel (1787),[13] for example, noted the phenomenon with potassium sulphate crystallizing from an aqueous solution; C. G. Schönwald, with a mixture of sodium sulphate and potassium sulphate crystallizing from aqueous solution, and he noted that the crystals also became luminous when rubbed. E. Wiedemann applied the term **tribo-luminescence** to the property exhibited by many crystalline substances of emitting a characteristic phosphorescent light when rubbed or crushed, while the emission of a phosphorescent light during crystallization is called **crystallo-luminescence**. The phenomenon was also observed by J. A. Giobert, and he said that if the potassium sulphate contains magnesium sulphate as impurity, the phenomenon does not occur, and he adds that previous exposure to sunlight strengthens the effect, although this observation has not been confirmed. K. S. L. Hermann observed the light during the crystallization of cobalt sulphate at —12°. The phenomenon with potassium sulphate has also been the subject of comment by J. J. Berzelius, F. Wöhler, and M. Sager; with strontium nitrate by C. H. Pfaff and E. Stieren; with potassium acetate by J. A. Büchner; with potassium chromate, selenate, sulphate, and chloride, and arsenious oxide by H. Rose. Numerous other salts have been added to the list by E. Brandrowsky, M. Trautz, J. Guinchant, D. Gernez, W. J. Pope, E. F. Farnan, etc. H. Rose thought the phenomenon with arsenious oxide was due to the change from an amorphous to a crystalline state; O. Lehmann said from one crystalline form to another—rhombic to cubic (octahedral). E. Brandrowsky disproved both these suggestions, and he tried to show that it was an electrical effect of the union of charged ions in the act of crystallizing from aqueous solution. He thought that the light was white, but H. B. Weiser showed that with sodium chloride the light is blue. The general cause of crystallo-luminescence is now attributed to chemical action due to the union of ions—*e.g.* $Na'+Cl'=NaCl$—but it is not at all clear what is really the nature of the reaction, if one such does occur. The light also has been spectroscopically examined, and so has the varying effects of the nature and concentration of the precipitant; of agitating the precipitating solution; of adding a colloid; of increasing the viscosity of the solution; and of variations of temperature. J. Plotnikoff has described a *triboluminiscope* for exhibiting the phenomenon.

The Florentine Academicians (1660) were the first to note the tribo-luminescence of many substances—flint, sugar, salt, agate, jasper, and quartz—when rubbed in darkness.[14] R. Boyle (1663) noted that diamonds exhibited the phenomenon; C. Mentzel (1675), W. Homberg (1730), J. Bernoulli and J. Cassini (1707), F. Hauksbee (1709), C. F. du Fay (1723), and many others, made analogous observations in the eighteenth century. A great many observations were afterwards recorded showing that the phenomenon is fairly general. L. Tschugaeff, for instance, tried over five hundred substances and found that about 25 per cent. showed tribo-luminescence, and he found some cyclic carbon compounds exhibited the phenomenon to a marked degree. The early observers thought tribo-luminescence is due to small particles of the solid becoming heated to incandescence by friction, but T. de Saussure demonstrated that this explanation is very improbable when he was able to obtain the effect by stroking a mass of calcium phosphate with a quill. J. P. Dessaignes[15] tried to demonstrate that the luminescence is an electrical effect, but J. Schneider showed that neither electrification nor heating are adequate explanations of the phenomenon. After an examination of the main hypotheses propounded to explain the phenomenon, H. B. Weiser concluded that tribo-luminescence is caused by chemical action, and photographic observations are in agreement with the same hypothesis. The colour of the light is specific in that it depends on the nature of the chemical reaction by which it is produced. All crystallo-luminescent substances are tribo-luminescent, but converse of this does not obtain.

The emission of light in luminescence has been explained, in part, in terms of the electronic hypothesis. In electro-luminescence, where the effects are produced by cathode rays, X-rays, Becquerel rays, or canal rays, the result is connected with the displacement or separation of electrons from the constituent atoms of a substance; in tribo-luminescence, where the effects are produced by friction or by crushing, frictional electricity is likewise involved in the displacement or separation of electrons; in chemi-luminescence, where the effects are produced by chemical action, the result is attributed to the rupture of a chemical bond which in turn is effected by the rupture of a valency electron; and finally, in photo-luminescence whether it be transient (fluorescence) or persistent (phosphorescence), where the effect is due to the action of light, it is also supposed that the partial or complete separation of electrons from the constituent atoms is directly concerned in the emission of light.

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§ 4. The Crystallization of Solids en masse

In crystals, we see one of the many ways of judging the internal world of molecules and atoms, and one of the weapons for conquering the invisible world of molecular mechanics which forms the main object of physical chemistry.—D. I. MENDELÉEFF.

When a supercooled liquid commences to solidify, rays of the solid grow into the liquid with a definite velocity,[1] and H. A. Wilson has shown that the relation between the velocity of solidification and the supercooling of some liquids fits the hypothesis that solidification is due to the difference between the internal pressure in liquid and solid, and that the molecules at the surface of a liquid are urged from liquid to solid by this difference in internal pressure. Modifying J. H. van't Hoff's method for calculating the osmotic pressure of a salt in solution from the lowering of the vapour pressure, he obtained the formula: Velocity of solidification$=k(T_m-T)/V$, where T_m represents the melting point of the solid on the absolute scale; T, the temperature at the surface separating liquid and solid, so that T_m-T measures the supercooling of the liquid; V, denotes the viscosity of the liquid; and k is a constant. Hence, the velocity of solidification of a pure substance is directly proportional to the actual supercooling of the solidifying liquid, and inversely as the viscosity. The results obtained with a number of substances agree with this hypothesis, although there is a disturbance due to the production of heat which accompanies solidification, and which raises the temperature at the surface of solidification.

Metals, during solidification, have a characteristic tendency to assume dendritic forms rather than simpler crystals. Even in the natural state, crystals of native gold, silver, and copper—all in the cubic system—frequently appear as dendritic growths. E. S. Dana, in a paper on the *Crystallization of native copper,*[2] has indicated a variety of these forms. The idealized representation, Fig. 12, illustrates a common method of growth.

It seems as if the nuclei of a crystallizing metal first stretch out long branching lines, each nucleus secures for its own crystal a large share of territory,[3] and then proceeds "in a leisurely manner to fill up the gaps." Under high magnification, it appears as if the branches radiating from adjacent crystals stop growing before they actually meet, and so form a kind of neutral territory between the tips of the branches. When the growth of all the radiating branches has been arrested in this way, the effect is almost the same as if each nucleus was enclosed by a cell-like boundary. As shown by D. K. Tschernoff and others, the crystal grains of ordinary cast metals thus appear to be produced by the mutual interference of adjacent dendrites, as illustrated diagrammatically in Fig. 13.

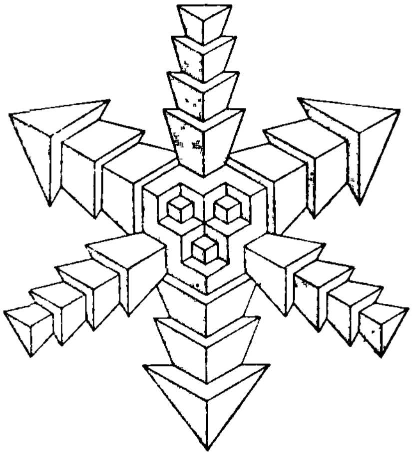

Fig. 12.—Idealized Dendrite of Copper.

O. Lehmann,[4] in his *Molekularphysik,* gives a satisfactory explanation of the phenomenon of dendritic growth in the case of supersaturated solutions: In the immediate vicinity of a growing crystal, a zone of liquid no longer supersaturated is formed owing to the removal of the solute, by the crystal. Further growth can occur only when the concentration of the solution in the immediate neighbourhood of the growing crystal is increased by diffusion or convection. The growth of the crystal thus depends upon the rate of supply of dissolved material from the surrounding supersaturated solution. The concentration currents—*Diffusionsströme*— thus set up are stronger where the difference of concentration is greatest, and this must be at the sharp angles of the growing crystal, because the crystal there presents the greatest surface to the liquid. Growth is thus accelerated with increasing velocity in the vicinity of the crystal angles. As a result, the crystal extends most rapidly in the direction of the concentration currents or supply columns bringing the food, so to speak, necessary for further growth. When the supersaturation is so reduced that the crystal can grow but slowly, the concentration currents will virtually cease, and the spaces between the branchlets will be gradually filled up.

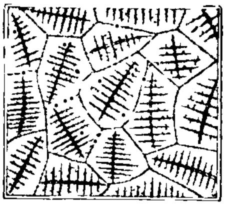

Fig. 13.—Diagrammatic Illustration of the Crystallization of Pure Metals.

O. Lehmann's explanation can be extended to the case of a cooling metal, where a certain amount of heat (latent heat of fusion) must be locally developed about each crystallizing centre; and the crystal must cool down to the crystallizing point before further growth can occur. Local currents of undercooled liquid will flow quickest from the surrounding liquid in the direction of the sharpest angles of each growing crystal, because there the temperature gradient is steepest. Hence, growth will be fastest in the direction of the currents of undercooled liquid.

G. Quincke's hypothesis of the cellular structure of metals.—When two partially miscible liquids—*e.g.* benzene with a little concentrated potash lye; or paraffin with one per cent. of a one per cent. soap solution—are shaken together, an *emulsion* is formed; and when one of the liquids is in large excess, the other may be distributed throughout the mass in such a way as to form what G. Quincke[5] called *foam cells—Schlaumkammern*—consisting of thin cell-walls of the liquid present in small quantity, enclosing drops of the other liquid. In G. Quincke's study of the formation of the emulsoidal structure, he showed how a similar structure might be obtained with solutions in which the cell-wall differed from the contents only in the concentration of the solute. He also suggested the hypothesis that the first stage in crystallization is the separation of the liquid into two immiscible phases, one of which is in relatively small quantity, and that the two liquids assume the foam-cell structure. He said that the purest of liquids still contains enough impurity to produce an eutectic which forms the cell-walls separating the primary metal. Crystallization then takes place within the foam cells, and the cell-walls are represented in the solid mass by the boundaries of the crystal grains. The arrangement of the crystalline particles, when actual solidification begins, is determined by the size and shape of the foam cells. This attempt to explain the cellular structure of metals does not appear to be satisfactory, since, although a homogeneous liquid at a certain temperature may separate into two immiscible liquids on cooling, there is nothing at all to show the phenomenon is so general as is required by G. Quincke's hypothesis. In those cases where crystallization has been observed under the microscope, the nuclei first formed control the ultimate structure, and there is no sign of a pre-existing foam-cell form. C. H. Desch has sought evidence of the assumed phenomenon and concluded that the grains of a solidifying metal have a tendency to assume the shape of foam cells, but he was not able to decide if foam cells are actually formed, or if the solidification of the metal proceeds from nuclei.

A cellular or tesselated structure is sometimes observed on the surface of cooling liquids. E. H. Weber (1855)[6] has recorded the formation of polygonal areas during the slow evaporation of a mixture of alcohol, water, and gamboge on a microscopic slide; and L. Frankenheim (1860) noticed a similar phenomenon during the evaporation of a solution of sulphur in turpentine. J. Thomson (1882) obtained a similar structure on the surface of soapy water; and C. Dauzere on the surface of mixtures of beeswax and paraffin or salol. According to H. Benard (1901), the best results can be obtained by exposing a layer of spermaceti, 0·4 to 2·0 mm. thick, in a metal trough 15 cm. diameter. The lower surface must be uniformly heated, and great care taken to eliminate disturbing influences. The partitioning approximates to an arrangement of regular hexagons. According to J. Thomson, the upper surface of the liquid is cooler than the portion below. Convection currents are set up, and the warmer liquid below ascends in vertical columns, spread out, and descends vertically downwards. The polygonal areas are the boundaries where the descending currents meet. The currents can be rendered visible, and photographed, by using fine particles of gamboge, lycopodium, graphite, etc., in suspension in the liquid. The surface polygonal areas are thus the upper surfaces of a series of prismatic columns produced by convection currents—*tourbillions cellulaires*—their axes are always vertical, never horizontal, and therefore the phenomenon is not the same in kind as that which gives rise to the cellular structure of metals. The phenomenon was studied mathematically by Lord Rayleigh in 1916.

Pure metals are aggregates of crystals which have been prevented from assuming a regular geometrical form by the crowding which occurs during the growth of neighbouring crystals. The crystals have grown more or less simultaneously and independently from a number of independent centres of crystallization. The facts must have been known to Robert Hooke[7] in 1665, and to R. A. F. de Réaumer in 1722; but H. C. Sorby was the first to show, in 1864, that a polished and etched surface of a metal is cut up into a number of polyhedral parts suggesting that the metal has a kind of cellular structure when examined under a suitable magnification and illumination. Under the microscope, also, the crystal boundaries appear as dark lines which are developed by the etching liquid attacking the surfaces of the various crystals at different rates. Although the internal structure of opaque crystals cannot be established so readily as would be the case if the crystals were transparent and could be examined under polarized light, yet, by etching the surface with suitable liquids, or by casting metals like cadmium or tin against a smooth glass surface, the evidence of an internal oriented structure is unmistakable. Thus, J. A. Ewing [8] has shown that—

> The surface of each grain consists of a multitude of geometrically similar pieces, parallel to one another so that their corresponding facets are all oriented one way. They are oriented in different ways as we pass from grain to grain, but in any one grain they face one way, and in consequence of that the light which falls on the grain is reflected in a perfectly uniform manner over the whole expanse of that grain, although it is reflected in a very different manner from the surface of any other grain. Over each grain the brightness is uniform, because the little surfaces are acting equally as regards the reflection of light.

The idea is well shown by the photograph by J. E. Stead, Fig. 14, from a specimen of iron with 4·5 per cent. of silicon in solid solution, and deeply etched. Cubic crystals of iron and octahedral crystals of copper have been obtained in an analogous form.

Although the cohesion of the molecules of a homogeneous liquid or amorphous solid can be explained by intermolecular attractions, auxiliary hypotheses must be invented to explain the stability of crystals, for the orientation of the structural units makes it appear as if the attractive forces are to some extent polar, because they act most favourably in certain directions. With aggregates of crystals, the distance between the surface molecules in two different systems of adjacent crystals must be much greater than between the molecules within each of the crystals; and consequently, it would appear as if the attraction of crystals for crystals should be less than the molecular attraction within the crystals themselves; or as if intracrystalline cohesion should be greater than intercrystalline cohesion. The intercrystalline boundaries or joints of a piece of metal of normal purity might therefore be expected to be a surface of weakness. W. Rosenhain [9] has emphasized the fact that the converse is usually the case. J. A. Ewing and W. Rosenhain have shown that the fracture of a piece of Swedish iron under a tensile load does not usually follow the intercrystalline boundaries, but rather cuts across the crystals themselves; otherwise expressed, **the intercrystalline boundaries of normally pure metals are not surfaces of special weakness, but are rather surfaces of special mechanical strength.**

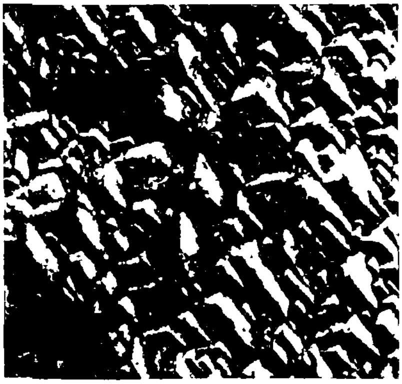

Fig. 14.—Surface of Silicon Steel. (J. E. Stead.)

The attempt has been made to explain the greater strength of the intercrystalline boundaries by assuming that the crystals grow, not by accretion layer by layer, but rather by the shooting out of dendritic branches which continue to grow until they meet one another, and finally interpenetrate one another so that the crystals are bound together by the interlacing of dendritic branches. W. Rosenhain and D. Ewen, however, reported that the "study of a large number of crystal boundaries does not seem to show sufficient evidence that the process is universal enough to account for the whole of the phenomena," and they favour the hypothesis that **there is a cementing medium between adjacent crystals in the intercrystalline boundaries which makes the crystals adhere together with special firmness.**

Although J. O. Arnold [10] has shown that a deleterious impurity may considerably weaken intercrystalline boundaries, for the presence of 0·1 per cent. of bismuth in gold was sufficient to surround the ductile crystals of the latter metal with a brittle envelope which readily fractured under a blow, yet many metals are known to be of sufficient purity to render highly improbable the assumption that the intercrystalline cement consists of impurities, more fusible metals, or eutectics. Consequently, Rosenhain concludes that the cement, if it exists at all, must be chemically the same material as the crystals themselves, and it is accordingly inferred that **the crystals of a metal of normal purity are surrounded by a thin layer of metal in an amorphous condition which acts as a cement, and which determines the mechanical strength of the metal itself.**

It is assumed that the forces at work during crystallization are such as to prevent the last vestiges of mother liquid from crystallizing, and that this liquid retains the amorphous condition while the metal cools down to the ordinary temperature. If the formation of a crystal requires not only the orderly arrangement of the structural units in the crystal, but also a grouping together of the molecules into aggregates to form the structural units, the liquid residue in the interstices when the growing crystals are nearly in contact will be unable to crystallize because there is not sufficient space for the aggregation of the molecules into the structural units.

The mechanical strength of a metal is determined by the strength of the intercrystalline cement; and if this cement be weakened or destroyed, the metal will show intercrystalline weakness. An intercrystalline cement was postulated by M. Brillouin, J. E. Sears, C. D. Bengough, and others [11] to explain the behaviour of metals when subjected to deformation under various conditions. For example, the effect of temperature on the tensile and elastic properties of metals is explained by assuming that at low temperatures the cement will accommodate itself to stresses in virtue of its elasticity while the crystals accommodate themselves to stresses by plastic deformation ; as the temperature rises, the cement weakens, and its elasticity diminishes ; when the cement has weakened sufficiently, the fracture under stress will be intercrystalline, and permanent elongation will occur under very small stresses because the cement does not prevent the crystals from sliding over one another.

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§ 5. The Internal Structure of Crystals

Imagine two hundred brilliant violin players playing the same piece with perfectly tuned instruments, but commencing at different places selected at random. The effect would not be pleasing, and even the finest ear could not recognize what was being played. Such music is made for us by the molecules of gases, liquids, and ordinary solids. They may be highly gifted molecules with a marvellous internal structure, but in their activity, each disturbs the others. A crystal, on the other hand, corresponds with the orchestra led by a vigorous conductor when all eyes intently follow his nod, and all hands follow the exact beat. This picture enables us to understand how crystals can exhibit whole ranges of phenomena quite wanting in other bodies. To me, the music of physical law sounds forth in no other department in such full and rich accord as in crystal physics.—W. VOIGT.

Crystals are not only peculiar in the regularity of their external shape, but they also possess a definite internal structure.—In illustration, E. Bartholinas (1669) noticed that if a rhombohedral crystal of Iceland spar be placed over a black spot on a strip of white paper, Fig. 15, the spot appears to be doubled and one of the two spots appears clearer than the other. If the rhombohedron be rotated, the spot which seems to be nearest to the eye appears to rotate about the other. There is, however, one direction in which the dots viewed through the crystal seem to coincide. It is readily demonstrated that the beam of light in passing through the prism (in all but one direction) is split into two rays, for if a single beam of light be passed through the crystal, two beams of light will emerge. This property of splitting the ray of light into two different rays is called **double refraction,** and the crystal of Iceland spar is said to be *doubly refracting*—while the crystal is *singly refracting* in the one direction in which the image of the two spots is not doubled. One of the two rays obtained by double refraction is called the **extraordinary ray**—R. H. Haüy's *rayon d'abèrration*—and the other the **ordinary ray**—R. J. Haüy's *rayon ordinaire.* In 1690, C. Huyghens discovered that each of these rays has certain peculiar properties different from those of an ordinary ray of light. Each ray is said to be *polarized.* The splitting of a ray of light into two rays by double refraction is called **polarization of light.** The effect of polarization on a beam of light can be illustrated as follows : The ray of light is supposed to be vibrating in all possible directions perpendicular to the path of the ray ; ✱ ; on passing through the prism these vibrations are resolved into vibrations in two planes at right angles to one another : + ; and are at the same time separated into two rays, — and |, vibrating in different planes at right angles to one another. The resolution of the heterogeneous mixture of vibrations into linear vibrations in one direction is called the **plane polarization of light.** If a crystal of tourmaline, also doubly refracting, be placed between the eye and the crystal of Iceland spar, Fig. 15, and then rotated, the two spots will alternately appear and disappear.

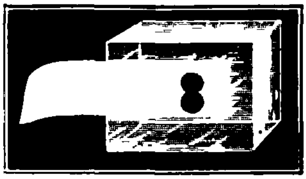


FIG. 15.—Illustration of the Double Refraction of Iceland Spar.

That direction in the crystal of Iceland spar in which light is singly refracted is called the optic axis of the crystal, and generally the directions parallel to which there is no double refraction are called the **optic axes** of a crystal. Crystals which have one optic axis—or one axis of no double refraction—are said to be **uniaxial crystals** in contrast with crystals with two optic axes—or two axes of no double refraction—which are said to be **biaxial crystals.** Examples of uniaxial crystals are calcite, quartz, borax, sugar, sodium nitrate, potassium thiosulphate, potassium or ammonium phosphate, etc. Examples of biaxial crystals are potassium nitrate, sodium sulphate (glauberite), cerussite, aragonite, gypsum, etc.

Polarizing microscope.—In the polarizing microscope, a prism of Iceland spar—called a **Nicol's prism** or simply a **nicol**—is so arranged that the ordinary ray from a parallel ray of light is reflected to one side, and the extraordinary ray alone passes through the prism. The extraordinary ray of polarized light can then be passed through a second Nicol's prism which can be turned about its axis. When the nicols are crossed, the field will appear dark in spite of the fact that there is nothing but two transparent prisms between the eye and the source of light. The first Nicol's prism is called the *polarizer* and the second the *analyzer*. When the two prisms are at right angles to the position where the field has its maximum darkness, the nicols are said to be parallel. When the nicols are parallel, the field appears of maximum brightness, and the extraordinary ray passes through both prisms.

If a doubly refracting crystal be placed between crossed nicols, instead of complete darkness, the crystal appears to be more or less illuminated on a dark background (double refraction). D. Brewster (1821) showed that the behaviour of crystals in polarized light (between crossed nicols) is an important means of distinguishing doubly refracting crystals from cubic crystals. Very few crystals fail to show light between crossed nicols when examined in a suitable instrument, the polarizing microscope; and crystals can be classified into families according to their peculiar action on polarized light, because each system interferes with polarized light in a characteristic way. Let a crystal be laid flat on a glass plate on the stage of a microscope and the eyepiece, with cross wires, so fixed that an edge of the crystal is parallel to one of the cross wires; let the polarizer and analyzer be placed perpendicular to each other. The angle through which the crystal must be rotated in order to produce darkness is called the **angle of optical extinction**. If the crystal extinguishes or disappears when the edge of reference is parallel with the cross hairs of the eyepiece, and is brightest midway between, the crystal is said to have **parallel or straight extinction** with respect to that edge; and if the position of extinction is inclined or oblique to the cross-hairs, the crystal has **oblique extinction.** Tetragonal, hexagonal, trigonal, and rhombic crystals show parallel extinction, while monoclinic and triclinic crystals give oblique extinction.

A pencil of parallel polarized light.—If the direction of vibration of the plane polarized light is continuously rotated as it passes through the crystal, the phenomenon is called **rotatory polarization,** and the crystal is said to be **optically active.** Optically active crystals rotate the plane of polarization of light even in sections perpendicular to the optic axes. In 1811, D. F. Arago discovered the optical activity of quartz. Sodium chlorate also exhihits the phenomenon. When a pencil of parallel light rays is passing through the polarizer, the interposition of a plate of glass or of an isotropic crystal between the crossed nicols will not affect the field of vision which will remain dark; on the contrary, with plates of certain other crystals—quartz, sodium chlorate, cinnabar, etc.—cut perpendicular to the optic axis, the field of vision becomes more or less clear according to the thickness of the plate interposed, and this in spite of the fact that the nicols are crossed. The plates should be not less than 0·2 mm. thick. In order to re-establish the original darkness, the analyzer must be rotated through a certain angle, showing that the interposed plate of, say, quartz rotated the plane of vibration of the polarized rays from the first nicol. If the analyzer be turned through a certain angle clockwise (viewed from the front) in order to restore darkness, the crystal is said to be **dextro-rotatory,** because the crystal rotates the plane of polarization from the left to the right of an observer receiving the light and not towards the right in the direction the wave of light progresses. The converse of this applies for **lævo-rotatory** crystals. Since the angle of rotation is proportional to the thickness of the crystalline plate under examination, it is conventionally referred to a plate 1 mm. thick. The angle of rotation is also dependent on the wave-length of the light used, and therefore the character of the light should be specified—yellow sodium light, designated after Fraunhofer's *D*-line in the solar spectrum, is commonly employed, and the angle of rotation is symbolized a_D. Examples: The angle of rotation a_D for sodium bromate, $NaBrO_3$, is 2·17°; for sodium thioantimoniate, $Na_3SbS_3.9H_2O$, 2·37°; for sodium chlorate, $NaClO_3$, 3·14°; potassium lithium sulphate, $KLiSO_4$, 3·44°; potassium dithionate, $K_2S_2O_6$, 8·39°; quartz, 21·723°; and for sodium periodate, $NaIO_4.3H_2O$, 23·3°. When these substances are dissolved, or fused, the rotatory power is lost; and it is accordingly inferred that the cause of the rotatory power must reside in the way the molecules are structurally grouped in the crystals. On the other hand, a great many compounds of carbon possess this rotatory power when in the liquid state, in solution, and sometimes even in the state of vapour, *e.g.* camphor, etc. Consequently, it is inferred that with these substances the rotatory power is not due to the structure of the crystal, but is produced by arrangement of the atoms in the molecule itself, and is concealed by the orientation of the molecules in the crystal. Strychnine sulphate is optically active in solution and still more so in the solid state, so that the optical activity is determined by the orientation of the molecules in the crystal, as well as by the arrangement of the atoms in the molecule.

It is not possible to calculate the rotatory power of a substance with certainty from the rotatory power of its aqueous solution. In 1838, J. B. Biot [1] noticed that the rotatory power of tartaric acid in aqueous solution increased with increasing dilution, but R. Pribram failed to obtain constant values for the rotatory power even with very great dilutions. The decrease in the specific rotatory power of dilute solutions of the alkali tartrates with increasing dilution was attributed by R. von Sonnenthal to ionization. G. H. Schneider found that concentrated solutions of malic acid were dextro-rotatory; dilute solutions, lævo-rotatory; and that 34 per cent. solutions appeared inactive. Hence, it is highly probable that the so-called inactive solvent does exert some kind of action on the solute—maybe by breaking down molecular aggregates; forming unstable hydrates; changing the configuration of the atoms in the molecules, or by ionizing the salt in solution.

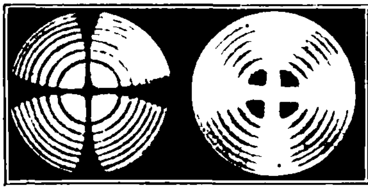
In 1817, J. B. Biot showed that the magnitude of the angle of rotation of solutions of optically active substances depends upon (i) the thickness of the layer of solution observed; (ii) the concentration—*i.e.* the mass per unit volume; (iii) the temperature; and (iv) the wave-length of the light employed. The **specific rotatory power** or the specific rotation of a substance at a particular temperature for a particular wave-length of light is the rotation produced by a decimetre of solution which contains one gram of the active substance per cubic centimetre. If w grams of an optically active substance are dissolved in v c.c. of a solvent, and the observed angle of rotation a with a column of liquid l decimetres long, the specific rotatory power, $[a]$, of the solution will be $[a]=av/lw$, on the assumption that the solvent is without influence on the result. This assumption is usually justifiable in the case of aqueous solutions, but not with other solvents. The change in the rotatory power of certain substances when dissolved in solvents upon which they exert no apparent chemical action, is explained by assuming that the solvent either unites with the solute, or else exerts a specific attraction so that the motions of the molecules of the solute are modified. A temperature of 20° is often taken as a standard of reference.

EXAMPLE.—If 20·2 grms. of a substance is dissolved in 79·8 grms. of water and the solution has a specific gravity of 1·0842; and when a layer 2 d.m. thick has an angle of rotation $a_D=29°$, what is the specific rotation? Here, $l=2$; $w=20{\cdot}2$; v=weight÷specific gravity$=(79{\cdot}8+20{\cdot}2)\div1{\cdot}0842$; $a=29$; hence, $[a]_D=66{\cdot}21°$.

The product of the specific rotatory power and the molecular weight of a substance is called the **molecular rotatory power.** The numbers so obtained are often divided by 100 in order that smaller numbers may be used. Special instruments called *polarimeters* are used to measure the rotatory power of optically active solutions, for they do this more accurately than is possible in the ordinary polarizing microscope.

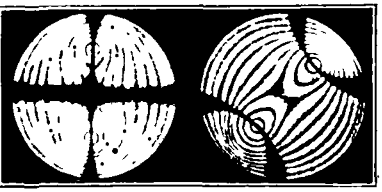
A converging cone of light.—A thin plate of a doubly refracting uniaxial crystal, cut at right angles to the optic axis, and placed between crossed nicols with a cone of convergent light incident on the polarizer, furnishes a series of circular, coloured, and concentric rings traversed by a dark cross, Fig. 16; and a biaxial crystal treated in a similar manner exhibits a double series of elliptical (lemniscate) rings traversed by a narrow bar, and separated by a broad bar, Fig. 17. These figures are called **interference figures.** When the analyzer is rotated, the distribution of the colours varies, and the interference figures change in a characteristic way in crystals of different mineral species. The black cross of uniaxial crystals changes into a white one, Fig. 16, and the colour of the rings changes to the complementary tints when the nicols are parallel. Similarly, with biaxial crystals, Fig. 17, rotating the analyzer breaks up the cross and develops two dark brushes, Fig. 17, each of which traverses one of the systems of rings. The crystals of some substances require the analyzer to be rotated to the right, and other crystals to the left in order to develop a given succession of colours—*e.g.* different specimens of quartz, for example, may show what J. Herschel called right- and left-handedness, and some samples again, principally the purple crystals of quartz (amethysts), may show both right- and left-handedness in one specimen.

The properties of crystals are not always the same in different directions.—The hardness, elasticity, crushing strength, rate of solution in acids, optical, thermal, and electrical properties, are generally different in different directions. This means that different results are usually obtained when the elasticity, refraction of light, thermal expansion, etc., of a crystal are measured in different directions. Thus, the coefficients of thermal expansion of quartz along the axes designated *a* and *c* are respectively 1515×10^{-8} and 807×10^{-8}—so that one is nearly twice as large as the other; with adularia (felspar) the coefficients along the three axes are respectively 1569×10^{-8}, $65{\cdot}9\times10^{-8}$, and 291×10^{-8}—corresponding nearly with the ratio 24 : 1 : 4. A substance, apparently homogeneous, may therefore exhibit *privileged directions* for the propagation of any particular form of energy—thermal, electrical, optical, magnetic, or elastic. Any medium in which any natural phenomenon is not produced with the same intensity in every direction is said to be **anisotropic** (ἄνισος, unequal; τρέπειν, to turn) or **æolotropic** (αἰόλος, changeful) for that phenomenon, for the body is dissymmetrical with regard to that phenomenon. A body whose optical, magnetic, thermal, electrical, elastic, or other property depends upon direction, is anisotropic. All these forms of anisotropy can exist simultaneously in a body. When the properties of a substance are the same in all directions, it is said to be an **isotropic** substance (ἴσος, equal)—*e.g.* gases, most liquids, unstrained glass, and, so far as the optical, thermal, and electrical properties are concerned, unstrained crystals belonging to the cubic system.



Nicols crossed. Nicols parallel.

FIG. 16.—Interference Figures—Uniaxial Calcite.



Nicols crossed. Analyzer rotated 45°.

FIG. 17.—Interference Figures—Biaxial Potassium Nitrate.

In *H. de Sénarmont's experiment* (1847),[2] a slice of quartz is cut perpendicular to the long axis and another slice is cut perpendicular to this; each slice is covered with wax, and pierced at the centre so that a hot wire can be inserted. The wax naturally melts about the hot wire. In the former case, the molten wax will form a circle—*A*, Fig. 18;

and in the latter case, an ellipse—*B*, Fig. 18. This shows that the *thermal conductivity* of the crystals is different in different directions. In H. L. Bowman's experiment one end of a heated wire in contact with a face of a crystal of gypsum gave a white, opaque, elliptical area owing to dehydration. The ratio and direction of the axes of the ellipsoid varied for different faces—on the cleavage face, the ratio was 1·129.

If a crystal of calcite be hung in a beaker of dilute hydrochloric acid by means of a platinum wire, solution does not occur at a uniform rate over the whole surface, but the *rate of solution* of the crystal is faster in one direction than in another. Plates have been cut parallel to the different faces of different crystals, and the edges protected with wax, and measurements made of the amount dissolved after the plates had been immersed in the selected solvent for a given time. The velocity of the attack by hydrochloric acid is about 1·15 times greater when the surface exposed to the action is perpendicular to the principal axis than when the surface is parallel therewith.[3] A. Wolff found all the faces of crystals of Mohr's salt dissolve at the same rate; and A. Körbs noticed very little difference in the rates of solution of the different faces of crystals of sodium chloride, alum, and potassium nitrate, but with copper sulphate and potassium ferrocyanide wide differences were observed—in the former case, 37 per cent.; and in the latter, 86 per cent. Still further, the velocity of propagation of *light* through crystals of the cubic system is the same in all directions, but not with members of the other systems.

The attack of a crystal face by a reagent does not necessarily commence at the same time at all points, but proceeds more rapidly in some parts than in others. If the attack be stopped at the right time, the attacked face will be pitted with little angular cavities, many of microscopic size, called **etch figures**, or **corrosion figures.** Passing a moist cloth rapidly over the surface of an octahedral crystal of alum will suffice to develop triangular cavities with sloping sides, and similar to those sometimes found naturally on the octahedral faces of the diamond. With the right conditions—solvent, time, and temperature—the etch figures will be in parallel positions plane for plane. The etch figures on similar faces will be all alike, but unlike on dissimilar faces. The etch figures conform to the symmetry of the class to which the crystal belongs, and they therefore serve as an important clue in determining the symmetry of a crystal. The etch figures on cubes of galena are symmetrical to the nine planes of symmetry, while those on cubes of sylvite are symmetrical only to the axes. The etched pits are bounded by a number of minute faces with complicated indices which are generally known as *vicinal faces.*

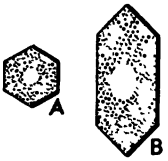


Fig. 18.—H. de Sénarmont's Experiment.

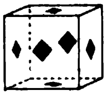


Fig. 19.—Etch Figures of Galena (diagrammatic).

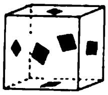


Fig. 20.—Etch Figures of Sylvite (diagrammatic).

Experiments on the rates of solution of crystal faces must always be affected by errors owing to modifications in the surface area by (i) the pitting of the faces; and (ii) the rounding of the edges. V. Goldschmidt[4] has studied the etch-figures of crystal faces and of the successive forms assumed by a sphere of calcite when subjected to the action of phosphoric, hydrochloric, nitric, formic, or acetic acid. The sphere is first etched in tracts which correspond with the natural faces most prone to attack; the etch-figures then disappear; the entire surface is then affected so that the poles of the faces most prone to attack become most sharply pronounced corners of curved faces. Consequently, growth and dissolution are inversely related This relation is called **V. Goldschmidt and F. E. Wright's law of polarity**: *the corners of a dissolving crystal become the poles of the faces of a growing crystal.*

The inversion corners shift slightly as the crystal dissolves, until at last a final form is reached which dissolves without change of shape. This final form depends on the original form of a natural crystal and on the nature and concentration of the acid. P. Hochschild obtained similar results with zinc blende; and A. E. Fersmann and V. Goldschmidt have shown the relation between these results and the corrosion forms shown by natural crystals of the diamond. W. Schnorr also studied the alteration of form brought about by a reversal of the growth process of crystals of rock salt by the solvent action of slightly unsaturated solutions of sodium chloride with a little carbamide. The first action is to bevel the cube edges—the final form is the icositetrahedron. The final form obeys V. Goldschmidt and F. E. Wright's law of polarity.

The essential difference between crystalline and amorphous substances is one of internal structure, not necessarily external shape.—The external form of crystals is their most obtrusive characteristic, and it was naturally the first to arrest attention; but the geometrical shape is by no means the most characteristic property of crystals, because the external geometrical form may be destroyed, and yet the fragments do not cease to be crystals, for they behave in polarized light like perfect crystals. On the contrary, the most perfect glass model of a crystal is not a crystal, because it lacks the characteristic internal properties of crystals. According to L. Vegard,[5] crystals of thorite show nearly perfect tetragonal forms and internally they appear to be amorphous. The shapes of gems cut and polished to accentuate the ornamental value of the gem must not be confounded with crystal structure; similarly, the term "crystal" applied to cut glass has a different meaning from the special use of the word crystal in the text. Transparent glass is not crystalline; some varieties of opaque glass are microcrystalline. In the case of granite, the crystals of felspar, quartz, and mica have been so crowded during their growth that they have had no chance to develop their characteristic external shape. The internal structure of each mineral, however, is characteristic. A crystal has therefore been defined as "a solid body bounded by plane surfaces arranged according to definite laws, and possessed of definite physical properties. Both the external form and the physical properties result from a definite and unique internal structure." Amorphous substances show no signs of the definite structure characteristic of crystals. The term "amorphous" is applied, somewhat vaguely—often wrongly—to the pulverulent substances, *i.e.* to substances occurring as fine-grained powders particularly when the powders have not the definite external shape characteristic of crystals, or when the grains are opaque and do not permit the application of the usual optical tests to find if they have the internal structure characteristic of crystals. P. P. von Weimarn has raised the question whether the finest precipitates are ever amorphous; he is right in saying that many precipitates usually classed as amorphous are really crystalline, but there is no doubt that many precipitates are really analogous with supercooled liquids, like glass. P. P. von Weimarn, however, says that a "super-cooled glass" is crystalline, and he even says that liquids and gases are crystalline; this makes it obvious that his definition of a crystalline substance is different from that usually employed, and need not here be considered.

An amorphous substance is one which, during solidification, has not taken the definite external shape characteristic of crystals, the properties when measured in any one direction are the same as when measured in any other direction, and there are no signs of a definite orientation of the molecules. In this case it is assumed that the constituent molecules are arranged haphazardly or in a chaotic manner. In crystals, on the contrary, where the properties along parallel directions are the same, but different in directions that are not parallel, it is assumed that the ultimate molecules, or their motions, are oriented or arranged in a definite regular manner. W. Voigt (1906) aptly illustrates this idea by the metaphor cited above.

The words "haphazard," "chance," and "chaotic," applied to the arrangement of atoms or molecules in amorphous substances, are not intended to imply that there is such a thing in nature as a "fortuitous concourse of atoms." The man of science believes, by faith, that the irregular path described by a mote dancing in a beam of sunlight is determined as certainly as the orbit of the planet about its sun. Words like these are conventional modes of expressing our ignorance of the great design. If this be ever discovered, we believe, by faith, that what is now regarded as a chance coincidence will be part of an everlasting harmony.

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§ 6. The Seven Styles of Crystal Architecture

> In crystallography there is a beautiful instance of successful classification connected with a nearly perfect physical hypothesis.—W. S. JEVONS.
>
> A symmetrical shape is one which consists of parts exactly similar, repeated a certain number of times, and placed so as to correspond with each other. The symmetrical parts of a crystal are, under like circumstances, alike affected.—W. WHEWELL.

Crystal faces usually occur in sets so arranged as to preserve the symmetry of the crystal with respect to certain imaginary points, axes, or planes which are characteristic of certain groups or families of crystals. J. B. L. Romé de l'Isle expressed the idea in 1783 by stating: "Every crystal face has a similar face parallel to it," and the symmetry of the faces and angles of crystals has been emphasized by calling it the **law of crystal symmetry: In normally formed crystals, every face has a similar face in all positions consonant with the symmetry of the particular class to which the crystal belongs.** When a crystal shows the highest grade of symmetry pertaining to its system—that is, when a crystal possesses all the faces required by the law of symmetry—the crystal is said to be holosymmetrical or **holohedral**—from ὅλος, whole; ἕδρα, base or face. An unsymmetrical crystal may be derived from a holohedral crystal by the suppression of half its faces, when it is termed **hemihedral,** from ἡμι, half—the tetrahedron, for instance, is the hemihedral form of the octahedron; or by the suppression of three-quarters of its faces, when it is termed **tetartohedral**—from τέταρτος, a quarter.

G. D. Liveing[1] assumes that if a solid be bounded by plane faces, the surface tensions at the edges will have a resultant which tends to compress the mass; and, for equilibrium, there must be an opposing pressure on the opposite side of the crystal, or else there will be internal stresses. Hence, a reason for the law of crystal symmetry can be seen, for if *one* face of the crystal be developed, the *opposite* face will also be developed; and if one edge or angle be truncated, all the corresponding edges or angles will be truncated; if otherwise, there would be a stress in the interior tending to deform the crystals. The surface tension, which produces this stress, depends on the nature of the surfaces in contact, on their temperature, electrical condition, etc. If therefore the surface tension on one face be balanced by inequalities of temperature, etc., unsymmetrical faces may be developed, and when the stress produced by, say, an inequality of temperature is relieved, an internal stress due to unequal surface tensions would persist. Such crystals would exhibit signs of internal stresses. Crystals with unsymmetrical faces generally do exhibit signs of internal stresses by developing electrifications of opposite signs at the two ends when heated or cooled—*pyro-electrification*—or they may affect polarized light differently. In illustration, symmetrical crystals of tourmaline do not usually exhibit pyro-electrification, while the unsymmetrical crystals do. Likewise, substances which show rotatory power in solution develop unsymmetrical crystals—*e.g.* the tartrates.

A crystal is said to possess a **centre of symmetry** when to every face of the crystal there is a corresponding parallel face at the opposite side of the crystal.

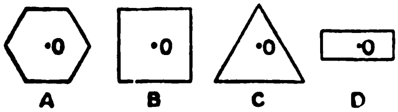

FIG. 21.—Axes of Symmetry.

A **plane of symmetry** is an imaginary plane which divides the crystal into two parts such that one part is the exact but inverse counterpart of the other. In other words, the two parts bear to one another the same relation that the image in a mirror bears to its object. The mirror is the equivalent of a plane of symmetry. A crystal of potassium iodide, for example, has nine planes of symmetry indicated in Fig. 24. The crystal of gypsum, Fig. 44, has only one plane of symmetry; and a crystal of barium sulphate has three planes of symmetry, Fig. 41. Crystals can be classified into groups, according to the disposition and number of their planes of symmetry.

Then again, a crystal may be rotated about a definite axis through an angle, which is a simple fraction—$\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{4}$, or $\frac{1}{6}$ of the angle of complete rotation, 360°—such that the faces, edges, and corners are brought into similar or symmetrical positions, and the aspect of the crystal is the same as before rotation. The axes of rotation are then called **axes of symmetry.** Thus we speak of dyad, triad, tetrad, hexad axes of symmetry according as there are 2, 3, 4, or 6 positions of symmetry during a complete rotation. These positions correspond with rotations of 180°, 120°, 90°, and 60°. Thus, Fig. 21, *A*, represents a horizontal cross-section of a crystal with one hexad axis of symmetry, because during the rotation of the crystal about the axis *O*, there are six positions—60°, 120°, 180°, 240°, 300°, and 360°—where the original aspect of the crystal is the same. In Fig. 21, *B, C, D*, respectively, denote tetrad, triad, and dyad axes of symmetry. P. H. R. von Groth (1876)[2] has shown that other grades of symmetry—pentad, heptad, octad, etc.—are not possible in crystals, and J. W. Evans proved that the only possible axes of symmetry are those with cyclic numbers 2, 3, 4, or 6, provided that the crystals have a homogeneous cellular structure. In the subjoined outline discussion of the crystal systems, the maximum symmetry is alone indicated.

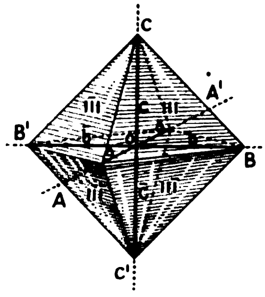

FIG. 22.—Crystallographic Constants.

Miller's system of crystal notation.—Under ordinary conditions the earth is the standard of reference for both position and direction. This is merely for convenience; other standards are used in astronomy. In analytical geometry, position and direction are referred to a set of arbitrary lines called *axes*. Similarly, in the geometrical description of a crystal, it is convenient to refer the position of the faces or bounding planes of the crystal to a set of imaginary coordinate axes within the crystal, and which are called the **crystallographic axes.** There are generally three, sometimes four, of these axes. The comparative length and mutual inclination of the axes depend upon the symmetry of the ideal crystal. The axes are chosen so as to furnish the simplest expression to describe the faces of the crystals, and to allow similar faces to be described by similar terms. In

Fig. 22, let AOA', BOB', COC' represent the three axes of a crystal, and call them respectively the a-, b-, and the c-axis. The virtual axis is called the c-axis; that passing forwards and backwards is the a-axis, and that passing right and left the b-axis. The form and nature of the crystal is supposed to be determined by the length and mutual inclination of these axes. The angles between the axes are called the **axial angles.** The axial angle BOC is symbolized α, the axial angle COA, by β; and AOB, by γ. The axial angles with the axial ratios $a:b:c$ are a characteristic for the crystals of each individual substance, and are called the **crystallographic constants** of the crystals. Each of the crystallographic axes can be drawn from the intersection or origin O in two directions; one direction is arbitrarily called the *positive* and the other the *negative* direction. A bar over the letters A, B, C represents conventionally the negative direction, the opposite directions are called positive. Mark off the equal lengths a and $\bar{a}$ on the $AO\bar{A}$ axis, b and $\bar{b}$ on the $BO\bar{B}$ axis, and c and $\bar{c}$ on the $CO\bar{C}$ axis. Suppose a set of planes to lie in such a position that the extremities meet the AOA' axis at a distance a, the $O\bar{C}$ axis at $\bar{c}$, and OB axis at b, and so on. The lengths a, b, c and $\bar{a}$, $\bar{b}$, $\bar{c}$ are called **parameters.** In the diagram, Fig. 22, the plane ABC with the parameters abc is called the abc-plane; the plane ABC' is the $ab\bar{c}$-plane; $AB'C'$ is the $a\bar{b}\bar{c}$-plane, etc.

The faces can be fixed when the directions of the a-, b-, and c-axis and the parameters a, b, c, are known. Suppose a plane to cut the axis a at half the length of a, b at $\frac{1}{3}$ the length of b, and c at $\frac{1}{4}$ the length of c, then the position of this plane about the given axes would be fixed by $\frac{1}{2}a$, $\frac{1}{3}b$, $\frac{1}{4}c$. Such a notation is considered clumsy, and the reciprocals of the fractional values alone are used in describing the plane, which would then be called the 234-plane. Similarly, a 123-plane is one which passes through points corresponding with a, $\frac{1}{2}b$, $\frac{1}{3}c$. Similar remarks apply to the other planes, allowing for the negative values as just indicated; the plane $\overline{abc}$, for instance, becomes the 111-plane. Each number is called an **index,** and conventionally, the first index always refers to the a-axis, the second to the b-axis, and the third to the c-axis. Suppose that a plane corresponded with $\frac{1}{1000}a$, $\frac{1}{1000}b$, c, it would be described as the 1000, 1000, 1-plane; this is true, however small the fractions be taken. The smaller the parameter, the steeper the plane, until finally the plane ∞a, ∞b, c is written 001, is parallel to the axes in question. The cyphers thus represent planes parallel to the a- and b-axes respectively. The three indices of a plane may be multiplied or divided by any desired number without altering their relations one to another. Thus the plane 222 must be parallel to the 111-plane, and also to the 333-plane, etc. Hence, it is usual to reduce the ratios to their simplest form. This system of notation was adopted by W. H. Miller in a classical work entitled *Treatise on Crystallography* (Cambridge, 1829). There are several other systems in use, but Miller's promises to oust them in the course of time.

R. J. Haüy's law of rational indices.—It might be supposed that the angles between the planes of crystals could have any indices, and the planes any inclination. Observations show that this is not the case. R. J. Haüy noticed that the indices can be generally represented by simple whole numbers, but never by what mathematicians call irrational numbers.[3] Thus the indices of a plane might be 123, 457, etc., but never $1\sqrt{23}$, $45\sqrt{7}$, etc. The fact that **the indices of all crystal planes can be expressed by rational whole numbers** is called R. J. Haüy's law of rational indices. The simplicity of the indices of course is largely determined on the happy though arbitrary choice of the axial directions AA', BB', and CC'. Like most other so-called laws, the rationality is seldom fulfilled with strict accuracy, but it comes so near the truth that it is regarded as an outward and visible symbol of the internal structural simplicity of crystals

Sometimes the symbols hkl, $\bar{h}\bar{k}\bar{l}$, etc., are used in a general way to express any set of rational numbers. If the symmetry of a crystal and one face of a crystal form are known, the other similar faces can be derived from the known face. A group of similar faces is called the **form of a crystal**, and the form of a crystal can be represented by the same symbol as that used for one of the faces. In that case the symbol for the face is enclosed in brackets, thus, (*hkl*) represents all the faces included in the groups of faces similar in every respect to the face *hkl*.

The seven systems of crystal architecture.—The study of the physical properties and forms of crystals *quâ* crystals is a special branch of chemical physics—**crystallography**—and the study of the forms of the different varieties of crystals is called the *morphology* of crystals. It is assumed that crystals are built of similar molecules which are either similarly related to all the adjoining molecules, or else similarly related to the adjoining molecules which are in the same plane, but differently related to those in different planes. In the one case the arrangement of the molecules is rectangular, and in the other case, oblique. All the physical properties of crystals are closely correlated with the form of the crystal; and the form of a crystal is determined by the relative length, and the mutual inclinations of the crystallographic axes.

It is supposed that the imaginary axes of all except hexagonal crystals can be varied with respect to *length* in three ways, for they may be (1) all equal; (2) all unequal; and (3) one may be unequal and two equal. The axes can conceivably be varied in *direction* or slope in four ways: (*a*) All may be at right angles to one another; (*b*) two axes may be at right angles, and the third perpendicular to one of them and oblique to the other; or (*c*) the third axis may be oblique to both; and (*d*) all three axes may be oblique to one another. There is also an additional type which has three axes lying in one plane and a fourth axis perpendicular to these three. Every known crystal can be referred, on the basis of its symmetry, to one of the following seven systems:

				SYSTEM.
Axes	Three	All rectangular	All equal	Cubic
			Two equal, one unequal	Tetragonal (uniaxial)
			All unequal	Rhombic (biaxial)
		One perpendicular to two mutually oblique, all unequal		Monoclinic (biaxial)
		All oblique and	Unequal	Triclinic (biaxial)
			Equal (with angles equal but not 90°)	Trigonal (uniaxial)
	Four	One rectangular, to three oblique and equal		Hexagonal (uniaxial)

These seven systems are further subdivided into classes, each of which has its own characteristic symmetry—described in standard works—*e.g.* A. E. H. Tutton's *Crystallography and Practical Crystal Measurement* (London, 1911).

With the exception of the members of the cubic system, the crystals of no two compounds are exactly alike; but crystals of the same compound have their faces inclined at the same angles. Consequently, it is possible to identify crystals quickly from measurements of the angles between similar faces of one or two crystals by reference to tables containing measurements of all those crystalline substances whose angles have been measured. This mode of identifying crystalline substances is called **Fedoroff's crystallochemical analysis.**[4]

I. Cubic system.—The first class of crystals possesses three axes—*a*, *b*, *c*—of equal length, and they make equal angles—α, β, γ—with one another, as illustrated in Fig. 23. The axes are interchangeable, so also are the angles, so that what is true of one axis or angle is true also of the other two. This is expressed in symbols: $a=b=c$, and $\alpha=\beta=\gamma$. The crystals have nine planes of symmetry as illustrated in Fig. 24, three of the planes of symmetry are principal planes, and six are secondary. There are six dyad, three tetrad; and four triad axes of symmetry. The primary or simplest representative form is the cube—hence the name cubic system. By cutting off the corners of the primary cube by planes variously inclined to the axes, the octahedron, dodecahedron, and various secondary forms are derived. Since each of the three crystallographic axes is exactly like the other two, every facet formed on one corner of a crystal must be repeated symmetrically with regard to the other axes; hence the forms produced are symmetrical or regular, and in place of the cubic system, the term *regular system* is synonymously employed. In addition to the terms cubic or regular system, this class of crystals has also been called the *isometric*, *monometric*, *tesseral*, *tessural*, and *octahedral* system.

Typical crystals for examination are cuprite and garnet. These cubic crystals are defined by the numerical values of the indices of the component forms. For example, *cuprite*, Fig. 25, has *a*(100), *d*(110). This particular crystal, described by A. E. H. Tutton, is apparently holohedral; but H. E. Miers has shown that in general cuprite is hemihedral. *Garnet*, Fig. 26, has *d*(110), *i*(211). Potassium iodide, barium nitrate, chrome alum, potash alum, sodium chlorate, and arsenic trioxide also furnish good crystals for examination.

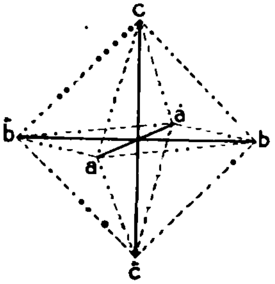

FIG. 23.—Crystallographic Axes of the Cubic System.

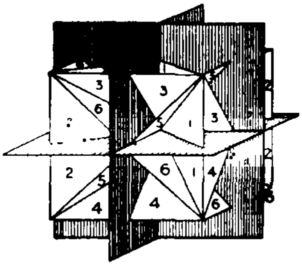

FIG. 24.—Planes of Symmetry in the Cubic System—3 Principal and 6 Secondary Planes.

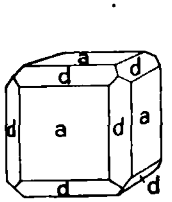

FIG. 25.—Cuprite.

EXAMPLES.—Diamond; potassium chloride; sodium chloride; alum; fluorspar; iron pyrites; lead nitrate; magnetic oxide of iron; barium nitrate; arsenic trioxide; galena; garnet; ammonium chloroplatinate; silver chloride; boracite; indium; aluminium; iron; platinum; lead; phosphorus; gold; copper; silver; nickel; arsenic; metacinnabarite; cerargyrite; ammonium chloride; amalgam—HgAg; nitrous oxide; carbon dioxide; ammonia; potassium thio-stannate—$K_2SnS_3.3H_2O$; beryllium sulphate—$BeSO_4.6H_2O$; uranyl sodium acetate; stannic iodide; bismuth; fahlerz; spinel: argentite; leucite; franklinite; nosean; tetrahedrite; tennantite; allmannite—NiSbS; barium nitrate; analcite; cobaltite: cuprite; sodalite; sodium chlorate; sodium bromate; zinc blende; mercury.

The equality and symmetry of the three axes in the members of the cubic system is a mathematical expression of the fact that the vectorial properties of the crystals belonging to this system are alike in all direction—*e.g.* the optical properties. When light or heat rays enter one of these crystals, the rays spread with equal rapidity in all directions just as they do in homogeneous gases, liquids, and unstrained amorphous solids—*e.g.* glass. The crystals are not doubly refracting unless the elasticity is modified by compression. Otherwise expressed, the crystals are optically isotropic, with an index of refraction which is the same in all directions; there is no change between crossed nicols; and there are no interference figures. When the crystals are heated, they expand equally in all directions. Consequently, the mere statement that a crystal belongs to the cubic system, is a sufficient indication that it possesses these qualities in common with other members of its class.

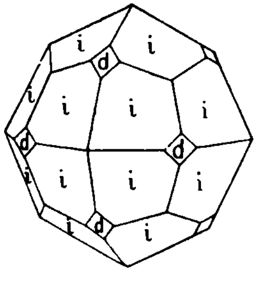

FIG. 26.—Garnet.

II. Hexagonal system.—The system is so named because a horizontal section is usually hexagonal—from ἑξάγωνια, having six angles or corners. Here the crystals have four axes—a_1, a_2, a_3, c—of which the three—a_1, a_2, a_3,—lying in one plane are of equal length, $a_1=a_2=a_3$, and meet one another at angles of 60°, Fig. 27; the fourth or *c*-axis is perpendicular to the *a*-axis, and is called the principal axis.

These facts are symbolized $a_1=a_2=a_3\lesseqgtr c$; $\alpha_1=\alpha_2=\alpha_3=90^\circ$, $\gamma=60^\circ$. The crystals have seven planes of symmetry, Fig. 28; and one hexad, and maybe six dyad axes of symmetry. The crystals are uniaxial; the interference figure is a symmetrical black cross with concentric spectrum coloured rings; there are two principal indices of refraction.

Typical crystals for examination are beryl and apatite. The crystals are defined by the form development and the values of the interfacial angles from which the axial ratios can be calculated. For instance, *apatite* has $a:c=1:0·7346$ and $m(10\bar{1}0)$, $x(1011)$; *beryl* has the angle $a:c=1·0499$, and $a(1010)$, $r(1121)$, $c(0001)$. Lead iodide, and cadmium iodide also, furnish good examples for examination.

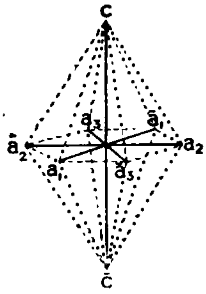

Fig. 27.—Crystallographic Axes of the Hexagonal System.

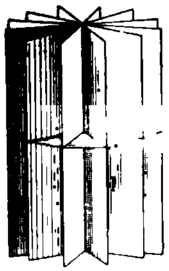

Fig. 28.—Seven Planes of Symmetry of the Hexagonal System.

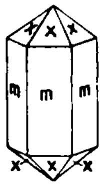

Fig. 29.—Apatite.

EXAMPLES.—Beryl; apatite; copper sulphide; lead iodide; magnesium; beryllium; zinc: cadmium; calcium; pyrrhotite; proustite; pyrargyrite; silver iodide; strontium and lead antimonyl tartrates; pyromorphite; mimetite; vanadinite; iodyrite; nephelite; etc.

Owing to the disposition of the axes in the tetragonal, trigonal, and hexagonal systems, the physical properties are alike in all directions perpendicular to the principal axes, but are different in other directions. The crystals are not doubly refracting in the direction of the principal axis, but they are doubly refracting in other directions. Thus, a crystal of beryl does not exhibit double refraction in the direction of the principal axis, but light is doubly refracted in every other direction. Accordingly, these crystals are uniaxial. Heat is conducted at the same speed in directions parallel to the principal axis, but with different speeds in directions perpendicular to this axis.

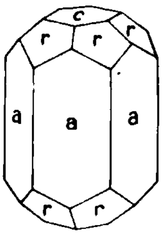

Fig. 30.—Beryl.

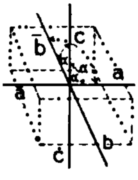

Fig. 31.—Crystallographic Axes of the Trigonal System.

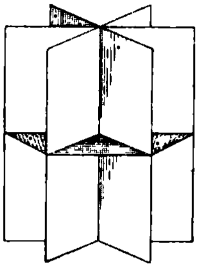

Fig. 32.—Trigonal Planes of Symmetry.

III. Trigonal system.—The name comes from τρίγωνον, having three angles or corners. The crystals of this system have three axes $a=b=c$, all equal and equally included at an angle which is not a right angle, so that $\alpha=\beta=\gamma$, Fig. 31. The crystals have three planes of symmetry, Fig. 32, one triad, and maybe three dyad axes of symmetry. The crystallographic axes are not axes of symmetry, but are lines parallel with the edges of the fundamental rhombohedron. This system is sometimes called the *rhombohedral* system, and it is sometimes regarded as a special development of the hexagonal system. The crystals are uniaxial; the interference figure is a symmetrical black cross with concentric spectrum coloured rings; there are two principal indices of refraction.

Typical crystals for examination are calcite and quartz. The crystals are defined by the form development, and the values of the interfacial angles from which the axial ratios are calculated. For example, calcite (Figs. 36 and 37) has $\alpha=101° 54'$; and $m(2\bar{1}1)$, $r100$, $v(201)$, $e(110)$; quartz (Fig. 3) has $\alpha=93° 57'$; and $m(211)$, $r(100)$, $r'(122)$, $s(4\bar{2}1)$, $x(4\bar{2}1)$. Sodium orthophosphate, $Na_3PO_4.12H_2O$, strontium chloride, $SrCl_3.6H_2O$, sodium nitrate, $NaNO_3$, furnish examples for examination.

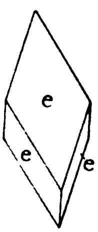

FIG. 33.—Rhombohedral Calcite.

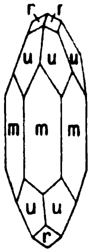

FIG. 34.—Calcite (Dog's Tooth Spar).

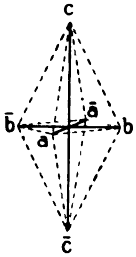

FIG. 35.—Crystallographic Axes of the Tetragonal System.

EXAMPLES.—Sodium periodate—$NaIO_4.3H_2O$; quartz; tourmaline; antimony; bismuth; calcite; ice; graphite; sodium nitrate; arsenic; tellurium; nickel sulphide—millerite; cinnabar; calcium chloride—$CaCl_2.6H_2O$; corundum; cadmium carbonate; bismuth iodide; ferrous carbonate; zinc carbonate; manganese carbonate; chabazite; brucite; corundum; lead, barium. strontium, and calcium dithionates; calamine; dolomite; dioptase—$CuSiO_3.H_2O$; benitoite—$BaO.TiO_2.3SiO_2$; ilmenite; phenacite; etc.

IV. Tetragonal system.—The name comes from τετραγωνία, having four angles or corners. The members of this system have three axes, two of which, a and b, are equal to one another $a=b\lessgtr c$; the axes intersect at right angles, Fig. 35, so that $\alpha=\beta=\gamma=90°$. The crystals may have five planes of symmetry, Fig. 36, one tetrad, and maybe four dyad axes of symmetry. The crystals are uniaxial; the interference figure is a symmetrical cross with concentric rings; the crystals are isotropic in one position, and the optical extinction is parallel in the other two; there are two principal indices of refraction. This system is sometimes called the *pyramidal*, *quadratic*, or the *quaternary dimetric* system.

Typical crystals for examination are nickel sulphate, $NiSO_4.6H_2O$, and cassiterite. The crystals are defined by the form development, and the values of the interfacial angles from which the axial ratio is calculated. For example, *nickel sulphate* (Fig. 39) crystallized from a warm solution has $a:c=1:1·912$; and $o(111)$, $x(112)$, $c(001)$, $a(100)$, $r(101)$, $s(203)$. *Cassiterite* (Fig. 38) has $a:c=1:0·673$, and $m(110)$, $a(100)$, $r(101)$, $s(431)$. Potassium cupric chloride, mercuric cyanide, and potassium arsenite also furnish good crystals for examination.

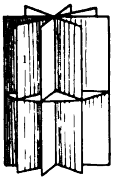
FIG. 36.—Planes of Symmetry of the Tetragonal System.

EXAMPLES.—Rutile; cassiterite; zircon; mercurous chloride; nickel sulphate; potassium hydrogen phosphate—KH_2PO_4; native lead molybdate or wulfenite—$PbMoO_4$; sodium meta-antimonite—$NaSbO_2$; potassium hydrogen arsenate—KH_2AsO_4; scheelite; tin; strychnine sulphate; anatase; lead tungstate—$PbWO_4$; stolzite; yttrium niobate or fergusonite; pinnonite; vesuvianite; urea; wernerite; mercury chloride, iodide, and cyanide; barium antimonyl tartrate; phosgenite; idocrase; apophyllite; scapolite; braunite; etc.

V. Rhombic system.—Here the crystals have three unequal axes all inclined at right angles, so that $\alpha=\beta=\gamma=90°$; and $a<b\leqq c$, Fig. 39—b is conventionally taken as unity. The larger of the two lateral axes is called the *macrodiagonal*—μακρός, long—and the smaller the *brachydiagonal*—βραχύς, short. The crystals may have three planes of symmetry, Fig. 40; and three dyad axes of symmetry. The crystals are biaxial; optical extinction is parallel in all three main positions of the crystal; and there are three principal indices of refraction—the smallest index is in the direction of greatest elasticity, and *vice versa*. This system is sometimes called the *orthorhombic*, *trimetric*, or the *prismatic* system.

Typical crystals for examination are barytes (Fig. 41) and topaz (Fig. 42). The crystals are defined by the development forms and the values of the interfacial angles from which the axial ratios can be calculated. Thus, barytes has $a:b:c=0·815:1:1·314$; and $c(001)$, $o(011)$, and $d(102)$. Topaz has $a:b:c=0·529:1:0·954$; and $c(001)$, $m(110)$, $n(140)$, $i(223)$, $l(120)$, $f(021)$, $y(041)$, $u(111)$. Ammonium sulphate, potassium nitrate, potassium sulphate, zinc sulphate, sodium nitroprusside, and mercuric chloride also furnish good crystals for examination.

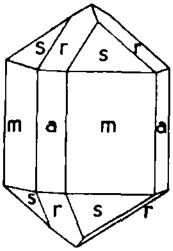

FIG. 37.—Cassiterite.

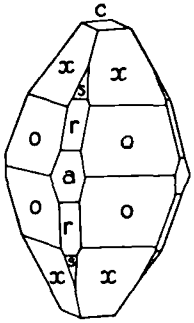

FIG. 38.—Nickel Sulphate Hexahydrate.

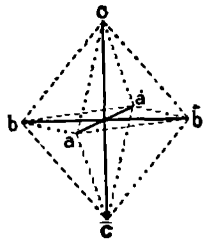

FIG. 39.—Crystallographic Axes of the Rhombic System.

EXAMPLES.—Zinc sulphate—$ZnSO_4.7H_2O$; magnesium sulphate—$MgSO_4.7H_2O$; ammonium magnesium phosphate—$NH_4MgPO_4.6H_2O$; potassium sulphate; aragonite; anhydrous sodium or silver sulphate; sulphur from solution; barium, strontium, and ammonium sulphates; sodium arsenate; sodium phosphate—$NaH_2PO_4H_2O$; iodine; potassium nitrate; tartar emetic; potassium perchlorate; potassium permanganate; topaz; marcasite; tridymite; silver nitrate; lead carbonate; silver sulphide; prehnite; calamine; atacamite; goslarite; stephanite; chrysoberyl; topaz; andalusite; chalcocite; acanthite; hypersthene: struvite; tartaric acid; manganese peroxide; barium chloride; mercuric chloride; orpiment; antimonic oxide; ammonium nitrate; Rochelle salt; citric acid: iodine; selenium; olivine; cerussite; strontianite; redruthite; bournonite; hemimorphite; stibnite; etc.

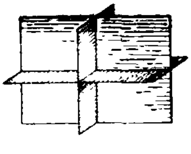

FIG. 40.—Planes of Symmetry in the Rhombic System.

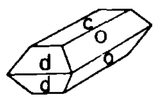

FIG. 41.—Barytes.

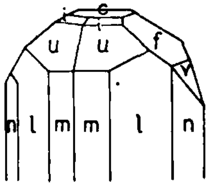

FIG. 42.—One end of a Topaz Crystal.

The physical properties of members of the triclinic, monoclinic, and rhombic systems vary in all three directions; for example, heat is conducted at different rates in all three directions; again, in the mineral iolite, $Al(F_2OH)SiO_4$, crystallizing in the rhombic system, light transmitted in the direction of the principal axes often appears blue, greyish-blue when viewed through the 100 face, and yellow through the 010 face. This phenomenon is known as pleochröism. Light is singly refracted in two directions, and doubly refracted in all other directions, hence the crystals are optically biaxial.

VI. Monoclinic system.—The name is derived from *μόνος*, one, and *κλίνειν*, to incline—having one oblique intersection in allusion to the fact that the members of this system can be referred to three unequal axes, of which two, c (the vertical axis) and a, are inclined to form one oblique angle β, and third lateral axis, b, is at right angles—to the other two—Fig. 43. The inclined lateral or a-axis is called the *clino-axis* or *clino-diagonal*—*κλίνειν*, to incline—and the rectangular lateral or b-axis is called the *ortho-axis* or the *ortho-diagonal*—*ὀρθός*, straight. Hence, $\alpha=\gamma=90°$, and $\beta \lesseqgtr 90°$, and $a \lesseqgtr b \lesseqgtr c$, and there are no closed symmetrical forms, and accordingly, the crystal must be a combination of different forms. These crystals may have one plane of symmetry, Fig. 46, and there may be one dyad axis of symmetry. The crystals are biaxial; optical extinction is parallel in two positions and oblique in the third; and there are three principal indices of refraction. This system has also been styled the *mono-symmetric*, *clino-rhombic*, or the *oblique* system.

Typical examples for examination are gypsum (Fig. 44) and ammonium magnesium sulphate (Fig. 45)—the crystals by the development forms, and the values of the interfacial angles from which the axial ratios can be calculated. Thus *gypsum* (Fig. 44) has $a:b:c=0·690:1:0·412$; $\beta=80°\ 42'$; and $l(111)$, $m(110)$, $b(010)$.

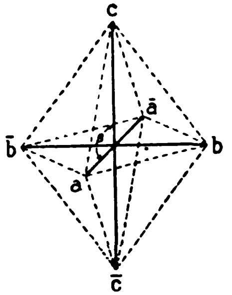

FIG. 43.—Crystallographic Axes of the Monoclinic System.

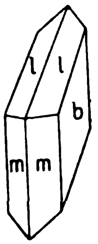

FIG. 44.—Gypsum.

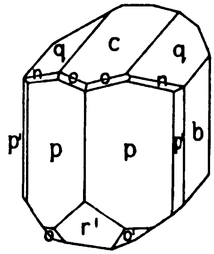

FIG. 45.—Ammonium Magnesium Sulphate.

Ammonium magnesium sulphate $(NH_4)_2SO_4.MgSO_6.6H_2O$ (Fig. 45), has $a:b:c=0·740:1:0·492=107°\ 6'$; and $b(010)$, $c(001)$, $p(110)$, $p'(130)$, $q(011)$, $r'(201)$, $o(111)$, $o'(111)$, $n(121)$. Potassium chlorate, potassium ferrocyanide, potassium chloride, barium chloride, and nickel chloride also furnish good crystals for examination.

EXAMPLES.—Borax—$Na_2B_4O_7.10H_2O$; gypsum; ferrous sulphate—$FeSO_4.7H_2O$; potassium and sodium carbonates; felspar—orthoclase; sodium sulphate—$Na_2SO_4.10H_2O$; ammonium magnesium sulphate—$(NH_4)_2SO_4.MgSO_4.6H_2O$; potassium chlorate; potassium tetrathionate—$K_2S_4O_6$; tartaric acid; sulphur—from fusion; potassium sulphate; cane sugar; arsenic disulphide—realgar; ammonium dichromate; rubidium magnesium sulphate; acid mercuric fluoride; clinohedrite; scolecite; lead chromate; oxalic acid; sodium acetate; augite; hornblende; vivianite; epidote; etc.

VII. Triclinic system.—Crystals of this system can be referred to three oblique axes, Fig. 46. There are no closed symmetrical forms, and hence each crystal must be a combination of different forms. The crystals have no axes nor planes of symmetry, but they may have a centre of symmetry; $a \lesseqgtr b \lesseqgtr c$, and $\alpha \lesseqgtr \beta \lesseqgtr \gamma$. The crystals are biaxial; the optical extinction is oblique in all three positions; and there are three indices of refraction. This system has also been designated the *anorthic*, *clino-rhomboidal*, *asymmetric*, or the *double oblique*.

Typical examples for examination are crystals of copper sulphate (Fig. 48) and of potassium dichromate (Fig. 47). The crystals are defined by the development forms, and the values of the interfacial angles from which the axial ratios can be computed. For instance, potassium dichromate (Fig. 47) has $a:b:c = 0{\cdot}558:1:0{\cdot}551$; $\alpha:\beta:\gamma = 82°\ 0' : 90°\ 51' : 83°\ 47'$; $a(100)$, $b(010)$, $c(001)$, $q(011)$, $p(110)$; *copper sulphate*, $CuSO_4.5H_2O$ (Fig. 49), has $a:b:c = 0{\cdot}5715:1:0{\cdot}5575$; $\alpha:\beta:\gamma = 82°\ 16'$; $107°\ 26'$; $102°\ 40'$; and $q(011)$, $q'(011)$, $t(021)$, $t'(021)$, $s(\bar{1}21)$, $s'(\overline{121})$, $o(111)$. Potassium persulphate, manganese sulphate, and boric acid furnish good crystals for examination.

EXAMPLES.—Potassium dichromate; copper sulphate—$CuSO_4.5H_2O$; calcium thiosulphate—$CaS_2O_3.6H_2O$; boric acid; potassium ferricyanide; anhydrous manganese sulphate; copper selenate; anorthite—lime felspar; cryolite; chromic phosphate—$CrPO_4.6H_2O$; labradorite; chalcanthite; rhodonite; albite; oligoclase; axinite; bismuth nitrate; etc.

The relation between crystal form and molecular complexity.—J. W. Retgers (1894) noticed a general relation between the molecular complexity of over nine hundred substances and their crystalline form. Table I shows the approximate percentage distribution of compounds of different molecular complexity in the different crystal systems. The hexagonal system here includes the trigonal and hexagonal systems.

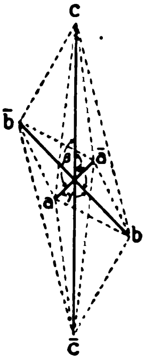

FIG. 46.—Crystallographic Axes of the Triclinic System.

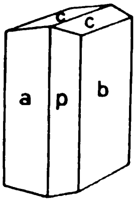

FIG. 47.—Potassium Dichromate.

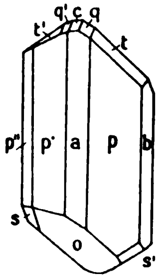

FIG. 48.—Copper Sulphate Pentahydrate.

TABLE I.—PROPORTION OF SUBSTANCES OF DIFFERENT MOLECULAR COMPLEXITY CRYSTALLIZING IN THE DIFFERENT SYSTEMS.

Complexity of molecules.	Number of substances considered.	Per cent.					
		Cubic.	Hexagonal.	Tetragonal.	Rhombic.	Monoclinic.	Triclinic.
Elements .	40	50	35	5	5	5	0
2-atoms .	67	68·5	19·5	4·5	3·0	4·5	0
3-atoms .	63	42	11	19	23·5	3	1·5
4-atoms .	20	5	35	5	50	5	0
5-atoms .	50	12	38	6	36	6	2
6-atoms or more	673	5·8	4·6	7·0	27·3	37·3	8

The results indicated in Table II can be expressed differently by including the cubic and hexagonal systems in one group, and the remaining systems in another group. From this it follows that substances with complex molecules are more inclined to crystallize in systems with a low order of symmetry; and the simpler the molecules of a substance, the greater the probability of its crystallizing in the hexagonal or cubic systems with a high order of symmetry. G. Tschermak[5] has shown that when 2, 3, or 6 atoms are present in the molecular formula, the compound usually crystallizes in the rhombohedral or hexagonal system, and the crystals are characterized by axes of two-, three-, or six-fold symmetry—*e.g.* Fe_2O_3, $FeCl_3$, Ag_3SbS_3, PI_3, $SrCl_2.6H_2O$, etc.—those compounds which have the number 4, but not 6, in their molecular formulæ, usually crystallize in the tetragonal system, and they possess a two- or four-fold, but not a six-fold, symmetry—*e.g.* $ZrSiO_4.4H_2O$, etc. Compounds in which the numbers 3 and 4 occur in the molecular formulæ, have a tendency to crystallize in the cubic system the axes of which possess a three- and four-fold symmetry—*e.g.* $2KF.ZrF_4$, Ag_3PO_4, As_4O_6, etc.

TABLE II.—PROPORTION OF SUBSTANCES OF DIFFERENT MOLECULAR COMPLEXITY CRYSTALLIZING IN THE CUBIC AND HEXAGONAL SYSTEMS.

Crystal system.	Elements (per cent.).	Atoms per molecule.				
		2	3	4	5	6 and over.
Cubic and hexagonal . .	85	88	53	40	50	20·4
Other systems . . .	15	12	47	60	50	79·6

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[2] J. W. Evans, *Min. Mag.*, **18**. 324, 1919; P. von Groth, *Physikalische Krystallographie*, Leipzig, 1876.

[3] T. V. Barker, *Ann. Rept. Chem. Progress*, **12**. 256, 1915.

[4] T. V. Barker, *Chem. News*, **106**. 199, 1912.

[5] G. Tschermak, *Tschermak's Mitt.*, **22**. 393, 1903.

§ 7. The Growth of Crystals

The very molecules appear inspired with a desire for union and growth.—J. TYNDALL.

We do not understand the phenomenon of crystallization, nor do we know how crystals grow. The facts indicated in the preceding sections have made it almost certain that the space occupied by a crystal is not all matter; that their structure is discontinuous; and that crystals grow by accretion, molecule by molecule, like bricks in the hands of the builder, and in accord with "an architectural plan more elaborate and exact than that of any human architect." We are quite ignorant of the shape of the structural units. C. Huyghens saw that the regularity of crystals depends on the arrangement of the smallest particles from which they are built, and he assumed the structural units of calcspar to be rotational ellipsoids. For convenience, they are usually taken to be spherical, as Robert Hooke did in his *Micrographia* (London, 1665), when he said:

> All these regular figures that are so conspicuously various and curious, arise only from three or four several positions or postures of globular particles. . . . And this I have *ad oculum* demonstrated with a company of bullets and some few other very simple bodies; so that there was not any regular figure which I have met withal of any of these bodies and I could not with the composition of bullets or globules . . . imitate even almost by shaking them together.

C. F. G. H. Westfeld (1767) and T. Bergmann (1773),[1] in his *Variæ cristallorum formæ a spato ortæ*, also held the view that many crystal forms could be obtained by laying together little rhombohedra; and in 1772, J. B. L. Romé de l'Isle pointed out that the various shapes of natural crystals can be derived from a fundamental figure or *primitive form*, and that the variety of form which is found in natural crystals is due to the variety of the secondary faces. About 1801, R. J. Haüy[2] developed the idea, that all crystal forms, other than the primary ones, could be exactly imitated by building on the faces of the primary forms, successive layers of what he called integrant molecules—*molécules intégrantes*— each successive layer being regularly diminished by the abstraction of one or more rows either parallel to each edge, or to the diagonals of the faces of the primitive form or in some other way. R. J. Haüy's integrant molecules were of three shapes—the parallelopiped, tetrahedron, and the trigonal prism. R. J. Haüy deduced the shapes of his crystal units from the shapes of the cleavage fragments. W. H. Wollaston,[3] like R. Hooke, suggested the presence of *cleavage molecules* in crystals, but he also remarked that, in place of spheres, mathematical points endowed with forces of attraction and repulsion can be postulated with equal success. In 1831, J. F. C. Hessel[4] showed in his book, *Krystallometrie oder Krystallonomie und Krystallographie* (Leipzig, 1831), that only thirty-two types of symmetry are possible with a solid bounded by plane faces conforming to R. J. Haüy's law of rational indices. At that time comparatively few of these thirty-two types were known. In 1865, A. Gadolin independently made the same discovery as J. F. C. Hessel, and during the next three years V. von Lang established the external geometry, so to speak, or the symmetry of the thirty-two classes of crystals.

Speculations were gradually diverted away from the external form of the crystals, and attention focused more on to the internal orientation of the centres of the particles; L. A. Seeber (1824) and G. Delafosse (1843)[5] regarded the crystal structure as a kind of network of molecular points repeated as identical units throughout space without regard to their shape or constitution, and thus arose the idea that the arrangement of the middle points of the structural units resembles a parallelopipedal network or **space-lattice**—German, *Raumgitter*; French, *réseau.* Thus, said G. Delafosse (1843):

> The molecules of the crystal must be situated in a uniform and symmetrical manner, having their centres of gravity at the points of intersection of a series of parallel planes, and thus present the picture of a lattice with parallel-figured meshes.

The idea of a space-lattice can be gathered from Figs. 49 to 68; it has been likened to a kind of three dimensional net, in which the particles are situated at the corners of parallel and equal parallelopipeda, so that the strings of the net represent the lines of intersection of the planes, and the knots, nodes, or points, their points of intersection. M. L. Frankenheim[6] examined the different kinds of networks of points and compared them with the various types of symmetry presented by crystals; and M. L. Frankenheim's geometrical investigation was supplemented with elegant proofs by A. Bravais[7] in 1848. Whatever be the actual size and shape of the structural unit, it is equally certain that all phenomena peculiar to crystals depend upon the structure or upon the orientation of the constituent molecules of the crystals. The possibility of assigning imaginary crystallographic axes to all known crystals shows that the molecules must be so related to one another that (1) the structural units or molecules of crystals of the same chemical substance, under similar conditions, must be alike in size, and in the distribution of their attractive forces; and (2) the relative position of any one molecule must be symmetrical with that of every other molecule. No other arrangement can be regarded as possible in a crystal. Hence the study of crystal structure, the orientation of the structural units, is reduced to the purely geometrical investigation of the possible arrangements in space of networks of structural units which satisfy these conditions.

Among the problems concerned in elucidating the structure of crystals are: (1) What is the nature of the structural units? (2) How are these units arranged or oriented in space? and (3) What is the nature and character of the vectorial or directed forces which fix the relative positions and determine the orientation of the structural units which make up the crystals? Great success has been attained with the second problem, which has been studied geometrically quite independently of the nature of the material. Geometricians have investigated: **the nature of the symmetrical arrangement of particles in space which will confer on matter the symmetry shown by crystals.** As a result, the theory of the homogeneous partitioning of space, *i.e.* of the homogeneous repetition of identical parts in a uniform structure, has probably reached its final form.

The history of the development of this theory is interesting because it shows how the testing of the deductions of the mathematician's definitions of homogeneity by comparison with the morphological properties of crystals from time to time, compelled the mathematicians to make the definition of homogeneity wider and wider until it included all known forms of crystals. A. Bravais, for instance, based his geometrical treatment of the homogeneous partitioning of space on the assumption that if the properties of crystals depend upon the nature and arrangement of the crystal units, their properties are alike in *parallel* directions, and that fourteen types of space-lattice are possible with a symmetry, corresponding with the maximum symmetry of one or other of the seven systems of crystal architecture.

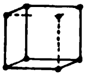
FIG. 49.—Simple Cubic Lattice.

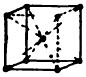
FIG. 50.—Body-centred Cubic Lattice.

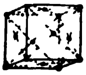
FIG. 51.—Face-centred Cubic Lattice.

The fourteen space-lattices are illustrated in Figs. 49–68, where the dots are supposed to represent the positions of the centre of gravity of the atoms. The lattices belonging to the cubic system are indicated in Figs. 49 to 51. There is: I. *The simple cubic lattice*, Fig. 49, with a particle at each corner of a cube. If the atoms are all nearly equal in size, the symmetry is apparently cubic holohedral—*e.g.* sodium chloride, NaCl; galena, PbS, etc. If two sizes of atoms are present, the symmetry is plagihedral—*e.g.* sylvine, KCl; potassium bromide, KBr; etc. II. *The body-centred cubic lattice*. Here the cube has a particle at each corner and one at its centre. The symmetry when the atoms are all alike is cubic holohedral, Fig. 50, *e.g.* iron, nickel (in part), and sodium. III. *The face-centred cubic lattice*. Here the cube has a particle at each of its corners and one at the centre of each of its faces. The symmetry is cubic holohedral when the atoms are all alike, Fig. 51, *e.g.* copper, silver, gold, lead, aluminium, nickel (in part), etc. The space lattice may consist of two or more mutually penetrating lattices. For example, two interpenetrating face-centred cubic lattices furnish the *double face-centred lattice* of the diamond and zinc blende types illustrated in Fig. 52. The atoms may be all alike when the symmetry is cubic-tetrahedral in some respects, but holohedral by compensation—*e.g.* diamond, silicon, etc. If the atoms are all alike and more than quadrivalent, the symmetry is hexagonal—trigonal, or rhombohedral—*e.g.* antimony, bismuth, arsenic, tellurium. If two kinds of atoms are present, the symmetry will be cubic tetrahedral—*e.g.* sphalerite, ZnS. If three or more kinds of atoms are present, and the atoms are numbered 1, 2, 3, then reading from the top layer downwards, 1, 2, 3, 2, 1. For instance, in chalcopyrite with Cu, 1; S, 2; and Fe, 3, alternate layers taken vertically consist exclusively of each kind in turn. The symmetry is scalenohedral– *e.g.* chalcopyrite, $CuFeS_2$; stannite, Cu_2FeSnS_4. If the atoms be supposed in contact, the shapes of the spaces available for them are illustrated in Figs. 53 to 56, when the constituent atoms are all equal in size. Atoms of one kind may form a simple cubic lattice with an interpenetrating symmetrical face-centred cubic lattice containing atoms of another kind. The symmetry is cubic-holohedral—*e.g.* calcium fluoride, CaF_2. In

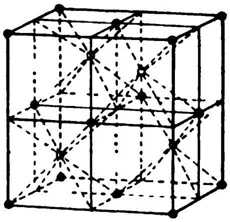
FIG. 52.—Double Face-centred Cubic Lattice.

hauerite, MnS_2, and pyrite, FeS_2, the symmetry is cubic-pyritohedral, and the space-lattice is similar to the former, excepting that the simple lattice is distorted. In cobaltite, CoSAs, the atoms on the distorted simple cubic lattice are of two kinds, and the symmetry is cubic tetartohedral. In cuprite, atoms of copper are on a body-centred cubic lattice, and the atoms of oxygen are on an interpenetrating distorted face-centred lattice; and the symmetry is cubic-gyrohedral.

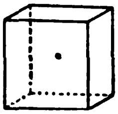
FIG. 53.—Atoms of Simple Cubic Lattice.

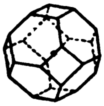
FIG. 54.—Atoms of Body-centred Cubic Lattice.

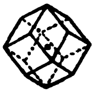
FIG. 55.—Atoms of Face-centred Cubic Lattice.

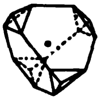
FIG. 56.—Atoms of Double Face-centred Cubic Lattice.

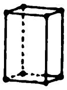
FIG. 57.—Square Prism Lattice.

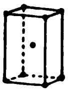
FIG. 58.—Body-centred Square Prism Lattice.

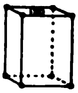
FIG. 59.—120° Prism Lattice.

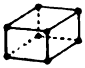
FIG. 60.—Rhombohedron Lattice.

The tetragonal system is represented by IV. *The square prism lattice*; Fig. 57; and by V. *The body-centred square prism lattice*, Fig. 58. The hexagonal and trigonal or rhombohedral system is represented by VI. *The 120° square prism lattice*, Fig. 59; VII. *The rhombohedron lattice*, Fig. 60.

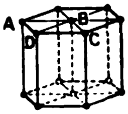

FIG. 61.—Hexagonal Prism.

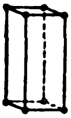
FIG. 62.—The Rhombic Lattice.

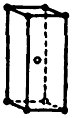
FIG. 63.—The Body-centred Rhombic Prism Lattice.

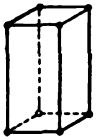
FIG. 64.—The Rectangular Prism Lattice—Rhombic.

The hexagonal prism, Fig. 61, may be regarded as a combination of three 120° prisms, each with a structure like the sixth lattice.

The rhombic system is represented by VIII. *The rhombic prism lattice*, Fig. 62; IX. *The body-centred rhombic prism lattice*, Fig. 63; X. *The rectangular prism lattice*, Fig. 64; and XI. *The body-centred rectangular prism lattice*, Fig. 65. The monoclinic system is represented by XII. *The clinorhombic prism lattice*, Fig. 66; and XIII. *The monoclinic parallelopiped lattice*, Fig. 67. The triclinic system is represented by XIV. *The triclinic prism lattice*, Fig. 68.

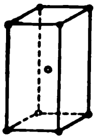
FIG. 65.—The Body-centred Prism Lattice—Rhombic.

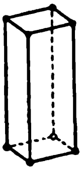
FIG. 66.—The Monoclinic Prism Lattice.

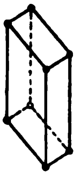
FIG. 67.—The Monoclinic Parallelopiped Lattice.

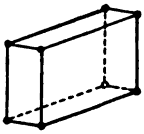
FIG. 68.—The Triclinic Prism Lattice.

In 1869, C. Wiener [8] and C. Jordan extended A. Bravais' assumption by laying down the principle that "regularity in the arrangement of identical atoms is presented when every atom has the remaining atoms arranged about it in the same manner; thus making homogeneity depend primarily on the continued repetition through space of the same relation between a unit and the entire structure as unlimited, instead of laying stress on orientation." L. Sohncke, in his *Entwicklung einer Theorie der Krystallstructur* (Leipzig, 1879), followed up the subject, and assumed that in a homogeneous structure the arrangement about any one point is the same as that about every other point, so that the aspect from any one point is the same as that viewed from any other point. He fulfilled this condition, by selecting one of A. Bravais' fourteen lattices, with one or more lattices identical with it, and thrusting the lattices into one another so as to satisfy the condition for homogeneity. This furnished L. Sohncke with 65 systems of points in place of A. Bravais' 14; and these fall into the 32 classes into which observation has classified all crystals known to exist. In 1887, L. Wulff and F. Haag showed that there is no provision in L. Sohncke's system for the crystals of the rare mineral dioptase, nor for the polar or hemimorphic forms of tartaric acid. L. Sohncke then modified his early theory, which assumed that the units were all of one kind and identically related to the structure as a whole. *A crystal consists of a finite number of interpenetrating, regular systems of points; each separate point system is occupied by similar material particles, which may be the same or different for the interpenetrating partial systems which form the complex system.* Each partial system of units taken by itself is homogeneously arranged, and all the different units are supposed to possess identical systems of axes, and to have the same set of translations common to them; but L. Sohncke did not stick to the purely geometrical problem, for he introduced hypotheses as to the physical character of the structural units, which he said can be rejected "only if they are held to be improbable."

In 1884, P. Curie [9] drew attention to the fact that crystals display not only identity of parts, but they also exhibit enantiomorphous similarity, and he deduced L. Sohncke's 32 varieties of external form, but did not pursue the subject further. Between 1891 and 1894, E. S. von Federoff,[10] A. Schönflies, and W. Barlow, working by three different methods, and in the order named, showed that L. Sohncke's definition provided for each unit being surrounded by all the other molecules in *like* manner where like referred only to identity and not to the resemblance which obtains between an object and its image in a mirror. In L. Sohncke's system two identical sets are superposable; in the extended theory, they are not necessarily superposable. H. A. Miers [11] illustrated this by showing that a point in the centre of a right-hand glove has precisely the same environment as a point in the centre of a left-hand glove, and yet the two are not superposable, for the one is as it were the reflection of the other. A. Schönflies admits the principle of reflection across a plane, inversion about a centre, or a combination of the two as an additional mode of repetition applicable to a system without changing its aspect. There are 230 possible ways of partitioning space into systems of points as types of homogeneous structures; and of these, Sohncke's 65 point-systems and A. Bravais' 14 space-lattices are special cases. Each of these 230 types of structure can be referred to one of the 32 classes into which all known crystals can be arranged, and these 32 classes can still further be grouped into the seven-systems of crystal architecture. "With the establishment of these 230 types of crystal structure," says A. E. H. Tutton, "the geometrical theory of crystal structure has attained what in all probability will prove to be finality." However, directly the space units or cells are invested with special shapes—the *parallelohedra* of E. von Federoff and Lord Kelvin, the *Fundamentalbereich* of A. Schönflies, or the *spheres of influence* of W. Barlow—complications are introduced, and controversial questions arise.

The birth of crystals.—As previously indicated, G. Quincke [12] assumed that the first stage in the crystallization of a liquid involves the separation of the solution into two immiscible liquids, one of which is formed in a relatively small quantity, so as to form a kind of emulsion; and H. F. Link (1839) thought that he could detect such globules at the moment of separation by using a magnification of 600 diameters. If the nuclear masses of the separating liquid are isotropic, with their physical characters alike in all directions, the nuclei would form spherical globules. The spherical globules would afterwards either (i) solidify and serve as nuclei for the subsequent growth of crystalline particles, or (ii) they would form particles in the act of solidification. H. Vogelsang (1875) inclined to the former hypothesis because he and C. Brame (1853) had observed what they considered embryonic sulphur crystals to separate as globular solids from solutions of sulphur in viscous solvents. H. Vogelsang called these embryonic crystals *globulites*.

The term **crystallite** is applied in several different ways—*e.g.* it has been employed for the structural units of crystals; for abnormally elongated and branched forms—crystal skeletons—in which the normal faces and angles are not developed; and for abnormally developed crystal nuclei which have received various names according to their shape or appearance—*globulites, longulites, margarites, belonites, cumulites*, etc.

The belief that small isotropic globulites first appear as nuclei during crystallization, and that only after these globulites have attained a certain size do they assume the crystalline state, has led W. Ostwald, G. Quincke, and others to believe that in the development of crystals, the crystal embryos are at first in the state of droplets of undercooled liquid, and only later become solid as they enlarge into crystals. This means that the molecules of the primary crystals are not vectorially oriented, a statement which has not yet been demonstrated.

H. Vogelsang's hypothesis is discredited, because C. Brauns (1899) showed that what are thought to be solid globules are in reality minute globular masses of undercooled solutions of high viscosity, as E. Weiss (1871) had previously supposed. If the second alternative be true the particles must be sub-microscopic, because T. W. Richards and E. H. Archibald (1901) found that instantaneous photographs of crystallizing barium chloride and potassium iodide showed that crystals have a definite character from the moment they are able to affect a photographic plate.

In his great work *On the equilibrium of heterogeneous substances* (1878), J. W. Gibbs showed that the stable form of a crystal is that for which, as a result of capillary forces, the total surface energy is a minimum. The same conclusion was drawn by P. Curie in 1885 and called **Curie's capillarity theory.** Each crystal face has a specific capillary constant which is measured by the work involved in increasing its surface face by unit area. Let the areas of the various faces be denoted by $s_1, s_2, s_3, \ldots$, and the respective capillary constants by $\sigma_1, \sigma_2, \sigma_3, \ldots$, then, adds J. W. Gibbs,[13]

On the whole it seems not improbable that the form of very minute crystals in equilibrium with solvents is principally determined by the condition that $\Sigma(\sigma_1 s_1 + \sigma_2 s_2 + \sigma_3 s_3 + \ldots)$ shall be a minimum for the volume of the crystal—except so far as the case is modified by gravity or the contact of other bodies—but as they grow (in a solvent no more supersaturated than is necessary to make them grow at all), the deposition of new matter on the different faces will be determined more by the nature (orientation) of the surfaces and less by their size and relations to the surrounding surfaces. As a result, a large crystal thus formed will generally be bounded by those surfaces alone on which the deposit of new matter takes place least readily, with small, perhaps insensible truncations.

Crystals take the habit which gives them the minimum surface energy, so that the relative areas of the faces depend on their capillary constants. While the principle probably operates with microscopic crystals it does not seem to be valid for large crystals. Droplets of liquid usually assume a spherical shape, corresponding with a minimum surface area per unit volume. A few crystals bounded wholly or partially by curved faces are known, and others are so richly faceted that they approximate to a spherical form. The most frequent styles of development are then plates or fine needles, shapes which approach a maximum area per unit volume. P. Curie assumed that plane faces are developed in preference to curved faces because the capillary constants of the former are the lower.

T. V. Barker has pointed out that if J. W. Gibbs' theorem be valid, a knowledge of the capillary constants would enable a prediction to be made of the form of a crystal. For example, in the case of a cubic crystal of common salt, in which both octahedral and cubic faces are observed, the crystal could develop only cubic or octahedron faces according as $s(100) : S(111)$ is less than $1 : \sqrt{3}$, or greater than $\sqrt{3} : 1$. S. Berent measured the capillary constant for water and a solution of carbamide where in the one case cubic faces are developed and in the other octahedron faces. The results demonstrated the existence of capillary differences, but they were unfavourably criticized by F. Pockels. Another deduction from the theory is that large crystals in favourable circumstances must grow at the expense of small ones, and this was verified by the work of G. A. Hulett on very minute crystals.

The theory of J. W. Gibbs also leads to the assumption that different faces have different solubilities. For a crystal departing from the equilibrium shape when placed in a solution of suitable strength should dissolve from some faces while others grow. M. le Blanc and G. Elissafoff showed that the only satisfactory way of testing the deduction is to find if a solution can be obtained of such a concentration that one face grows while another dissolves; and J. J. P. Valeton proved that it was not possible to obtain conditions at which the cubic or dodecahedron faces of alum dissolve while octahedron faces grow, but he did obtain a solution of such concentration that a variation of temperature even so small as 0·003° sufficed to transform unmistakable growth into unmistakable solution.. G. Wulff also measured the relative velocities of growth of the crystal faces of monoclinic Mohr's salt reckoned from the centre of the crystal. He found the relative rates of growth to be (110), 1·96; (001), 2·25; (111), 2·50; $(\bar{1}11)$, 2·64; (011), 2·77, when the rate for the $(\bar{2}01)$ face was taken as unity. S. Tolloczko also found the velocity of solution of gypsum on the (010), (110), and (111) faces were respectively 1, 1·76, and 1·88; and A. Ritzel found that water dissolved the octahedron faces of a crystal of sodium chloride faster than the cube faces, but with a dilute solution of carbamide this relation was reversed. G. Wulff and H. Liebmann also argued that the relative velocities of growth of the crystal faces are proportional to the capillary constants, but H. Hilton, G. Friedel, and C. Fastert have shown that the conclusion is faulty; and A. Berthoud has shown that the differences in the solubilities of the different faces of a crystal are so minute in comparison with the difference in the rates along different axes as to be without influence on the crystalline habit.

L. Sohncke (1888) also attempted to establish a relation between the surface energy of a crystal face and what he called its face-density, meaning by that the number of mass-points (crystal units) existing in unit area of a crystal face. He showed that in a face of maximum face-density, the particles can come no nearer together, and therefore the minimum amount of work remains for the molecular forces to perform. This means that the surface energy of such a face is a minimum. Hence, the crystalline face which is most thickly studded with mass-points will occur most frequently. The density of such points on a face is known as the *reticular density* (A. Bravais). L. Sohncke also attempted to find a relation between the principal cleavage form and the structure of a crystal.

The main factors which determine the crystalline habit are (1) the internal structure of the crystals; (2) the degree of supersaturation; and (3) the nature of concentration (diffusion) currents in the solution during deposition. A. A. Noyes and W. R. Whitney (1897) showed that the dissolution of a crystal is governed by the rate of diffusion of the dissolved molecules across the zone of falling concentration which, being replenished instantaneously from the crystal, remains saturated. M. le Blanc applied the theory to the reverse process of crystallization, but C. L. Wagner and A. Berthoud have pointed out that M. le Blanc's hypothesis takes no account of the varying rates of crystal growth on different faces. C. L. Wagner postulated that the thickness δ of the diffusion zone varies from face to face, but, as L. Brunner showed, even with the most violent agitation δ is at least 0·03 mm., and the thickness δ is not likely to be appreciably influenced by forces of molecular magnitude at the crystal surface. A. Berthoud showed that the rate V at which equilibrium tends to establish itself between a given area s of crystal surface and the solution is proportional to the difference between the concentration C_0 of the saturated solution and the concentration C_1 in contact with the crystal. If k denotes the velocity constant of crystallization of the given surface; K, the diffusion constant; and C, the mean concentration in the diffusion zone, the velocity, $V=ks(C_1-C_0)$; or velocity, $V=sK(C-C_0)/(\delta+K/k)$. When K/k is very small in comparison with δ, which occurs when the solution is quite still, the formula reduces to A. A. Noyes and W. R. Whitney's expression. The more nearly this condition is attained in practice, the more nearly do the crystal faces approximate to equal rates of growth, and facets appear which are not seen when the solution is agitated. A. Ritzel also found the rate of solution of sodium chloride varied with the degree of under-saturation of the solution.

When a crystal is growing, curiously enough, the liquid in the immediate vicinity of the growing face is more concentrated, for it contains more of the dissolved substance per unit volume than the liquid a short distance away from the growing face. At first sight, it seems as if **the growing crystal exerts some kind of attraction on the molecules of the dissolved substance a short distance away.** For instance, if a saturated solution of zinc silicate in molten lead borosilicate tinted with cobalt silicate be allowed to crystallize, the crystals of willemite which separate will also abstract the cobalt silicate from the solution, and form patches of beautiful " azure blue " crystals in a colourless matrix. If no crystallization occurs, the matrix will be uniformly coloured an intense blue. Presumably, the concentration of the colouring agent at the crystal face is maintained by diffusion from the body of the liquid. These facts, as well as the phenomenon exhibited by liquid crystals, lend support to the view that as a liquid nears its crystallizing point, there is a marshalling of the molecules of a liquid about to crystallize which culminates at the moment of separation of the solid crystalline nucleus.

Growing crystals of hydrated strontium nitrate take up colouring matter from a solution coloured with logwood. P. Gaubert[14] showed that the different faces of a crystal have not the same power to absorb colouring matter, *e.g.* certain faces of the crystals of lead nitrate or urea nitrate growing in solutions coloured with methylene blue do not take up the dye; and picric acid crystals growing in solutions containing the same colouring agent, have some faces stained blue, while others remain yellow. R. Marc attributes the power possessed by crystallizing salts to take up organic dyestuffs to adsorption. It must not be supposed that crystals usually gather up impurities from the mother liquid (except by mechanically entangling the mother liquid with the crystal); the converse is often the case. The thrusting aside of impurities by the tip of a growing crystal can be readily observed under the microscope. The shape of growing crystals and the movements of the molecules in the solvent against the resistance exerted by the liquid are controlled by molecular forces which are not alike in all directions. It also follows that the physical character of the mother liquid must modify the rate at which the molecules are supplied to the growing crystal and determined to some extent its habit and form.

The kinetic theory of crystal growth.—The kinetic theory has taught us that during crystallization, it is probable that a series of exchanges between the molecules of the crystal and the molecules of the solution are going on all over the surface of the growing crystal. Molecules of the dissolved substance are attracted to the surface of the growing crystal, the molecules of the crystal continually pass into solution again. If the crystal is growing, more molecules are deposited on the crystal than are lost in unit time; and if the crystal is dissolving, less molecules are deposited on the crystal than are lost in a unit of time.

Let Fig. 69 represent, diagrammatically, a growing crystal, one face of which is incomplete; and assume that the structural units are spherical molecules. If a sphere lodges against a completed face, it can touch *three* other spheres, and whether or not the molecule leaves the growing crystal will depend upon the force of attraction exerted upon it by the three contiguous molecules. Again, suppose that a sphere lodges on the little ledge formed by the top layer of the incomplete face. It will then touch *five* instead of *three* spheres; and it will be held in place by the attraction of five contiguous spheres. Obviously, therefore, (1) during the exchange of molecules between the growing crystal and the solution, those molecules which have been deposited on the **growing face** will be retained more tenaciously than those deposited on a **completed face**; (2) as soon as a few molecules happen to be deposited in juxtaposition on the face of a crystal, subsequent growth on that face will be more rapid than the sporadic growth elsewhere; (3) an incompleted layer will rapidly extend until it covers the entire face of the crystal, etc. These deductions are in harmony with known facts.

G. D. Liveing's explanation of the phenomena is as follows: The surface tension at the boundary between a crystallizing solid renders a supply of energy necessary to generate a surface in the interior of the fluid; and the supersaturation of air with water vapour, and the supersaturation of solutions of salts, show that the generation of a free surface in the interior of a gaseous or liquid fluid is not easy. Similarly, if a surface is already formed in a fluid, as when a supersaturated solution meets the air, or the sides of the containing vessel, if the surface energy of either boundary be less than that at the boundary surface of the crystalline solid and the solution, energy will have to be supplied in order to produce a new surface—but not so much as if there were no such surface. Hence, crystals generally form on the top, or on the sides of the containing vessel. Part of the energy of the change of state from liquid to solid is generally available for producing a new surface; but when the mass deposited is small, the energy available will be correspondingly small—for *mass* varies as the cube of the diameter, while *surface* varies as the square of the diameter of a solid. Consequently, the first solid nucleus which separates from a solution is liable to be squeezed back into a liquid by its own surface tension, so as to form a supersaturated solution. A deposit will form most easily on a surface with the same energy as that of the deposit, because the additional energy required is only needed for the extension of the surface. This explains the seeding of supersaturated solutions by particles of the same salt as is in solution; and also how big crystals grow faster than little ones, for the ratio of the increase of surface to that of the volume decreases as the crystal grows.

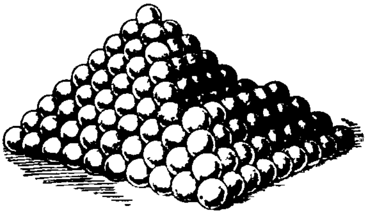

FIG. 69.—Imaginary Diagram of Growing Crystal.

If one part of a crystal be mutilated or damaged, the injured part may grow more rapidly than the other parts of a crystal until the injury disappears, and the perfect crystal is restored.[15] In his study *Die Regeneration der Krystalle* (Leipzig, 1895–6), G. Rauber was so impressed by the inherent power of a mutilated crystal to heal itself that he was led to propound the hypothesis that crystals are controlled by vital forces. D. N. Artemíeeff checked the healing process by exact measurements with the goniometer. According to T. V. Barker, he found:

> In the first period of growth the sphere exhibits a number of glittering spots corresponding with the most important faces. The rest of the surface remains matt, but later becomes covered with tiny crystals in parallel positions, each of which contributes a part to sharp goniometer reflections of the important forms: simultaneously, reflections corresponding with the less important forms appearing as glittering points. As growth proceeds, the less important faces disappear, the tiny parallel crystals coalesce, and the final result is a hemi-crystal bounded by common faces.

Further, if a crystal be removed from a solution in which it is growing, it does not lose its power of growth, for if the crystal be placed in a suitable environment at any future time, it will continue growing as if there had been no interruption. These two statements are demonstrated by the so-called *capped quartz* in which there is an overgrowth of transparent quartz on an old crystal covered with a film of clay or other material which has prevented the new growth adhering to the old so that the capping layer can be sometimes readily detached from the inner kernel. In *ghost quartz*, the film of "dust" has not been thick enough to prevent adhesion, but is sufficient to enable the outlines of the kernel crystal to be readily seen. In the remarkable photograph, Fig. 70, some quartz crystals, grown during some former geological period, have lost their external crystalline form by attrition as they "knocked about the world"—blown about as sand in the deserts, washed down the hillsides in streams of water, etc.—and they were finally deposited as rounded sand grains along with the mountain limestone from some prehistoric sea. There, the damaged crystals—sand grains—met a suitable environment in later years—probably water percolating through the limestone rocks, and carrying silicic acid in solution. The damaged crystals were repaired. Each sand grain, now embedded in each repaired crystal, served as a foundation for rebuilding the damaged quartz crystals on the original architectural plan. In the photograph it was impossible to get all the crystals in focus at the same time. Here, again, we can gaze only in ignorant wonder while the molecules of the solute deploy their mysterious forces in crystal building,

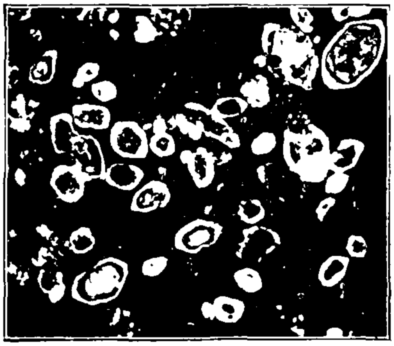

FIG. 70.—Growth of Quartz Crystals about Old Sand Grains.

> With rapt admiration we contemplate
> Immortal nature's ageless harmony
> And how and when, her order came to be.—EURIPIDES.

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§ 8. Analysis of the Structure of Crystals by X-rays

All effects are exactly proportional to their causes, therefore, unless their mutual relations be examined by accurate trials, theory must be lame and imperfect.—T. BERGMANN.

The works of nature which seem most desirous to escape our scrutiny are sometimes those which have most to show us.—R. J. HAÜY (1801).

It is shown in the text-books on physics that when a beam of light strikes against a series of very fine lines regularly ruled on the surface of a metal or glass plate, each line acts as a fresh centre from which a secondary train of light waves is diffracted. The diffracted waves enhance some of the normal light waves and damp down others, with the result that the beam of light is analyzed into a series of spectra ; the diffracted waves quench the coloured waves of normal light in the order and proportion of their wave-lengths.

B. Walter and R. Pohl found that the diffraction effects produced by the passage of X-rays through fine slits indicate that the wave-length of these rays is of the order 10^{-9} cm., a value but little less than the estimated distance between contiguous molecules in a crystal. In a paper *On the diffraction of short electromagnetic waves by crystals* (1912),[1] M. von Laue argued that a crystal must form a natural kind of grating on account of the regular disposition of the structural units. The units of a crystal are, however, so small in comparison with the wave-length of ordinary light that the crystal behaves as if it were a continuous medium when exposed to a ray of ordinary light ; on the other hand, the wave-length of the X-rays is so short —about $\frac{1}{10,000}$th of that of light—that the structural units of the crystal form a series of widely separated and regularly arranged particles each of which should diffract a small proportion of the energy of the incident X-rays ; each structural unit should be a centre of diffraction from which a secondary pulse of wavelets is diffracted producing interference effects somewhat analogous with the effect of a diffraction grating on ordinary light.

W. Friedrich and P. Knipping (1912) tested M. von Laue's hypothesis by allowing a primary pencil of X-rays to pass through a crystal, and afterwards impinge on a photographic plate. When the plate was developed the result with a crystal of zinc blende, ZnS, when the X-rays were parallel to the diagonal axis through the centre of the cubic crystal, was remarkable, four series of spots were formed symmetrically grouped about a central image, as illustrated by half a photograph, Fig. 71, also called a *röntgenogram* or *X-rayogram*, or a *radiogram*. Several hours' exposure were needed to produce good results because the greater proportion of the rays are not deflected by the crystal. The dark central spot represents the undeflected pencil of rays, while the smaller dark spots—called **Laue's spots**—symmetrically ranged about the central spot, represent secondary deviated beams due to diffraction or reflection effects of the internal planes of the crystal. The X-rays have presumably been diffracted by the structural units of the crystal *en route*, so that the secondary wavelets passed along and produced interference maxima.

M. von Laue supposed that the X-rays are electromagnetic radiations which set up vibrations in their passage through the crystal so that each structural unit becomes the centre of a wave disturbance. The resulting waves undergo interference, and a spot is produced in the diagram where a set of vibrations are so close in phase as mutually to reinforce each other. When a crystal is placed in the path of a beam of X-rays, the rays are partially reflected from the planes of the crystal which contain a relatively large number of atoms, but not from planes taken at random which do not contain many atoms. Each spot represents a partial reflection of the primary beam of X-rays by a plane rich in atoms. The general equations governing the interference of a three-dimensional grating have been developed. W. Friedrich and E. Wagner showed that the radiograms are the result of a continuous spectrum, and not of a monochromatic beam. It thus appears as if the diffracted rays should cause a general darkening of the whole of the photographic plate, and not produce well-defined spots. P. Debye got over the difficulty by assuming that the structural units at ordinary temperatures are not stationary, but possess some vibratory or oscillatory movement; and he showed that, in consequence, the intensity of the diffracted rays from most of the planes must be reduced to very low values, and only in the planes characterized by a fairly dense packing of particles will the effect survive this weakening. In support of P. Debye's assumption that the atomic vibrations are accelerated with a rise of temperature, M. von Laue and J. S. van der Lingen found that with mica, secondary spots are faintly visible at ordinary temperature under conditions where at 400° they do not appear; there is no trace of spots with rock salt at 620°; the reflected rays are weakened in intensity with a rise of temperature; and the mean distance apart of the atomic planes is augmented by the expansion of the crystal as indicated by a decrease in the glancing angle of the reflected rays. G. Friedel showed that the 32 classes of crystal symmetry can yield a total of eleven types of radiogram; and that the radiogram will not decide whether or not a crystal is endowed with a centre of symmetry. In the cubic system, for example, the holohedral, holoaxial, and tetrahedral classes all yield holohedral patterns, but the tetartohedral and pyritohedral classes give pyritohedral patterns.

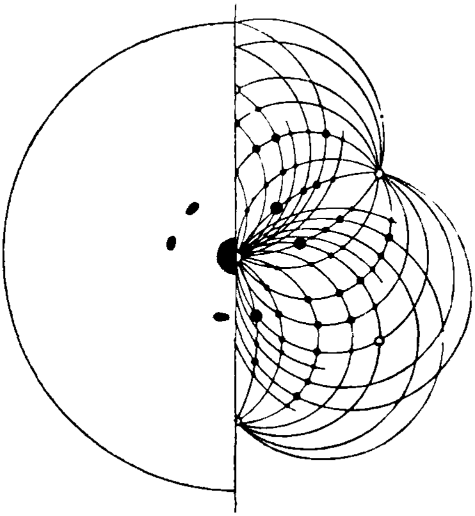


Fig. 71.—M. von Laue's Spots for Zinc Blende with W. L. Bragg's Projection.

J. Stark tried to explain Laue's spots by assuming that the X-rays are corpuscular, and that the corpuscles travel most easily in certain avenues in the crystal, each set of avenues giving rise to a spot. G. Wulff showed that this view is not tenable since there are many wide avenues not represented by spots in the radiogram. L. Mandelstam and H. Rohman suggested that the spots are due to reflections at the surface of cleavage cracks, which must be so fine as to escape detection by ordinary optical means, but M. von Laue showed that this view is untenable.

W. H. Bragg[2] (1912) found that when an incident beam of X-rays falls on a crystal face, the beam is reflected from the face itself; he further showed that the law of equality of the angles of incidence and reflection applies to the beam of X-rays. As a matter of fact, the reflecting plane is not merely the geometrical surface of the crystal, because the rays probably pass through a whole series of planes of molecules parallel to the face before an appreciable absorption occurs, and a small amount of energy must therefore be reflected by each of these planes. Thus E. Hupka roughened the surfaces of quartz and gypsum so that they scattered ordinary light completely, and found that the intensity of the reflected beams of X-rays was not appreciably influenced.

Let V_2, V_3, . . . be planes of atoms (or molecules) parallel to the crystal face V_1. Suppose a parallel beam of X-rays L_1L_2 falls on a crystal face V_1. The incident beam will be reflected by each atom, and the various atoms on the face will be centres of propagation of the reflected beam $L_1'L'_2$. The same will be true for the succeeding planes V_2, V_3, . . . If bS (Fig. 72) be perpendicular to the incident beam L_1L_2, and aS perpendicular to the reflected beam L_1L_2, the difference in the path travelled by a ray reflected from the plane V_1, and that reflected from the plane V_2, will be $bP+Pa$, but $bP=Pa$, and this is a projection of the distance l between the two consecutive planes V_1 and V_2 upon the direction of the incident and emergent beam. If θ denotes the glancing angles of the reflected beam, bP or $Pa=l \sin \theta$; and the whole difference of phase will be $2l \sin \theta$, that is, the trains of wavelets from each plane of the crystal will follow one another at intervals $2l \sin \theta$, and an interference maximum can occur only when this distance is equal to the wave-length λ or to a multiple of λ, say 2λ, 3λ, . . . Consequently, if the wave-length λ is such that $n\lambda=2l \sin \theta$, where n is an integral number, the waves will augment one another and produce a maximum interference. Consequently, if the incident beam contains rays of every possible wave-length, the crystal will appear to select the rays with those particular wave-lengths which follow the $2l \sin \theta$ rule, and produce maximum interference. The angles of reflection can be measured, and by using rays of the same wave-length, the distance l can be compared in different crystals, and with different faces of the same crystal.

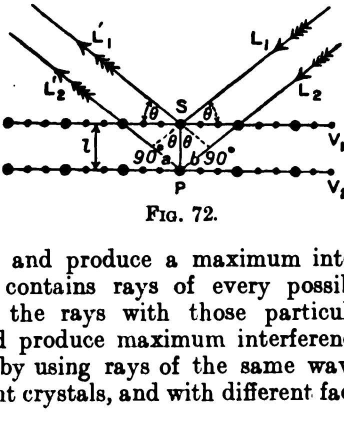


FIG. 72.

A diagrammatic representation of Bragg's apparatus—called an **X-ray spectrometer**—is shown in Fig. 74, and a perspective drawing in Fig. 73 with corresponding lettering.[3] The X-ray tube is placed in a lead box fitted with slits *A* and *B*, about a millimetre wide, to allow a fine pencil of X-rays to pass on to the crystal *C* placed on a little table with its axis passing through the crystal face and which can be rotated by the vernier *V* and scale *SS*; the ionization chamber *I* with its electrode *E* turns about the same axis. A second vernier V_2 indicates the angle at which the chamber *I* has been set in order that the beam of X-rays reflected by the crystal may fall upon and be admitted by the adjustable slit *D*. The ionization current of the chamber *I* with the electroscope *E* and reading microscope *M*, indicates the strength of the reflected beam of X-rays for each angle of incidence.

P. P. Ewald has shown that although apparently so different, M. von Laue's and W. H. Bragg's interpretations really amount to the same thing. M. von Laue worked with transmitted rays, W. H. Bragg with reflected rays. Bragg's method gives a rapid survey of the general structure of a crystal, and in the simpler cases it may furnish all that is required, but the more complex cases may require to be supplemented by Laue's radiograms, which introduce greater precision in the finer details. Laue's radiograms, if used alone, may be inconclusive and give erroneous results.

In P. Debye and P. Scherrer's method,[4] a narrow beam of X-rays is allowed to traverse an aggregate of small crystals, and the resulting diffraction pattern is photographed. The disposition of the crystals is assumed to be perfectly irregular, and A. W. Hull insures this by reducing the substance to a fine powder, and rotating the glass tube containing the powder while it is being exposed. In the latter case, the diffracted rays fall on photographic plates for some hours, and concentric bands are obtained which represent the X-rays reflected from all the important layers of atoms instead of from one at a time. M. de Broglie mounted the crystal, to be exposed in the path of the X-ray pencil, upon a rotating stage.

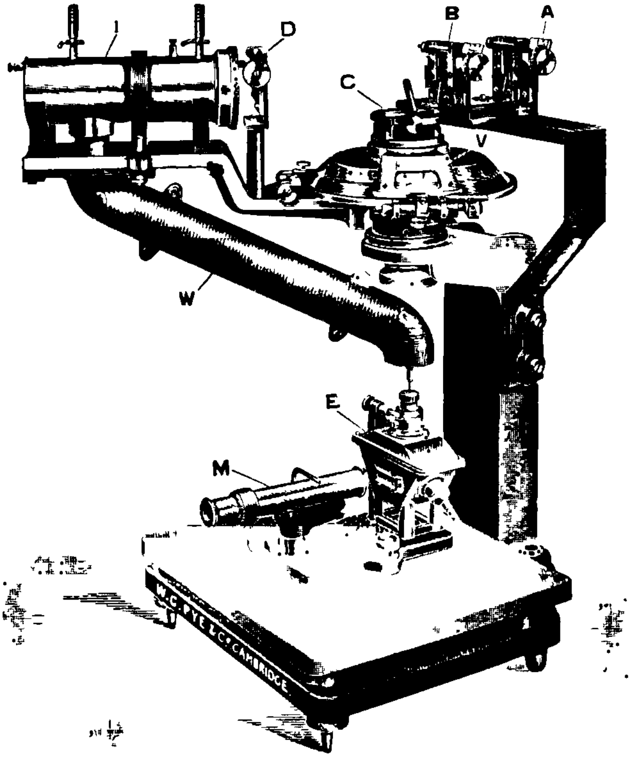


FIG. 73.—X-ray Spectrometer.

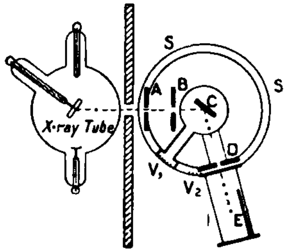


FIG. 74.—Diagrammatic Plan of Bragg's X-ray Spectrometer.

The measurements of the ionization current are usually plotted vertically while the angles of incidence are plotted horizontally. The curve is called an **X-ray spectrum.** This is done for *potassium chloride* and *sodium chloride* crystals in Fig. 75. There is a comparatively small reflection of the rays for all angles of incidence, but a very much larger reflection for special angles. This is shown by the peaks in the curves, Fig. 75. These peaks recur again for angles whose sines are twice those of the former angles, they recur again at triple these values, and so on. Since the wave-length λ and spacing l of the crystal planes parallel to a given face are connected by the equation $n\lambda=2l\sin\theta$, the second peak of the curve gives respectively for potassium and sodium chlorides $2l_1\sin\frac{1}{2}(10{\cdot}43^\circ)=\lambda$, and $2l_2\sin\frac{1}{2}(11{\cdot}8^\circ)=\lambda$, where l_1 and l_2 respectively denote the spacings for the (100)-plane of the crystals of potassium and sodium chlorides. Hence, $l_1=5{\cdot}48\lambda$ and $l_2=4{\cdot}85\lambda$. This shows that while the crystals of the two salts probably have a similar structure, the molecule of potassium chloride is more voluminous than that of sodium chloride, This agrees with the observed molecular volumes, for obviously, if M_1 and M_2 denotes the respective molecular weights of potassium chloride (37·8), and sodium chloride (27·8), and D_1 and D_2 the corresponding densities, then $l_1^3 : l_2^3$=Mol. vol. KCl : Mol. vol. NaCl$=M_1/D_1 : M_2/D_2$; and hence $l\sqrt[3]{D/M}$ should be a constant for different members of this series of salts. The computed value for potassium chloride is $5{\cdot}48\sqrt[3]{(1{\cdot}97 \div 75{\cdot}5)}\lambda = 1{\cdot}63\lambda$; for sodium chloride, $1{\cdot}62\lambda$; and for potassium bromide, $1{\cdot}63\lambda$. This is taken to mean that the structure of these salts is analogous.

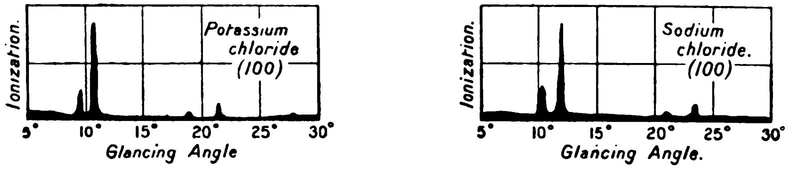


FIG. 75.—X-ray Spectra of Crystals of Potassium and Sodium Chlorides.

The curve in which the intensity is plotted against the glancing angle of incidence with the (100)-face of rock salt exhibits three peaks A_1, B_1, and C_1 at glancing angles 13° 48′, 11° 30′, and 10° respectively. These three peaks are produced with a platinum anticathode in the X-ray tube, and they have been found to correspond with three monochromatic beams of X-rays with wave-lengths $\lambda_A=1{\cdot}316\times10^{-8}$ cm.; $\lambda_B=1{\cdot}095\times10^{-8}$ cm.; and $\lambda_C=0{\cdot}96\times10^{-8}$ cm. The A_1, B_1, C_1 peaks are repeated by a less pronounced system of peaks A_2, B_2, and C_2 with glancing angles respectively 27° 36′, 23° 30′, and 20°; and these again by a third system B_3, and C_3 of still smaller intensity and with the respective angles 35° 50′ and 30° 48′. For the A-peaks, therefore, sin 13° 48′ : sin 27° 36′=0·238 : 0·463; for the B-peaks sin 11° 30′ : sin 23° 30′ : sin 35° 50′=0·199 : 0·399 : 0·585; and for the C-peaks, sin 10° : sin 20° : sin 30° 48′=0·173 : 0·342 : 0·512. These ratios correspond closely with 1 : 2 : 3. For corresponding maxima on the (100), (110), and the (111) planes for sylvine, KCl, the angles are respectively 5° 13′, 7° 18′, and 9° 3′, and their sines are in the proportion $1 : \sqrt{2} : \sqrt{3}$. The same ratios occur with the sines of the angles for corresponding maxima on these faces with rock salt, although their absolute values are different. Let $OBFAEGBC$, Fig. 76, represent a simple cubic space lattice, the (100)-planes are parallel to $OBDC$, and their distance apart $l_{100}=OA$; the (110)-planes are parallel to $CBFE$, and their distance apart is $l_{(110)}=OP$; and finally, the (111)-planes are parallel to ABC, and their distance apart is $l_{(111)}=OQ$. Geometrically, therefore,

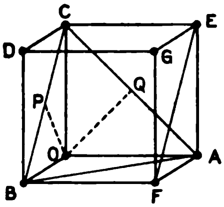


FIG. 76.

$$\frac{1}{l_{(100)}} : \frac{1}{l_{(110)}} : \frac{1}{l_{(111)}} = \frac{1}{OA} : \frac{1}{OP} : \frac{1}{OQ}; \text{ or } 1 : \sqrt{2} : \sqrt{3}$$

Experiment shows that for the crystals of sylvine

$$\frac{1}{l_{(100)}} : \frac{1}{l_{(110)}} : \frac{1}{l_{(111)}} = \sin 5^\circ\, 13' : \sin 7^\circ\, 18' : \sin 9^\circ\, 3'$$

which is very nearly that required for the simple cube lattice $1 : \sqrt{2} : \sqrt{3}$. These ratios with the three types of cubic space lattice (Figs. 49, 50, and 51) are

	$\frac{1}{l_{(100)}} : \frac{1}{l_{(110)}} : \frac{1}{l_{(111)}}$
Simple cubic lattice	$1 : \sqrt{2} : \sqrt{3}$
Body-centred cubic lattice	$1 : \frac{1}{2}\sqrt{2} : \sqrt{3}$
Face-centred cubic lattice	$1 : \sqrt{2} : \frac{1}{2}\sqrt{3}$

The measurements for both sodium and potassium chlorides are thus in agreement with the measurements for the simple cubic lattice.

Thus, the various glancing angles θ_1, θ_2, θ_3, at which a plane of crystal units serve as efficient reflectors, are determined. The wave-lengths of the rays emitted by anticathodes of platinum, rhodium, tungsten, or palladium are known. The results are then interpreted by means of the equation $n\lambda=2l \sin \theta$. The term n is unity with a reflection produced by the mutual reinforcement of pulses provided by successive chemically and crystallographically identical planes—first order reflection at angle θ_1; similarly, the co-operation of the second plane gives a second order reflection at an angle θ_2; likewise also with the co-operation of the third plane, the third order reflection at an angle θ_3 is obtained; and so on. The intensity of the reflection diminishes regularly in passing up the orders excepting in cases where successive planes of crystal units differ as to composition, or distances apart, so that the even orders may appear stronger than the odd orders, while certain orders may vanish altogether. With rock salt, the relative intensities of the reflections from the cubic and octahedron planes are:

	1st order.	2nd order.	3rd order.	4th order.
Cube planes, face (100)	100	18·7	6·25	—
Octohedral planes, face (111)	16·5	24·4	3·10	4·2

The regular decrease of intensity on ascending the scale of orders is interpreted to mean that the units are chemically identical, and the spacing of the successive cube planes is the same; on the other hand, the periodic rise and fall of intensity on the octahedral planes indicates some structural peculiarity; otherwise expressed, the reflecting units in successive cube planes are identical in all respect; but, assuming that the individual atoms, and not the molecules, are reflectors, it follows that the reflecting units in the octahedral (111) planes are alternate layers of sodium and chlorine atoms. This gives the arrangement shown in Fig. 77, where the solid circles represent chlorine atoms and the open circles sodium atoms.

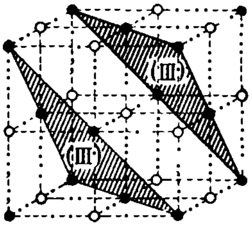


Fig. 77.—Space Lattice for Crystals of the Alkali Halides.

The patterns of the Laue spots for sodium and potassium chlorides, potassium bromide and potassium iodide are not identical. Potassium chloride gives the pattern characteristic of a simple cube lattice with points at each of the four corners; potassium bromide and iodide give patterns characteristic of the face-centred lattice; while sodium chloride gives a pattern which seems to be intermediate between the other types. It is known that the intensity of amplitude of the waves of the secondary radiation produced by X-ray impulses is nearly proportional to the masses of the atoms. It was therefore inferred that while in potassium chloride crystals the atomic weights of the potassium and chlorine are sufficiently close to make the two atoms almost equally active as centres of diffraction, the difference between the atomic weights of sodium and chlorine is sufficient to complicate the simpler potassium chloride pattern; while with *potassium bromide* or *iodide*, the difference between the atomic weights of the respective elements is so great that the effect produced by the lighter atom is overpowered by the heavier one. If the atoms of sodium be represented by open circles and the chlorine atoms by solid circles—Fig. 77—the space lattice must have an equal number of both kinds of spots, and the arrangement of the black and white points at the corners of the elementary cube will represent the effects produced by sodium chloride; while if the black spots are alone considered, the effective centres of diffraction will appear to be located at the corners and face centres of an elementary cube. In fine, the space lattice of sodium chloride may be regarded as being composed of two interpenetrating face-centred cubic lattices with the sodium atoms arranged on the one, and the chlorine atoms on the other. The structure of potassium chloride is much the same, the two interpenetrating space lattices—one chlorine and one alkali metal—are so intercalated that the chlorine space lattice is shifted over a distance of half the edge of the cube of the metal space lattice, so that each chlorine atom falls midway between two consecutive metal atoms, and similarly one metal atom falls between two consecutive chlorine atoms.

According to the kinetic theory, there are $6{\cdot}06 \times 10^{23}$ molecules per gram. The density of sodium chloride is 2·167; and therefore there are $2{\cdot}167 \times 6{\cdot}06 \times 10^{23} \div 58{\cdot}46 = 2{\cdot}3 \times 10^{23}$ molecules or $4{\cdot}6 \times 10^{23}$ atoms per c.c. The atoms of sodium are arranged cubically, and consequently the average distance apart of these molecules is the cube root of the reciprocal of $4{\cdot}6 \times 10^{23}$, or $3{\cdot}5 \times 10^{-8}$ cm.—very nearly one hundred-millionth of an inch.' This means that along the edge of a crystal of sodium chloride there are nearly a hundred million atoms per inch. The absolute dimensions of a space lattice can be calculated from the glancing angle θ—the angle of reflection of X-rays from crystals—which can be measured with great accuracy, and the known wave-length λ, by Bragg's equation $n\lambda = 2d \sin \theta$, where d denotes the spacing of the crystal planes parallel to the crystal face. If v denotes the volume of the elementary cell; M, the molecular weight; D, the density; n, the number of molecules in the cell; and N the number of molecules in a gram-molecule ($6{\cdot}06 \times 10^{23}$), $nM = NvD$. Consequently, the atomic weight of an element can be calculated from the observed data when the atomic weight of the other elements in combination with it are known.

These experiments give direct proof that the structural units of crystals are arranged in space-lattices. There is little indication of the way these units are united to form the so-called chemical molecule. Indeed, the crystal molecule as a structural unit seems to have lost its significance. (1) There is no evidence of chemical combination; (2) a sodium atom is no more closely attached to one chlorine atom than it is to any other; (3) there is no sign of a molecular structure in the chemical meaning of the term; and (4) each atom is an integral part of the whole crystal, and is not connected with any particular group of atoms which form its chemical molecule. The whole crystal endlessly extended in all directions seems to form one gigantic crystal molecule. It must be added that the scattering of X-rays is a purely atomic effect, consequently, although the exploration of crystal structure by these rays may reveal the mean positions of the atoms, yet, from the very nature of the case, it cannot throw direct light on the existence or non-existence of molecules in the crystalline condition.

The view that the radiograms demonstrate that no chemical molecules exist in crystals is not generally accepted. F. Rinne[5] claims that groups corresponding with molecules can be often recognized. A. L. W. E. van der Veen, and A. Smits and F. E. C. Scheffer claim that since the distances between the atoms in the solid state are small compared with their diameters, the atoms belonging to the same molecule can be but slightly closer than those belonging to different ones, and that the difference cannot be detected by the X-rays. A. Fock adds that even though the radiograms of sodium chloride show that six chlorine atoms surround one sodium atom this does not prove that one chlorine atom is not combined with one sodium atom. Isomorphism, electrical conductivity, and the fact that crystals and solutions of the same substance give the same molecular weight is taken by A. Fock to demonstrate the continued existence of molecules. P. Groth also claims that interatomic connections must remain even though the chemical molecule as such has lost much of its significance from a crystallographic point of view. The special nature of the symmetry elements in some crystals is closely related to the atomic structure of the chemical molecule itself, so that this cannot have any significance if there are no chemical molecules in the crystal. J. Beckenkamp holds that the ultimate structures of crystals are triclinic, and by submicroscopic twinning systems of higher symmetry are produced; and that the radiograms merely give the average positions of the atoms. A. C. Crehore mathematically investigated the mechanical forces between the atoms in a space lattice, and states that the essential difference between crystal and molecular structures is that in the former, the atoms, under certain mutual restrictions, may revolve about non-parallel axes, while in the latter, all atomic rotations are necessarily parallel.

W. L. Bragg found the results with zinc blende, ZnS; fluorspar, CaF_2; and calcite, $CaCO_3$, to be almost identical when the X-rays are taken diagonally through the centre of the cube. Each point in a space lattice is situated with respect to its neighbours like every other point; and, in the case of the three compounds just indicated, it is possible to satisfy the conditions only by assuming that each molecule acts as a single point in that it contains one atom heavier than the others which is responsible for the observed diffraction pattern. Hence, it is probable that single atoms are associated with each diffracting unit.

Still further, the value $l(D/M)^{\frac{1}{3}}$ is nearly constant for crystals of potassium chloride, KCl; sodium chloride, NaCl; zinc blende, ZnS; fluorspar, CaF_2; and pyrite, FeS_2. Hence, it is inferred that the number of molecules associated with each diffraction centre is the same; and since the crystals are so differently constituted, it is probable that one and only one molecule is associated with each diffracting centre. The volume of unit parallelopided of the space lattice for potassium chloride is about one-eighth that of the other crystals, because both its atoms, having nearly the same atomic weights, are equally effective as centres of diffraction, whereas with the others, only the heavier atom is effective.

W. H. and W. L. Bragg[6] found that in the double face-centred space lattice of the *diamond*, each carbon atom (black and shaded spots, Fig. 78) is surrounded by four other carbon atoms at equal distances away, and which are related to it like the four apices of a tetrahedron are related to the centre. If series of adjacent space lattices be examined, it will be found that the atoms appear to be arranged in a series of rings of six (heavy dotted lines, Fig. 78). This recalls the benzene, C_6H_6, ring. The diamond has also been investigated by L. Föppl, W. Barlow, A. L. W. E. van der Veen, and P. P. Ewald. W. L. Bragg found the space lattice of *zinc blende*, ZnS, to be similar to that of the diamond, if sulphur atoms (circles, Fig. 78) and zinc atoms (black spots, Fig. 78) be alternately substituted for carbon atoms. The zinc atoms now occupy the corners and face-centres of a cube with a sulphur atom in the centres of the alternate small cubes so that each sulphur atom is surrounded by four symmetrically placed zinc atoms; and each zinc atom is surrounded by four symmetrically placed sulphur atoms. The structures of zinc blende and of the diamond are thus based on the so-called double face-centred cubic lattice formed by the interpenetration of two face-centred cubic lattices. The space lattice for *fluorspar*, CaF_2, resembles that of zinc blende with the calcium atoms occupying the corners and face-centres of a cube, and fluorine atoms in the centres of all the small cubes, instead of in alternate cubes as was the case with the sulphur atoms of zinc blende. Each fluorine atom is now surrounded by four symmetrically placed calcium atoms, but each calcium atom has eight fluorine atoms arranged around it and related to the central calcium atoms as the eight corners of a cube are related to the centre. The crystals of *magnetite*, Fe_3O_4, show that the space lattice is fundamentally the same as the diamond with groups Fe_3O_4 taking the place of carbon atoms. Two out of the three atoms of iron are surrounded by four oxygen atoms arranged at the corners of an imaginary tetrahedron about each atom of iron as centre. The other atom of iron is arranged so that it is surrounded by six oxygen atoms belonging to the oxygen tetrahedra. It is therefore thought that the two iron atoms are probably bivalent, and one iron atom is tervalent representing a structural formula $Fe_2^{II}Fe^{III}O_4$. Quite similar results are obtained with spinel,

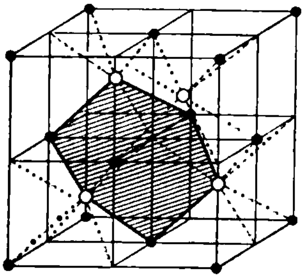


FIG. 78.—Space Lattice of Zinc Blende (and the Diamond).

Mg_2AlO_4, in which magnesium takes the place of bivalent iron in magnetite, and aluminium the place of ferric iron. L. Vegard reported that in *zircon*, $ZrSiO_4$, the atoms of zirconium and silicon are arranged alternately in a space lattice of the face-centred tetragonal type; each silicon and zirconium atom appears to be associated with two oxygen atoms forming SiO_2- and ZrO_2-groups as structural units of the space lattice. The oxygen atoms appear to be closer to the silicon atoms than to those of zirconium, probably because of the greater affinity of silicon for oxygen. Space lattices of crystals of *rutile*, TiO_2, and of *cassiterite*, SnO_2, resemble those of zircon, in which silicon and zirconium atoms are replaced by identical atoms of titanium or tin.

The space lattices of crystals of *copper*, *silver*, *gold*, and *lead* show that the structural units are arranged like a face-centred cube, Fig. 51. Each unit is surrounded by twelve equidistant units. W. L. Bragg found the space lattice of *pyrites*, FeS_2, is rather complex; it shows that the atoms of iron are arranged at the corners of a face-centred cube (circles, Fig. 79), and each iron atom has four equidistant sulphur atoms (black spots, Fig. 79) around it, and others at a slightly greater distance away. Each sulphur atom has three iron atoms arranged around it, with other iron atoms at a slightly greater distance away. W. L. Bragg also found that *hauerite*, MnS_2, *ullmannite*, NiSbS, and *cobaltite*, CoAsS, have a similar structure. *Cuprite*, Cu_2O, belongs to a similar class.

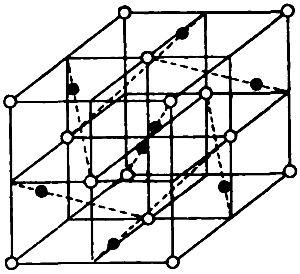


FIG. 79.—Space Lattice of Pyrites.

W. H. and W. L. Bragg found that the space lattice of *calcite*, $CaCO_3$, Fig. 80, shows that the carbon and oxygen atoms occur on triangular planes perpendicular to the crystal axis. The calcium atoms lie in planes just above and below the carbon and oxygen planes, so that each carbon atom is surrounded by six equidistant oxygen atoms. In Fig. 80, the large black dots represent carbon atoms, the small black dots oxygen atoms, and the circles calcium atoms. For the sake of clearness, the oxygen atoms are omitted from the upper part of Fig. 80, and the arrangement of the oxygen atoms is shown in the lower part of the diagram as a series of layers perpendicular to the trigonal axis. The position of the different planes is obvious from the lettering. Each carbon atom is associated with three oxygen atoms, while the latter are only associated with one carbon atom, and the distance between the calcium and carbon atoms is greater than the distance between the oxygen and carbon, or the oxygen and calcium. Each CO_3 group thus appears as a unit equidistant from the six calcium atoms. The space lattices of *rhodochrosite*, $MnCO_3$, *siderite*, $FeCO_3$, and *sodium nitrate*, $NaNO_3$, are similar to that of calcite. The change in the valency of the sodium and nitrogen in sodium nitrate from the basic element and carbon in the carbonates is noteworthy since it appears to make no difference in the general arrangement of the atoms in the crystals. In *dolomite*, $MgCO_3.CaCO_3$, the structure is similar to that of the carbonates with alternate atoms of calcium

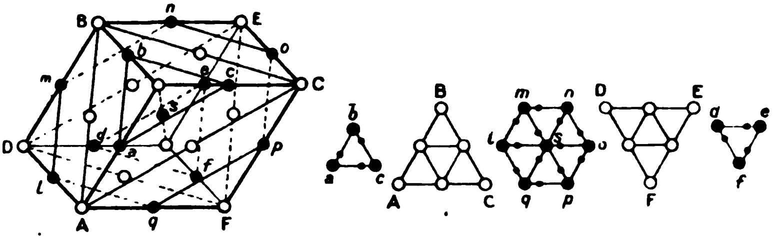


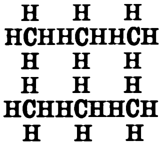
FIG. 80.—Space Lattice of Calcite.

and magnesium in place of calcium. The structure of *hæmatite*, Fe_2O_3, belongs to the calcite class with the carbon atoms removed and each calcium atom replaced by two iron atoms arranged like a dumb-bell parallel to the *c*-axis.

J. Herwig [7] investigated the space lattice of *gypsum* ; S. Nishikawa investigated the *spinel* minerals—magnetite, Fe_3O_4 ; ruby-spinel, $MgAl_2O_4$; W. L. Bragg investigated magnetite ; F. M. Jäger and H. Haga have examined *d*- and *l*-sodium chlorate ; ammonium-iron and potassium-chromium alums ; *d*- and *l*-triethylenediamine cobaltic bromide ; beryl, apatite, ethylsulphates of the rare earths, nephelene, calcite, dolomite, phenacite, tourmaline, quartz, cinnabar, aragonite, topaz, anhydrite, cordierite, hambergite, hemimorphite, struvite, sodium ammonium *d*-tartrate, *l*-asparagine, zinc sulphate, and benitoite ; F. Rinne has examined cyanite, diopside, epidote, scolecite, sucrose, anhydrite, aragonite, calcite, dolomite, quartz, carborundum, beryl, and cuprite. L. Vegard has studied silver, gold, lead, anatase, ammonium iodide, tetramethyl ammonium iodide, rutile, cassiterite, zircon, xenotime, and thorite. C. M. Williams has also studied the rutile group, and his results are not always in agreement with those of L. Vegard. Copper was examined by W. L. Bragg ; scheelite and wulfenite by R. G. Dickinson; iron, silicon, aluminium, sodium, lithium, nickel, magnesium, graphite, and the diamond by A. W. Hull; chalcopyrite, by C. L. Burdick and J. H. Ellis; barium, strontium, and lead nitrates, by S. Nishikawa and K. Hudinuki; garnet, by S. Nishikawa; different forms of silica, by S. Kyropoulos; and white and grey tin, by A. J. Bijl and N. H. Kolkmeijer.

I. Langmuir's theory of solids and liquids.—I. Langmuir believes that the work of W. H. and W. L. Bragg shows that in all probability crystals are not built of molecular units in the ordinary sense of the term. With potassium chloride, for instance, each atom of potassium is surrounded by six equidistant atoms of chlorine arranged as if they were placed at the corners of an octahedron ; each chlorine atom is similarly surrounded by six equidistant potassium atoms. The identity of the molecules of potassium chloride, KCl, thus appears to be lost, unless the whole crystal itself be regarded as itself forming one molecule. Each atom is united chemically with all the adjacent atoms, and these in turn are similarly united with those beyond. Consequently, the ordinary conception of valency no longer holds good, each atom appears to be united with far more atoms than corresponds with the normal valency. The valency of potassium, for instance, equally divided between six chlorine atoms, and the valency of chlorine between six potassium atoms. Considerations like these led I. Langmuir [8] (1916) to elaborate the definition of a molecule. A *molecule*, said he, is a group of atoms held together by atomic forces ; the *gas molecule* is defined in terms of Avogadro's hypothesis, while a continuous liquid or solid mass is called a *solid or liquid molecule.*

No structural formula consistent with the primary valency of the constituent atoms can be employed to represent the structure of crystalline solids like potassium chloride. I. Langmuir (1916), assuming that the primary valencies hold good for gaseous molecules of potassium or sodium chloride ; and that if there were no residual affinity or secondary valencies developed when the temperature is lowered or the pressure raised, these molecules could not condense to form a liquid or solid, supposes that in the solid state, what Werner calls the secondary valencies, altogether supplant the effects of primary valency. He also bases a similar assumption for molecules formed from bivalent and tervalent atoms upon Bragg's space lattices for zinc blende, ZnS ; fluorite, CaF_2 ; pyrites, FeS_2 ; hauerite, MnS_2 ; magnetite, Fe_3O_4 ; and spinel, $MgAl_2O_4$. In the case of the diamond, each carbon atom appears to be surrounded by four others equidistant from and arranged around the central atom much as the four corners of a regular tetrahedron are related to the centre. Consequently, the primary valencies of the quadrivalent carbon atom seem to exert some influence on the formation of the solid crystal. In cubic crystals of methane, CH_4, the carbon atom is probably surrounded by four hydrogen atoms held by primary valencies, and the crystal is held together by secondary valencies, so weak indeed that methane melts and boils at very low temperatures. Langmuir represents the constitution of a methane crystal diagrammatically as in Fig. 81, where each hydrogen atom is associated with a particular carbon atom ; each carbon atom is associated with four hydrogen atoms; and all other hydrogen atoms besides these four are combined with a different carbon atom. Langmuir calls aggregates



$$\begin{array}{c} \mathrm{H\quad H\quad H} \\ \mathrm{HCHHCHHCH} \\ \mathrm{H\quad H\quad H} \\ \mathrm{H\quad H\quad H} \\ \mathrm{HCHHCHHCH} \\ \mathrm{H\quad H\quad H} \end{array}$$

FIG. 81.

of atoms of this kind *group molecules*, because the atoms in the group may be distinguished from those outside the group. A crystal of zircon, $ZrSiO_4$, likewise contains group molecules ZrO_2 and SiO_2. Similar remarks apply to the quadrivalent atoms of titanium and zirconium in zircon, ZrO_2, rutile, TiO_2, and cassiterite, SnO_2, where röntgenograms by L. Vegard (1916) show that the molecular groups ZrO_2, TiO_2, or SnO_2 form the structural elements in the space lattices.

When the vapour of potassium chloride is condensed to a solid and re-vaporized, it is probable that when a potassium atom escapes from the surface of the solid, it takes away one of the four adjacent chlorine atoms to form a gaseous molecule of potassium chloride, and judging from röntgenograms of the crystals, the chances are against the two partners being the same as were previously united before the condensation of the vapour. On the other hand, it is probable that if methane were treated similarly, the same four atoms of hydrogen would remain united to the same carbon atom in both the solid and gaseous states. I. Langmuir calls the largest aggregates of atoms which may pass from the gaseous to the solid or liquid phase and back again to the gaseous phase without exchanging atoms with other aggregates, a *fixed molecule*.

Still following I. Langmuir, since the secondary valencies of inorganic solids usually supplant the primary valencies exhibited by the substances in the gaseous state, (i) the composition of a solid should give little or no information about the primary valencies; and (ii) it should be possible to make more solid compounds than accord with the rules for primary valencies. If the arrangements of the atoms are regular so as to form a space lattice, the resulting solid should satisfy the tests for a chemical compound, even though it exhibits no relationship with the primary valencies of the constituent atoms. A large number of compounds are known in the solid state which do not accord with the ordinary doctrine of valency. For example, G. Tammann (1906–7)[9] obtained compounds corresponding with $AgMg_3$, $AgMg$, $AuZn$, Au_3Zn_5, Cu_3Al, $CuAl$, $CuAl_2$, Mg_4Al_3, $AlSb$, Zn_7Fe, $NaZn_{12}$, $NaCd_5$, etc., and he found that about 26 per cent. of the binary metal compounds which he investigated have formulæ in accord with those based on the primary valencies of the elements. In the case of minerals, and particularly the silicates, the number of exceptions to the valency doctrine is greater than with alloys. In these compounds, as also with potassium chloride, the atoms are held together by secondary valencies, and they have a definite composition because the constituent atoms are arranged as a space lattice. The reason solids so frequently accord with the ordinary rules for valency is that they are usually formed from solutions or from gaseous phases. Even in the case of alloys formed by solidification from a fused mixture, certain restrictions are necessarily imposed by the very method of formation. Hence, I. Langmuir argues that if methods for the preparation of solid compounds at sufficiently low temperatures could be devised, there is no conceivable limit to the number of possible compounds formed by secondary valencies.

If the units A and B in a space lattice could be replaced in an irregular manner by another unit C, the resulting crystal would not have a definite composition, and would not therefore be recognized as a chemical compound, but would rather be said to have formed a *solid solution* or *mixed crystals*. There is no reason to suppose that the forces holding the structural units together are any different in kind in the two cases; nor is there any reason, other than mere definition, to suppose that if one combination is a chemical compound the other is not a chemical compound. Again, a solid body built up from units—either atoms or group molecules—arranged irregularly in space would not form a space lattice, but it would be called an amorphous substance or a glass. The case of thorite is curious. L. Vegard[10] found that tetragonal crystals of thorite, $ThSiO_4$, are isotropic in polarized light, and show no indications of an optic axis; and Röntgen ray analyses show that while the crystal preserves the outward form of a tetragonal crystal, the original lattice resembling zircon has in the course of time been completely broken down and only the outer frame remains to indicate the original orientation of the atoms. The evidence thus seems to indicate that the internal structure is the same as that of an amorphous solid, and this in spite of its external crystalline form.

It is very doubtful if the nature of the forces holding together the units of amorphous substances or glasses are any different in kind from those in crystals. This recalls F. Wald's assumption that the composition of chemical compounds is variable, and out of all the possible variations which actually occur, chemistry reserves the term compounds for those of constant definite composition. This, says F. Wald, is quite an arbitrary choice. F. Wald also argues that the law of multiple proportions as well as the other stöchiometrical laws are really founded on similar conventions.[11]

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§ 9. Liquid Crystals; Crystalline Liquids; or Anisotropic Liquids

> The very name seems to be a self-contradiction. How can a liquid be a crystal, and how can a crystal be a liquid?—H. A. Miers (1896).

In 1876, O. Lehmann [1] found that at temperatures above 146°, silver iodide can flow like a viscous solid, and that although it is actually in the liquid condition, it still exhibits several properties characteristic of crystals. Further investigations, by F. Reinitzer (1888), on cholesteryl benzoate; by L. Gattermann (1890), on *p*-azoxyanisole and *p*-azoxyphenetole; and by O. Lehmann himself on ammonium oleate, etc., have shown that the phenomenon is not uncommon; rigid solidity is not an essential characteristic of crystals. If the temperature of these substances be gradually raised, while they are on the stage of a microscope—called a *crystallization microscope*—it will be observed that double refraction indicates that the molecules have a definite alignment at temperatures above their melting point when the crystals, if touched with a needle, wobble like jellies, for they are then soft, compressible, elastic, more or less viscid, turbid, anisotropic liquids. The term **liquid crystals**—*flüssige Kristalle*—was therefore proposed by O. Lehmann for substances which have the characteristic properties of crystals—excepting solidity and geometrical form. In order to avoid the hypothesis implied in the cognomen liquid crystals, some prefer the term **anisotropic liquids**, or *birefringent liquids*.

The molecules of a crystalline solid are arranged quite regularly, and they are retained more or less rigidly in position by elastic forces. Liquid crystals have the usual properties of liquids, but unlike ordinary liquids they also show: (i) double refraction; and (ii) interference colours in polarized light. It seems as if the directive cohesive forces which bring the molecules together, at the softening temperature, are not sufficient to fix them so rigidly about their centre of gravity as to prevent the mass wobbling. In consequence, the optical properties of liquid crystals show that (i) they have an internal structure which in some respects is characteristic of crystals, but that (ii) their external faces are more or less indistinct and mobile. I. F. Homfray [2] found the solubility of carbon dioxide in the liquid crystals is 18, and in the isotropic liquid, 26. The optical properties of liquid crystals have been studied by O. Lehmann, D. Vorländer, E. Dorn, and F. Wallerant.

C. Mauguin found that the liquid crystals of *p*-azoxyanisole take up a definite orientation on a fresh cleavage surface of muscovite mica; and F. Grandjean found the same result obtains, in ninety cases out of a hundred, with a number of such liquids on fresh cleavage faces of talc, muscovite, phlogopite, brucite, blende, orpiment, pyrophyllite, rock-salt, sylvine, and leadhillite. The orientation is sometimes independent of temperature, and in other cases it changes continuously or discontinuously with temperature. The continuous variation with temperature is taken to show that this property is not necessarily due to the alignment of the molecular axes of the liquid on a row of structural particles in a space lattice, but is an equilibrium property dependent on capillarity.

The surface tension of a liquid tends to make the surface occupy the smallest possible area; and a growing crystal likewise tends in the same direction, *viz.* minimum surface area. The molecules, however, during crystallization are also under the influence of opposing directive forces which make the crystal assume its characteristic geometrical form. If the surface tension were the stronger force, the crystal would assume a spheroidal form. The smaller the volume of a given mass, the greater the relative effect of surface tension, and conversely. With thin films, the effect of surface tension is very pronounced, and in 1857, M. Faraday [3] showed that when thin films of gold or silver on glass are heated, the mirror loses its reflecting power; the metal, under the influence of surface forces, and in spite of the directive crystalline forces, collects itself into globular aggregates just as occurs when a thin film of oil on the surface of water collects itself into globular aggregates.[4] The surface tension of the gold prevents the crystalline forces developing a characteristic geometrical shape.

When the temperature of a small portion of a crystalline solid is raised, the internal molecular motions are presumably augmented, and this weakens the directive forces which produce crystallization; surface tension is acting the whole time; ultimately, the directive forces yield to surface tension, and the crystals assume a more or less globular form. The solid is then said to have melted. It is claimed that in liquid crystals, the directive forces of crystallization are not completely overpowered by surface tension, although the two are almost balanced, for the fluid crystals are more or less rounded as illustrated in Figs. 82 and 83. The effects of surface tension are also seen when two round liquid crystals are brought into contact; union takes place, and a single rounded crystal is formed—the surface area of the single crystal is less than the sum of the surface areas of the two parent crystals. The elongated liquid crystals of potassium oleate unite only when the long axis of the one is nearly parallel with that of the other, and not if the two are in contact with their long axes at right angles to one another.[5]

Fig. 82.—Liquid Crystals of Ammonium Oleate.

Fig. 83.—Parazoxyanisole—crossed Nicols (O. Lehmann).

G. Friedel and F. Grandjean here show that the shapes of the liquid crystals of ammonium oleate have no similarity with the crystal forms, but are figures of revolution of great complexity; and C. Mauguin found that in some of the more mobile liquid crystals there is no definite shape, but a continuous internal movement in the smallest globule that can be isolated for observation. The movement increases in intensity as the temperature rises, but no definite regularity could be detected. O. Lehmann frequently emphasized his opinion that the globules are not liquid crystals but rather aggregates of such crystals.

Under certain conditions, some crystals can be so affected by heat, pressure, etc., that they pass suddenly into a new system more stable under the altered conditions—much as a half-opened pocket-knife closes with a snap. There are many examples of substances which pass abruptly from one solid modification to another without any transitional liquid state. For instance, H. A. Miers has shown that a section of boracite under the polarizing microscope appears to be traversed by doubly refracting lamellæ, and when the section is warmed to 265°, a cloud seems to pass over the crystal and it becomes dark—the twin lamellæ reappear on cooling down below the same temperature; and W. J. Pope has shown that molten chloral hydrate on a microscope slide cools to a film of uniaxial needle-like crystals, and these on standing gradually pass into biaxial lamellar crystals.

There is a temperature at which a crystalline solid loses its elasticity and becomes a turbid anisotropic liquid, which at a higher temperature loses its turbidity, clears and forms an isotropic liquid. With *p*-azoxyanisole, for example, there are two transition temperatures corresponding with these changes: Solid crystals→liquid crystals→ordinary liquids; and L. Gattermann found

$$p\text{-Azoxyanisole}_{\text{solid crystals}} \overset{116^\circ}{\rightleftharpoons} p\text{-Azoxyanisole}_{\text{liquid crystals}} \overset{134^\circ}{\rightleftharpoons} p\text{-Azoxyanisole}_{\text{liquid}}$$

A comparison of H. B. Roozeboom's diagram (1900),[6] Fig. 84, with the corresponding diagram for water, will show the conditions under which H. B. Roozeboom thinks that the liquid crystals are related on the one hand to the solid crystals, and on the other to the liquid and vapour. There are two triple or transition points instead of one. At one triple point *O*, solid, liquid crystals, and vapour are in equilibrium, and at the other triple point *O'*, liquid crystals, liquid and vapour are in equilibrium.

The change from an anisotropic to an isotropic liquid is characterized by a small heat absorption. E. Bose and F. Courat found the energy change to be very small in passing from the liquid to the liquid crystal phase, in comparison with that which obtains in passing from the liquid crystal to the solid phase; with anisaldazine, the former was about one calorie, the latter 20 cals. C. de Kock and R. Schenck found the molecular latent heat of *p*-azoxyanisole to be 0·68 cal. C. Tubandt and E. Lorenz also found that purified silver iodide forms no plastic or liquid phase at 550°, two degrees below its melting point. Similar remarks apply to the chloride and bromide of silver, and the three thallium halides which H. Stoltzenberg and M. E. Huth once believed to form liquid crystals. All these substances therefore must be definitely deleted from the list of liquid crystals. The point involved is not whether these crystals are so soft that it would be a misnomer to call it a solid, but rather whether the turbid double refracting liquids are restricted to organic compounds of some complexity, or whether representatives are to be found among the simple binary compounds. P. N. Pawloff, G. Wulff, and W. Voigt have also discussed the nature of liquid crystals.

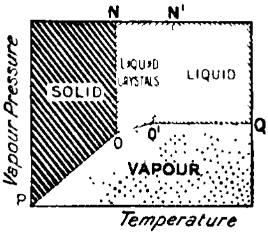

FIG. 84.—Vapour Pressure Curves showing Liquid Crystals (Hypothetical).

G. Quincke (1894) suggested that the effects obtained by O. Lehmann were produced by a trace of oil in the substance he examined; and G. Tammann (1905)[7] argued that the turbidity of liquid crystals in contrast with the clearness of solid crystals shows that the former are emulsions or suspensions and not homogeneous substances, but O. Lehmann replied that the turbidity of liquid crystals is not in evidence when they are examined under the microscope, and that the apparent turbidity is a secondary effect due to the aggregation of a large number of crystals differently oriented, just as marble appears opaque when observed *en masse*, even though it is really composed of a mass of transparent crystals of calcite. All attempts to separate the alleged emulsion into its constituent parts by G. Bredig and G. von Schukowsky and A. Cöhn by electrostatic or centrifugal processes have been futile. No clear proof of heterogeneity has been obtained. The temperature of liquefaction is constant, and is affected by pressure and admixture with foreign substances just as it is in the case with ordinary crystals. O. Lehmann (1910) studied the segregation of impurities during the formation of liquid crystals. Attempts have been made to explain some of the phenomena which occur in the vicinity of the melting point of metals by the existence of a liquid crystal phase.[8] Some metals assume a plastic condition at some distance below their recognized melting points.

The cause of the anisotropy of crystals is referred by A. Bravais [9] to the arrangement of molecules in parallel planes—that is, in certain privileged directions ; more usually it is referred to the orientation of dissymmetrical molecules. For example, the theory suggested by W. Weber in 1850 to explain magnetization assumes that the molecules are dissymmetrical in having two magnetic poles—one positive and one negative—and a body is magnetic only when a larger proportion of the constituent magnetic molecules are disposed with like poles in one direction. When the molecules of a body occupy random positions, so that the positive or negative charges are averaged in all directions alike, the body appears neutral. If an external stress comes into play and the molecules possess a certain degree of mobility, they will gradually turn in the same direction, and, little by little, one side will become positive and the other negative. The greater the controlling stress the more marked is the change. If the controlling force be withdrawn, the molecules gradually return more or less to their former position and the body remains more or less magnetized accordingly. Glass and many liquids were found by J. Kerr to become optically anisotropic or temporarily doubly refracting when acted upon by the poles of a high voltage electric machine—*J. Kerr's phenomenon.* A parallel phenomenon is produced by magnetic forces. Q. Majorana found that colloidal solutions of iron salts exhibited this phenomenon, and A. Cotton and H. Mouton obtained similar results. The explanation of the phenomena turns on the assumption that electric charges are accumulated on the molecules which, in consequence, possess electric poles so that the electric or magnetic field produces a slight change in the direction of the molecules, and the optical effect is the secondary result of the orientation of the molecules.

Again, when certain crystals are heated or cooled they exhibit positive and negative electrical charges—**pyro-electricity**—and the strength of the charge is proportional to the variation in temperature. R. J. Haüy was much impressed with the far-reaching consequences of this phenomenon. He said :

> I do not know whether there is anything better calculated to excite the interest of physicists than these minute electrical instruments built up by crystallization and confined within the compass of a crystal not more than 2 mm. in thickness.

Similarly when certain crystals are compressed or expanded, they undergo a change of form, and also exhibit positive and negative electrical charges—**piezo-electricity**—and the strength of the charge is proportional to the degree of elastic deformation. It is here assumed that a variation in the distance apart of the molecules caused by changes of temperature or pressure disturbs the orientation of the polar molecules, and the slight mobility of the molecules enables a small excess of them to orient themselves temporarily in a particular direction. If the temperature be raised sufficiently high, the resulting increase in the movements of the molecules stirs them up, so to speak, and tends to destroy the temporarily established order. Thus, a magnetized body may be demagnetized, and piezo- and pyro-electricity may disappear. In P. Lenard's opinion, also, the film next to the free surface of a liquid is a double layer of positive and negative charges which he explains by assuming that all the molecules in the surface present their electrical poles of the same kind towards the exterior, like, adds A. Perrier, the quills of a porcupine. The hypothesis here assumed is that the constituent particles of a body are dissymetrical in possessing electrical and magnetic poles, and that these particles are capable of revolving in such a way that they can occupy more or less parallel positions in particular directions ; as a result, the body acquires special properties in these privileged directions. Dissymmetry, said P. Curie, is necessary for the production of the phenomenon. *Si cette dissymétrie n'existe pas, le phénomène est impossible.*

In conformity with the above, O. Lehmann's liquid crystals can be regarded as microscopic systems in which the optical and magnetic properties show that certain groups of the constituent molecules have oriented themselves spontaneously in certain definite directions. According to **E. Bose's swarm theory**,[10] if two or more elongated molecules approach so closely that the mean distances of their centres of gravity are less than half the length of the molecule, all free rotation must cease except about the direction of elongation, and the molecules will tend to orient themselves in parallel formations. A swarm of such molecules disposed in a parallel direction, and in a perfectly fluid condition, without any suspicion of a space-lattice arrangement, will possess the symmetry of a figure of rotation and behave as a uniaxial crystal. Each swarm of such molecules will appear as a clear transparent liquid-crystal; and the turbidity of a large mass of liquid is simply due to the reflection and diffusion of light at the mutual boundaries of the swarms. The average size of the swarms will decrease on heating, and the point at which the swarms become smaller than the wave-length of light will be the clearing point; above this temperature the liquid will appear singly refracting. The idea is illustrated by Figs. 85 and 86. D. Vorländer prepared a number of complex organic compounds which when melted on a glass slide yielded a clear mass of a doubly refracting liquid which in converging light gave a normal uniaxial interference figure, Fig. 87, and, if the substance has an enantiomorphous molecular configuration, the interference figure shows rotatory polarization. If thicker than 0·3 mm. the masses may become turbid. The indices of refraction for the ordinary and extraordinary rays have also been determined for ethylbenzylideneamine α-methyl- and α-ethyl- cinnamates by E. Dorn and W. Lohmann. The change from a solid crystal to an anisotropic liquid is regarded by H. W. B. Roozeboom as a polymorphous transition point, and the clearing point as a true melting point; if the liquid crystals are merely liquids with groups or swarms of molecules aligned in parallel, H. W. B. Roozeboom's transition point must be regarded as a true melting point; and his melting point as the temperature at which the average size of the swarms becomes smaller than the wave-length of light.


FIG. 85.—Molecules disposed in all Directions.


FIG. 86.—Molecules swarming into Parallel Groups.

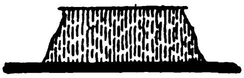
FIG. 87.—Molecular Arrangement for D. Vorländer's Uniaxial Interference Figures.

L. Pucciante and R. Schenck found the viscosity of the crystalline liquid to be usually less than that of the isotropic liquid. E. Bose found that the viscosity of an anisotropic liquid increases quite normally with a fall of temperature down to the point where the turbidity appears, and then decreases very sharply to a minimum at 2° below the clearing point. The viscosity then begins to suffer the normal increase with a fall of temperature, but not to the extent of the isotropic liquid. The lower value of the viscosity of an anisotropic liquid as compared with that of an isotropic liquid has been called the viscosity anomaly. E. Bose and F. Courat showed that if the form of the molecule be that of an elongated ellipsoid of rotation, the viscosity of a swarm can theoretically fall to two-thirds the value of the same substance in an isotropic condition, the ratio of the two viscosities for anisaldazine is anisotropic : isotropic=0·65. The change from an isotropic to an anisotropic is always attended by a moderate increase in density, corresponding with the closer packing possible with elongated molecules.

It will thus be observed that the question whether liquid crystals really have a crystalline structure turns on the definition of a crystal. O. Lehmann, in his *Ueber die Definition des Begriffes Krystall* (1890), regards the regular arrangement of the particles into a homogeneous anisotropic solid to be an accidental and not an essential feature. It is highly probable that the molecules of liquid crystals are grouped in swarms in each of which there is a definite alignment; but if a *crystal* is a homogeneous mass of material, arranged on a space-lattice pattern, the term *liquid crystal* is probably a misnomer. Hence, wrote H. A. Miers:

> It will be wise to retain the names crystal and crystalline in their old signification, rather than to extend them so as to include the birefringent liquids whose existence has been established by Lehmann.

Several of the characteristic tests for a crystalline structure are quite inapplicable —*e.g.* elasticity and cleavage. D. Vörlander says that no biaxial liquid crystals are known, while some fifty are definitely known to be uniaxial, and these are all complex organic compounds. Nearly all compounds with a complex molecular structure crystallize in a biaxial systems. These facts, said T. V. Barker, are of superlative importance inasmuch as they present a statistical proof that the structure of the so-called liquid crystals is not crystalline.

> The whole of the firmly established properties—dichroism, and the invariable straight extinction when the "crystal" is resting on a "prism" face, the apparent absence of double refraction in parallel light, and the perfect uniaxial figure in convergent light when the "crystal" is resting on its base—are in complete harmony with a structure analogous to that of an even-grained piece of wood.

The effect of an electromagnetic field on liquid crystals is said by W. Nernst[11] to furnish a decisive proof of the correctness of the swarm theory. O. Lehmann first noted that a magnetic field clears the droplets of *p*-azoxyanisole; and E. Bose noted that the effect can be perceived with the application of 600 Gauss units of force, and with a few thousand units, the layers of liquid 4 mm. thick are immediately cleared when the liquid is viewed along the lines of force; if the current be cut off, the liquid again becomes turbid. The phenomenon thus interpreted recalls Weber's theory of magnetization. H. von Wartenberg and C. Mauguin extended the work, and found that when a homogeneous film is exposed to a transverse magnetic field, the optic axis is gradually deflected in the plane containing the lines of force, but on releasing the force, the optic axis immediately returns to its normal position.

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§ 10. Isomorphism—Mitscherlich's Isomorphic Law

The laws of nature represent design; they are embodied design.—P. CARUS.

Dans les substances cristallisés, la forme des molécules intégrantes, et, par suite, des cristaux, dépènd du nombre et de la position respective des atomes dont les molécules sont composées.—A. M. AMPÈRE (1814).

According to E. Wohlwill,[1] Basil Valentine prepared mixed crystals of the vitriols, and the mixed crystals were mentioned about the middle of the eighteenth century by J. F. Henkel and by A. G. Monnet. In 1772, J. B. L. Romé de l'Isle noticed that a mixture of copper and iron sulphates furnishes crystals in the form characteristic of iron not copper sulphate, and in 1787, N. Leblanc [2] made the same observation. This appeared to be an exception to D. Guglielmini's generalization or Haüy's law—that the angles between similar faces of the crystals of a given substance are characteristic of one definite compound. Analogous results were observed with crystals from mixed solutions of iron and aluminium potash and ammonia alums; many minerals also are almost identical in crystalline form through possessing a different chemical composition. In 1801, N. Leblanc confirmed J. B. L. Romé de l'Isle's observation and found many other examples. He noted that the aluminium of alum could be replaced by iron without altering the crystalline form. In 1797, L. N. Vauquelin also noted that the potassium in alum could be replaced by ammonium, without changing the crystalline form; and in 1816, J. L. Gay Lussac found that crystals of very different composition could be obtained from mixed solutions of different alums. A. Bernhardi (1809) investigated mixed crystals, and found that different substances can have the same crystalline form—*e.g.* magnesium and zinc vitriols, and he observed that in crystallizing a mixture of copper and iron vitriols the one can so influence the other that the two salts crystallize in the same form, and C. F. Bucholz proved by analysis that there must be at least 13 parts of copper vitriol to 87 of zinc vitriol in order to give to the mixed crystals the peculiar form of the former salt. F. S. Beudant made important contributions to the subject about 1817. W. H. Wollaston investigated the mixed crystals of zinc and copper vitriols in 1818, and a year later, B. de Villiers, in his *De la cristallisation* (Strasbourg, 1819), also discussed this question.

The analyses of M. H. Klaproth, L. N. Vauquelin, P. Berthier, and others showed that the variable composition of mixed crystals applies not only to laboratory preparations but also to numerous minerals. J. N. von Fuchs (1815) also showed that certain constituents of a compound can be replaced by other so-called *vicarious constituents*—*vicariende Beständtheile*—without altering its general character; for example, gehlenite is essentially calcium aluminium silicate, $3CaO.Al_2O_3.2SiO_2$, and yet the calcium can be more or less replaced by magnesium or ferrous iron, and the aluminium by ferric iron, without changing the general physical properties of the mineral. In the Berthollet-Proust controversy, C. L. Berthollet argued from such examples that chemical compounds may have a variable composition, while J. L. Proust argued that these crystals are really mechanical mixtures; R. J. Haüy maintained that when two substances crystallize together in this manner the dominant crystalline form will be characteristic of the component which is in excess. R. J. Haüy explained the results by postulating that one constituent might determine the crystal-form of a substance even though present in very small amounts, while the other constituent remained without influence on the crystal form.

E. Mitscherlich's investigations opened up the subject in a most interesting manner. His work is recorded in memoirs: *On the relations between chemical composition and crystalline form,* published in Sweden between 1818–1821.[3] While making preparations of the arsenates and phosphates of potassium and ammonium, he noticed that the crystals were so like each other as to be indistinguishable by simple inspection; and a closer examination led E. Mitscherlich to conclude: (1) That bodies of different chemical composition may have the same crystalline form; (2) substances of similar constitution have the same crystalline form. E. Mitscherlich wrote:

> The same number of atoms combined in the same manner produce the same crystalline form; the crystalline form is independent of the chemical nature of the atoms, and is determined solely by their number and mode of combination.

This relation is now known as **Mitscherlich's law.** He noticed that the acid arsenates and phosphates of potassium, sodium, or ammonium crystallize in similar tetragonal forms, Fig. 7 (left), that one element or groups of elements may be exchanged for another which appears to act in an analogous manner. Thus arsenic may be exchanged for phosphorus, and potassium for ammonium without affecting the form of the crystal. In Mitscherlich's words:

> Every arsenate has its corresponding phosphate, composed according to the same proportions, combined with the same amount of water of crystallization, and endowed with the same physical properties: in fact, the two series of salts differ in no respect, except that the radicle of the acid in the one series is phosphorus, while in the other it is arsenic.

It is not difficult to understand how atoms of different elements may be so related that they can be mutually interchanged without altering the crystalline form and general character of the compound. The idea is illustrated by an old simile: the lines of a tesselated pavement are not altered if the blue tiles are replaced partly by red or by green ones, so long as the different-coloured tiles retain the original size and shape of those they replace.

Besides the phosphates and arsenates, Mitscherlich observed that a certain group of mineral carbonates—calcite, $CaCO_3$; dolomite, $CaMg(CO_3)_2$; siderite or chalybite, $FeCO_3$; calamine or smithsonite, $ZnCO_3$; and dialogite or rhodocrosite, $MnCO_3$—all form isomorphous crystals in the trigonal system (Fig. 88), and an application of the X-ray spectrum has enabled W. L. Bragg (1914) to demonstrate the structural similarity of rhodochrosite, chalybite, and dolomite. Again, the mineral sulphates—barytes, $BaSO_4$; celestine, $SrSO_4$; and anglesite, $PbSO_4$—all form similar rhombic crystals; while aragonite, $CaCO_3$; witherite, $BaCO_3$; strontianite, $SrCO_3$; and cerussite, $PbCO_3$, form isomorphous rhombic crystals. Numerous other examples could be quoted. E. Mitscherlich applied the term **isomorphism**—from ἴσος, equal; μορφή, shape—to connote the fact that analogous elements can replace one another without affecting the apparent shape of the crystals. It is therefore inferred that **in a crystalline solid, each constituent atom occupies a certain domain or portion of the space occupied by the whole molecule.**

E. Mitscherlich's law of isomorphism, as well as the phenomena of polymorphism, appear to contradict R. J. Haüy's law, and there was some reluctance in France to accept E. Mitscherlich's conclusions. For instance, in some *Reflexions sur le mémoire de M. Mitscherlich qu'on était recueillies dans une conversation avec M. Haüy par un de ses éléves,*[4] it is said that Haüy considered : *Si la théorie de M. Mitscherlich était juste, la minéralogie serait la plus pitoyable des sciences.* R. J. Haüy,[5] however, specially remarked on the crystallographic resemblances between certain minerals like barytes and strontianite by saying :

> There is almost an identical primitive form—*noyau*—in each, and the crystals themselves furnish ocular resemblances, so that they may be compared with what botanists term family resemblances—*air de famille.*

E. Mitscherlich, no doubt, had in mind absolute identity of crystal form as the basal principle of isomorphism, but later investigations have shown that the crystals of isomorphous substances are nearly but not absolutely identical, but only similar in form ; and thus confirmed the earlier observations of W. H. Wollaston (1812) [6] that the rhombohedral cleavage angles of the native carbonates of the calcite series are nearly but not quite the same ; and E. L. Malus that :

> Des recherches posterieures des nous enseigneront comment cette loi générale sera modifiée par la petite différence qui se trouve quelquefois dans les angles des combinaisons isomorphes.

There are small but real differences in similar interfacial angles of the members of an isomorphous series of compounds. For example, the corresponding angles *P* (Fig. 88) of the following isomorphous carbonates of the calcite series are far from identical, even if they are approximately similar :

	Calcite, $CaCO_3$	Dialogite, $MnCO_3$	Chalybite, $FeCO_3$	Magnesite, $MgCO_3$	Smithsonite, $ZnCO_3$
Angle . . .	105° 5′	106° 51′	107° 0′	107° 20′	107° 40′

The idea will perhaps be clear from Fig. 88, where the change in the interfacial angle *P* in passing from calcite to smithsonite is shown in section. With the carbonates of the aragonite series, the angles between the prism faces are :

	Aragonite, $CaCO_3$	Strontianite, $SrCO_3$	Witherite, $BaCO_3$	Cerussite, $PbCO_3$
Angle . . .	116° 10′	117° 18′	117° 48′	117° 18′
Axial ratio $a : b : c$	0·623 : 1 : 0·721	0·609 : 1 : 0·724	0·595 : 1 : 0·741	0·610 : 1 : 0·723
Specific gravity .	2·95	3·74	4·32	6·60
Specific heat .	0·1992	0·1445	0·1078	0·0814
Molecular heat .	19·66–20·18	21·31	21·34	21·73

and for the isomorphous sulphates of the barytes series, the angle of the rhombic prisms are respectively 101° 46′, 103° 48′, and 104° 11′ with barytes, $BaSO_4$, anglesite, $PbSO_4$, and celestine, $SrSO_4$. With the isomorphous sulphates, $ZnSO_4.7H_2O$, $MgSO_4.7H_2O$, and $NiSO_4.7H_2O$, the angles are respectively 89° 22′, 89° 26′, and 89° 56′; and with the trigonal series: potassium platinate, $K_2Pt(OH)_6$, stannate, $K_2Sn(OH)_6$, and plumbate, $K_2Pb(OH)_6$, the angles are respectively 74° 18′, 75° 14′ and 75° 19′.

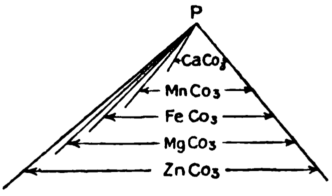


FIG. 88.—Diagramatic Representation of the Variation in the Angle *P* of the Isomorphous Carbonates.

A. E. H. Tutton [7] found that in the isomorphous selenates and sulphates of potassium, rubidium, and cæsium, specific chemical replacements are accompanied by clearly defined changes in the crystal structure along specific directions. Thus, when the basic element, say, potassium, in an alkaline sulphate or selenate is replaced by another of the same alkali family group, rubidium or cæsium, the greatest alteration occurs in the crystal angles corresponding with an elongation of the vertical axis; and when the acid-forming element sulphur is replaced by selenium, its family analogue, the greatest expansion takes place along the horizontal axes of the crystals. A. E. H. Tutton's diagram, Fig. 89, shows in an exaggerated manner, the effect of replacing potassium in potassium sulphate or selenate by the basic elements rubidium and cæsium.

Eutropic series.—According to A. E. H. Tutton, *in a strictly isomorphous series, where the interchangeable elements belong to the same family group of the periodic classification, the whole of the properties of the crystals—morphological, optical, thermal, and physical—are, in general, functions of the atomic weights of these elements*, and for the purpose of emphasizing the closeness of the relations connecting the several members, it is called a eutropic series—εὔτροπας, well nourished. Thus, thallium sulphate and selenate, and ammonium sulphate are isomorphous with the potassium, rubidium, and cæsium sulphates and selenates, because the radicle thallium or ammonium can replace the alkali metal without causing angular or structural changes greater than those produced by an interchange of the same family of elements. All the salts bear some definite chemical analogy, and crystallize in the rhombic system in forms whose angles rarely differ by more than 3°. In addition, the members of a eutropic series are not only isomorphous, but the interchangeable radicles belong to the same family group—*e.g.* the thallium, ammonium, potassium, rubidium, and cæsium sulphates from an isomorphous series, but the two former are not included in the eutropic series formed by the three latter; aragonite, strontianite, witherite, and cerussite form an isomorphous series, but the last is excluded from the eutropic series.

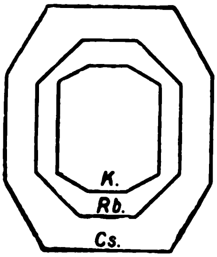


FIG. 89.

F. M. Jäger[8] similarly investigated the hexagonal crystals of the isomorphous rare earth ethyl sulphates of the type $R'''(EtSO_4)_3.9H_2O$, in which R''' denotes yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, dysprosium, erbium, thulium, and neo-ytterbium. The variation in passing from one member of the series to another is but a few minutes, so that the probable value of $c:a$ for the whole series is $c:a=0{\cdot}5062 \pm 0{\cdot}0012$. The molecular volumes are distinctive. A. E. H. Tutton has shown that F. M. Jäger's results might have been anticipated if the factors operating towards the extreme closeness of the angular values be considered: (i) Small variations in the atomic weights of the elements concerned; (ii) the mass effect of the remainder of the molecule; and (iii) the high symmetry of the hexagonal system.

The ratios in an isomorphous series whose members are not related eutropically, do not stand as an arithmetical or harmonic series of integral numbers. G. Linck[9] found empirically that if V denotes the crystal volume, D the specific gravity, and M the molecular weight, the quotients VD/M of the members of a eutropic series are related with one another as an arithmetical or harmonic series. This is illustrated in Table III.

Morphotropic series.—According to the structural theories of E. von Federoff, A. Schönflies, and W. Barlow space is partitioned into *space units*, *space lattices*, or *elementary cells*, Fig. 90, which E. von Federoff called *polyhedra*, A. Schönflies, *Fundamentalbereich*, and W. Barlow, *spheres of influence*. Further, following H. A. Miers, analogous portions of matter are supposed to be distributed in each space unit. No hypothesis is made as to the characteristics of these portions of matter; nor of the arrangement of the atoms in the molecules. Each space lattice is considered to be made up of units or points which represent either the centres of gravity of the constituent molecules, or the centres of rest about which those centres of gravity oscillate. The physical properties of crystals make it clear that whatever be the nature of the vibratory motions of the molecules, the movement does not take place outside a certain imaginary ellipsoidal domain or sphere of influence. Consequently, the molecules can then be discussed as if they were arranged like a system of points at rest. On this view, crystals are regarded as aggregates of ellipsoids or spheres, piled up in such a way that the corresponding axes are arranged in accord with some definite geometrical plan. Each molecule then appropriates to itself a space equal to one space unit—illustrated by the heavier lines in Fig. 90. It can then be assumed that the volume of each space unit can be represented by the quotient of the molecular weight by the molecular volume. W. Muthmann,[10] F. Becke, and A. E. H. Tutton attempted to determine the structure or rather the relative distances between homologous points in the space lattices of known crystals by measuring the relative distances of the crystal molecules from each other along different directions in a series of isomorphous crystals. P. Groth had previously emphasized the fact that on substituting a univalent atom or radicle in place of hydrogen, a change in the form of the crystal may take place in a particular direction, and he called the phenomenon **morphotropy.** A related phenomenon was noticed by A. Laurent (1840), and by F. de la Provostaye (1870), when chlorine was substituted for hydrogen in certain organic compounds—*e.g.* naphthalene, etc. The subject also received the attention of L. J. Wallmark, W. G. Hankel, L. Bodart, J. Nicklès, T. von Alth, L. Pasteur, etc. Numbers representing the relative dimensions of the space units can be derived from measurements of the crystallographic axes, etc. The axial ratios $a:b:c$ are used in describing the form of a crystalline substance, and they usually change, more or less, in passing from one substance to another; but since the axial ratios of a substance represent ratios of the actual dimensions of the corresponding homogeneous structure, they do not indicate the change in dimensions which occurs on passing from one substance to the other. It has therefore been found convenient to link up the axial ratios $a:b:c$ with the molecular volume V of the substance so as to furnish ratios χ, ψ, ω, which are proportional to the ratios $a:b:c$, and

TABLE III.—EUTROPIC SERIES OF CRYSTALS.

Salts.	Axis ratios, $a:b:c$	Crystal vol. V	Specific gravity, D	Molecular weight, M	VD/M	Ratio.
			Rhombic sulphates.			
K_2SO_4 . .	0·5727 : 1 : 0·7418	0·4248	2·666	174·4	0·006496	9
Rb_2SO_4 . .	0·5723 : 1 : 0·7485	0·4284	3·615	267·1	0·005798	8
Cs_2SO_4 . .	0·5712 : 1 : 0·7531	0·4302	4·246	361·9	0·005048	7
			Cubic nitrates.			
$Ca(NO_3)_2$ . .	1	1	2·6440	164·08	0·016116	8
$Sr(NO_3)_2$ . .	1	1	2·9857	211·68	0·012404	7
$Ba(NO_3)_2$ . .	1	1	3·2435	261·48	0·012404	6
			Monoclinic magnesium sulphates.			
$K_2Mg(SO_4)_2 6H_2O$.	0·7413 : 1 : 0·4993 $\beta = 75° 12'$	0·35784	2·028	402·9	0·0018012	36
$Rb_2Mg(SO_4)_2 6H_2O$	0·7400 : 1 : 0·4975 $\beta = 74° 1'$	0·35391	2·382	495·4	0·0017017	34
$Cs_2Mg(SO_4)_2 6H_2O$	0·7279 : 1 : 0·4946 $\beta = 72° 54'$	0·34410	2·670	590·6	0·001556	31

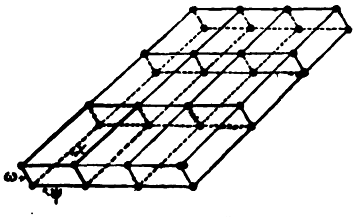


FIG. 90.—Space Lattice.

which represent the linear dimensions of the elementary cell, Fig. 90. Let χ, ψ, and ω represent the lengths of the sides of a unit cell; and V its molecular volume; further, for the sake of simplicity, suppose the cell be rectangular, and let the directions of the sides coincide with the crystallographic axes. Then $V=\chi\psi\omega=M/D$, where M denotes the molecular weight of the substance, and D its specific gravity. Hence χ, ψ, and ω may be taken to represent molecular intervals along the edges of the cell. Let a, b, and c represent the crystallographic axes coincident with the edges of the rectangular cell, then, by a well-known theorem in trigonometry,

$$\frac{\chi}{a}=\frac{\psi}{b}=\frac{\omega}{c}=\mu\,;\quad V=abc\mu^3\,;\ \text{or}\ \mu=\sqrt[3]{\frac{V}{abc}}$$

Consequently,

$$\chi=\sqrt[3]{\frac{a^2V}{bc}}\,;\quad \psi=\sqrt[3]{\frac{b^2V}{ac}}\,;\quad \omega=\sqrt[3]{\frac{c^2V}{ab}}$$

Consequently, the relative dimensions of the space units in a series of related crystals can be calculated from measurements of the crystallographic axes, etc. The values χ, ψ, ω so determined are called the **topic parameters,** or **topic axes,** or *molecular distance ratios*, and for a series of related substances, they represent the changes in the molecular magnitude of corresponding translations of the homogeneous structure common to the substances which occur in passing from one member of the series to another.[11]

The topic characters are calculated in an analogous way for crystals belonging to other systems. If the angle between the lines ω and ψ be α; between ω and χ be β; and between χ and ψ be γ, then, for a *triclinic* crystal, $V=\chi\psi\omega\sin\alpha\sin\beta\sin\gamma$; for a *cubic* crystal, $a=b=c$, and $\alpha=\beta=\gamma=90°$ and sin 90° is unity, therefore $\chi=\psi=\omega=\sqrt[3]{V}$; and for a *monoclinic* crystal, $\alpha=\gamma=90°$, so that $V=\chi\psi\omega\sin\beta$.

It is sometimes convenient to represent the cubic capacity—**crystal volume**—of a solid calculated from the axes ratios a, b, c and the angles α, β, γ of a crystal. In the *cubic system*, where $a=b=c$, and $\alpha=\beta=\gamma=90°$, the crystal volume is unity; in the *rhombic system*, where $a<b\lesseqgtr c$, and $\alpha=\beta=\gamma=90°$, the crystal volume is ac if $b=1$; ab if $c=1$; and bc if $a=1$; in the *tetragonal system*, where $a=b\lesseqgtr c$, and $\alpha=\beta=\gamma=90°$, the crystal volume is a^2, if $c=1$, and c if $a=1$; in the *hexagonal system*, where $a=b\lesseqgtr c$, and $\alpha=\beta=90°$, and $\gamma=60°$, the crystal volume is $\frac{1}{2}a^2\sqrt{3}$, if $c=1$; and $\frac{1}{2}c\sqrt{3}$, if $a=1$; in the *monoclinic system*, where $a\lesseqgtr b\lesseqgtr c$, and $\alpha=\gamma=90°$, and $\beta\lesseqgtr 90°$; the crystal volume is $ac\sin\beta$, if $b=1$; $ab\sin\beta$, if $c=1$; and $bc\sin\beta$, if $a=1$; and in the *triclinic system*, where $a\lesseqgtr b\lesseqgtr c$, and $\alpha\lesseqgtr\beta\lesseqgtr\gamma$, the crystal volume is $2ac\sqrt{\mu}$, if $b=1$; $2ab\sqrt{\mu}$, if $c=1$; and $2bc\sqrt{\mu}$, if $a=1$, where μ is put in place of $\sin s.\sin(s-\alpha).\sin(s-\beta).\sin(s-\gamma)$.

In his *Beiträge sur Volumetheorie der kristallisierten Körper*, W. Muthmann (1894)[12] calculated the topic axes of the acid phosphates and arsenates of potassium and ammonium, and also of the alkali permanganates. The relation between the axial ratios and the molecular distance ratios of the latter are:

	$a:b:c$	M	$\chi:\psi:\omega$
$KMnO_4$	0·7972 : 1 : 0·6491	58·526	3·8554 : 4·8360 : 3·1390
$RbMnO_4$	0·8311 : 1 : 0·6662	63·228	4·0322 : 4·8517 : 3·2312
$CsMnO_4$	0·8683 : 1 : 0·6853	70·042	4·2555 : 4·9009 : 3·3584
NH_4MnO_4	0·8164 : 1 : 0·6584	62·126	3·9767 : 4·8711 : 3·2071

Hence, while the axial ratios measure only the relative distances of translations, in homogeneous structure in the case of one substance, because one axial dimension, b, is taken as unity, the topic axes indicate the relative dimensions of corresponding translations in the several members of an isomorphous series; W. Muthmann concluded that with the alkali permanganates the differences between corresponding molecular distance ratios of the various salts indicate that the unit of crystalline structure is composed of four chemical molecules; but T. V. Barker's results with the alkali perchlorates, isomorphous with the permanganates, did not agree with

W. Muthmann's conclusions. A. E. H. Tutton likewise calculated the topic parameters of the alkali sulphates and selenates; J. A. le Bel and A. Ries, of the substituted ammonium chloroplatinates; G. Mez, of the derivatives of carbamide; etc.

If χ_1, ψ_1, ω_1; χ_2, ψ_2, ω_2; . . . be the topic axes of an isomorphous series in which it is assumed that the molecules are similar, that the arrangement of the molecules is similar, and that the crystals have the same elementary parallelopipedal cells which vary slightly in dimensions in passing from one series to the other, then, χ_1, ψ_1, ω_1 give the relative molecular intervals along three directions in the crystals of the one substance; χ_2, ψ_2, ω_2, the molecular intervals along three corresponding directions in the second substance. The ratio $\psi_1 : \psi_2$ represents the relative increased or decreased separation along the given direction in molecules of the two different substances, owing to the replacement of one element or radicle by another in the series. In illustration, W. Muthmann found that the molecules of the tetragonal phosphates separate almost uniformly in all directions when the atom *P* is replaced by an atom of As. When the K atom is replaced by the NH_4 radicle in either the tetragonal phosphate or arsenates, the molecules are again separated, but almost entirely in the direction of the principal axis. Hence, concludes W. Muthmann, the metallic elements occupy such a position in the molecule that the line uniting them to the acid radicles are parallel to the point axis.

If the symmetry of the crystal molecules be tetragonal like that of the crystal each physical molecule will be a complex cluster of at least eight chemical molecules, say KH_2PO_4, and he assumes that in this complex, eight $PO(OH)_2$ radicles are arranged at the corners of two superposed horizontal squares and a KO radicle is attached above or below each $PO(OH)_2$ radicle. A. E. H. Tutton employed analogous reasoning for the rhombic crystals of the alkali sulphates, and he considered the accord justifies the assumption that the crystal elements of the alkali sulphates are situated at the corners of a rectangular rhombic prism so that each cluster consists of four chemical molecules arranged in a definite symmetrical manner. The molecule of a crystal may thus include several chemical molecules, and G. J. Stoney[13] proposed to call the former *macromolecules* to distinguish them from the latter. W. Muthmann predicted that thallium and rubidium sulphates would have almost identical forms, and this prediction was later verified by A. E. H. Tutton. F. Slavik[14] has calculated the topic axes of the morphotropic series ammonium iodide, NH_4I, tetramethyl ammonium iodide, $N(CH_3)_4I$, tetraethyl ammonium iodide, $N(C_2H_5)_4I$; and tetrapropyl-ammonium iodide, $N(C_3H_7)_4I$, and found on writing Me for CH_3; Et for C_2H_5; and Pr for C_3H_7:

	Mol. vol.	$a:b:c$	$\chi:\psi:\omega$
NH_4I (cubic)	57·51	1 : 1 : 1	3·860 : 3·860 : 3·860
NMe_4I (tetragonal) . . .	108·70	1 : 1 : 0·7223	5·319 : 5·319 : 3·842
NEt_4I (tetragonal) . . .	162·91	1 : 1 : 0·5344	6·648 : 6·648 : 3·686
NPr_4I (rhombic) . . .	235·95	0·776 : 1 : 0·6283	6·093 : 7·851 : 4·933

Hence, while the value of ω is almost the same in the first three cases, the values of χ and ψ are increased by substituting four-methyl groups in place of hydrogen, and still more if four of the heavier ethyl-groups be introduced; with the still heavier propyl-groups more drastic changes take place in the spatial arrangement of the atoms, and a very marked change in the molecular volume is that the propyl-compound no longer possesses the same crystal symmetry.

C. A. Kenngott,[15] A. Schrauf, and F. Pfaff measured the relation between the *hardness* and *specific gravity* of isomorphous bodies, and found the mean hardness of the crystal faces to be related less definitely with the chemical composition than other physical properties. K. R. Koch measured the *elastic constants* of the two main alkali chlorides.

The *cleavage* of crystals is connected with their internal cohesion, and G. Tschermak[16] and A. Sadenbeck have given a number of examples showing the analogy in the cleavages of isomorphous substances. H. Baumbauer, G. Tschermak, and F. Becke [17] have examined the *corrosion figures* of isomorphous compounds. E. Jannettaz [18] has investigated the *thermal conductivity* of isomorphous crystals, and he concludes that:

> Les clivages les plus faciles ou leurs résultantes sont parallèles aux axes les plus grands de conductibilité thérmique, et inversement, même, dans les cas de trois clivages.

The *thermal expansion* of some isomorphous substances has been measured by H. Fizeau and F. Pfaff.[19] The *magnetic properties* of isomorphous substances have been studied by J. Grailich and V. von Lang,[20] and some analogies were observed.

Isomorphous bodies show close resemblances in their *optical properties*, although there are some irregularities; they have been compared with respect to the position and length of their optical elasticity axes; the index of refraction; double refraction, and dispersion. The pioneer work was done by H. de Sénarmont,[21] J. Grailich, V. von Lang, and H. Topsöe and C. Christiansen. In spite of the fact that H. de Sénarmont found

> The mechanical causes which determine the geometrical form are of a different order from those which determine the optical properties, inasmuch as the form remains the same in an entire series of isomorphous substances, whereas the optical properties show not only fundamental variations, but a complete inversion in their relative magnitude;

and J. Grailich and V. von Lang

> Different substances cannot enter into the molecule without changing the form of the crystal, but the optical qualities are more deeply affected the greater the change in the constitution of the molecule. . . . There is no direct relation between the optical properties and such properties as cleavage, hardness, and magnetic susceptibility which rest on the different arrangement of the molecules;

there are, however, many analogies between the optical properties—double refraction, index of refraction, etc.—of isomorphous bodies. The similarity in external form is one sign that there is an analogy of structure, so that isomorphous substances usually exhibit not only close chemical analogies but also close analogies in their physical properties. It is, however, possible that compounds of very different chemical composition have the same structure, and there is a risk in using isomorphism in the attempt to establish chemical relations where none exist.

The law of mixed crystals.—Extended observations have multiplied examples of substances which possess a similar chemical constitution and a similar crystalline form; but at the same time the observations have also brought into prominence the fact that substances which crystallize in similar or identical forms—particularly in the cubic system—may exhibit wide divergencies in chemical constitution. The converse of E. Mitscherlich's law does not, therefore, hold good. Similarity of chemical composition or similarity in crystalline form are not adequate tests for isomorphism. E. Mitscherlich also stated that "while substances of different crystalline form cannot combine other than in fixed proportions, substances of the same crystalline form can crystallize together in all proportions." F. S. Beudant [22] was the first to suggest that "mixed crystals" are *mélanges chimiques ou associations non mécaniques en proportion indéfinie.* He said:

> I have adopted the expression *mélange chimique* in order to distinguish by a specific term a chemical association of bodies which has characteristics different from other chemical associations to which the name *combinaisons chimiques* is applied. I do not, however, seek to imply that the components which can be associated in the *mélanges chimiques* in an infinitude of proportions, are really united chemically or simply mixed. The *mélanges chimiques* could be designated *combinaisons indéfinies* in which the product always possesses, more or less, the properties of one or other of the components.

Homogeneous crystals containing two salts mixed in indefinite proportions, and formed in solutions containing a mixture of both salts, were called ***Mischkrystalle***—*i.e.* **mixed crystals**—by H. W. B. Roozeboom in 1899; they have also been called **isomorphous mixtures,** but both terms are liable to misconception because the mixed crystals are mixtures only in the sense that ordinary homogeneous solutions are mixtures, and hence some prefer the older term **solid solution**, used by J. H. van't Hoff [23] in 1890, and regard crystals as homogeneous phases and not an aggregate of two or more phases. L. de Boisbaudran claims that he first applied the idea of solid solutions, *dissolvents solides*, in papers on fluorescence between 1886 and 1890, and that in an unpublished note—on supersaturation—before the *Académie des Sciences* in Paris in 1866, he stated:

> I do not hesitate to attribute the same cause, (i) to the solution obtained by dissolving one solid in another (isomorphisme de Mitscherlich); (ii) to the solution of liquids in another one; and (iii) to the solution of vapours in one another.

The formation of apparently homogeneous crystals is not accepted by chemists as a decisive test of the individuality of a chemical species, since, in crystals, certain elements may replace one another indefinitely without altering the form of the crystals. When mixed crystals of lead and barium nitrate are treated with a saturated solution of barium nitrate, the lead nitrate is dissolved out and a skeleton of barium nitrate remains which is not doubly refracting although the original mixed crystals exhibit this quality. The failure of mixed crystals to satisfy the law of constant composition has led chemists to agree *arbitrarily* that mixed crystals are mixtures and not definite compounds, although the phase rule regards mixed crystals as homogeneous single phases.

The colour of mixed crystals is usually intermediate between the colour of their component salts—thus, yellow cæsium chloroplumbate, Cs_2PbCl_6, and deep blue cæsium chloroantimoniate, Cs_2SbCl_6, give mixed crystals of a green colour; on the other hand, the two yellow salts, cæsium chloroplumbate, Cs_2PbCl_6, and cæsium chlorotellurate, Cs_2TeCl_6, give mixed crystals of an orange-red colour.

J. W. Retgers' colour test for mixed crystals.—Saturated solutions of the two salts which differ in colour are placed side by side on a microscopic slide and brought together with a glass rod. The crystals which form on evaporation are examined under a microscope. If the salts are isomorphous, the colour of the crystals varies gradually from one side to the other, the crystals of the pure compounds being visible on the extreme edges. If the two salts are not isomorphous, they do not mix, and near the centre, where the two solutions have been brought together, distinct crystals of each compound can be seen owing to their difference in colour. If the two salts have the same colour, J. W. Retgers uses a third salt of a different colour from the other two. If both the same coloured salts form mixed crystals with the salt of a different colour, the two salts under examination are isomorphous.

J. W. Retgers (1889) considers all important the property of forming mixed crystals in all proportions such that "if the percentages of one constituent of the mixture be plotted as abscissæ, and the corresponding magnitudes of the physical properties be plotted as ordinates, the different points lie in a continuous line." Two substances are really isomorphous only when the physical properties of their mixed crystals are continuous functions of their chemical composition; or **the physical properties of isomorphous mixtures are continuous functions of the percentage composition—Retgers' law.** Physical properties here include geometrical, optical, thermal, elastic, and electrical properties. This agrees with F. W. Küster's statement that all the physical properties of isomorphous mixtures which have been hitherto investigated are purely additive, and are continuous functions of their percentage composition. For instance, the refractive index curve of isomorphous mixtures of potassium and thallium alums lies on a straight line. H. de Sénarmont, A. des Cloizeaux, H. Dufet, G. Wyrouboff, E. Mallard, R. Brauns, A. Fock, T. Hiortdahl, etc., have shown that "the difference between the indices of refraction of a mixture of two isomorphous salts and those of the components is inversely as the number of the equivalents of the two salts in the mixtures," so that if μ be the index of refraction of the mixtures, μ_1 and μ_2 the indices of refraction of the component salts of molecular weight M_1 and M_2 respectively, then:

$$\mu=\frac{M_1\mu_1+M_2\mu_2}{M_1+M_2}$$

G. Bodländer also obtained analogous results with the circular polarization of mixed crystals of lead and strontium dithionates. The solubilities of isomorphous mixtures have been investigated by C. F. Rammelsberg, C. von Hauer, and F. Rüdorff. H. W. B. Roozeboom's work is indicated in the chapter on solutions, and he adds that if the osmotic pressure of a saturated solution of mixed crystals with an increasing content of one of the constituents, increases or diminishes, so is the proportion of this constituent in the solution greater or less than in the mixed crystal. Again, the melting points of isomorphous mixtures of albite and anorthite furnish a series which is almost a straight line representing albite by Ab and anorthite by An:

	An	$AbAn_5$	$AbAn_2$	AbAn	Ab_2An	Ab_3An	Ab
Melting point .	1532°	1500°	1465°	1419°	1367°	1340°	—

The melting point of albite has not been determined accurately within 150°. These results are in agreement with the much-discussed generalization of F. W. Kuster (1891) from observations on the melting points of mixtures of organic compounds. He found a simple linear relation, sometimes called **Kuster's rule : The solidifying point of an isomorphous mixture lies on a straight line connecting the melting points of the individual components, and it can be calculated from the percentage composition of the mixture.** This simple linear relation is supposed to represent perfect isomorphism. Imperfect isomorphism is assumed to be the cause of the slight concavity or convexity usually observed with these curves. On practical grounds, J. W. Retgers considers specific gravity, or the reciprocal of specific gravity—the specific volume—to be the most suitable property for investigation. This property was found by G. Tschermak, O. Pettersson, R. Brauns, J. W. Retgers, etc., to be a function of the specific gravity of the components such that if D and v respectively denote the specific gravity and specific volume of the mixture, D_1 and D_2, and v_1 and v_2, the specific gravities and specific volumes of the components when α denotes the volume percentage and β the weight percentage of the second component of the mixture, then:

$$D=D_1+\frac{\alpha(D_2-D_1)}{100}; \quad v=v_1+\frac{\beta(v_2-v_1)}{100}$$

An example by J. W. Retgers is indicated in Fig. 91, where the specific volume of mixed crystals of potassium and ammonium aluminium sulphates are plotted. The continuity of the curve shows that the specific gravity or specific volume and chemical composition of the mixed crystals are isomorphous. A similar continuous curve is obtained with mixtures of magnesium and manganese pyrophosphates. The curves sometimes show a break, as is the case with the dihydrogen phosphates of potassium and ammonium. Isomorphous mixtures are formed only when not more than 20 per cent. of the second constituent is present. Intermediate mixtures do not form homogeneous crystals. This is illustrated in J. W. Retgers' curve, Fig. 91, showing that the two substances are not miscible in all proportions, but the two portions of the curve are parts of one straight line corresponding with the isomorphous character of the two salts. Otherwise expressed, the solubility of each substance in the other may be limited like the solubility of many salts in water, or if the one in the other may dissolve the other in all possible proportions.

There has been some differences of opinion as to whether the formation of mixed crystals with isomorphous substances must take place in all proportions, or if gaps may occur; in other words, if the term isomorphous be applied only to those substances which form a continuous series of mixed crystals, and excluded from those which form only partial series of mixed crystals. In opposition to J. W. Retgers, W. Stortenbecker (1903) considers that if the substances are truly isomorphous, no gaps will occur, while B. Gossner (1906) also considers that isomorphous salts may exhibit gaps, and this the more, the greater the difference in the molecular volume (molecular weight divided by the specific gravity) of the respective compounds. This, in turn, is possibly conditioned by the relative sizes of the structural units of the two salts. According to B. Gossner (1907), also, if the molecular volume of the isomorphous substances be nearly the same—*e.g.* nickel or zinc fluosilicates and double alkali sulphates—the salts will form a continuous series of mixed crystals; while if the molecular volumes are very different—*e.g.* copper or cobalt fluosilicates and double alkali sulphates—there will be a break in the series of mixed crystals. If the continuous curve (Fig. 91) or broken curve (Fig. 92) are not in the same straight line, the two salts, even if perfectly miscible in all proportions, would not, according to J. W. Retgers' definition, be called isomorphous. For instance, ammonium and ferric chloride are not isomorphous, although octahedral ammonium chloride forms coloured mixed crystals by taking up a small amount of ferric chloride.

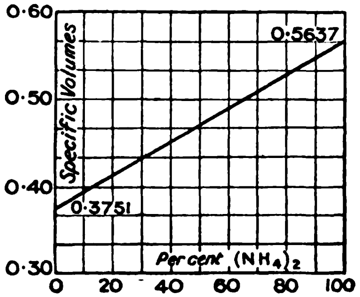


FIG. 91.—Specific Volumes of Mixed Crystals of Ammonium and Potassium Aluminium Sulphates.

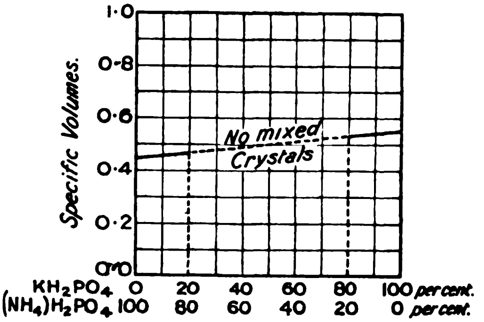


FIG. 92.—Specific Volumes of Mixed Crystals of Ammonium and Potassium Dihydrogen Phosphates.

The formation of mixed crystals is conditioned or favoured by substances of analogous structure, and this phenomenon is therefore regarded as strong evidence of isomorphism, but the formation of mixed crystals is not a *sufficient* criterion of isomorphism, since there is quite a large number of cases of their formation by substances of different form; nor is the formation of mixed crystals a *necessary* criterion of isomorphism, since the isomorphous salts may interact forming another chemical individual instead of producing mixed crystals. In other words, double compounds may be formed which interfere with the application of J. W. Retgers' rule—*e.g.* J. W. Retgers found with a mixture of rhombic silver nitrate and potassium nitrate, each can dissolve a little of the other still forming rhombic crystals, but the two salts crystallize together forming a double salt, $KAg(NO_3)_2$, which is monoclinic and has a specific volume 0·31. If the double salt were an isomorphous mixture, it would have a specific volume 0·38. The point corresponding with this mixture thus lies off the straight dotted line, as shown in Fig. 93. Similar results are obtained with mixtures of potassium and sodium sulphates, the point corresponding with $3K_2SO_4.Na_2SO_4$ is a long distance from the line connecting the two components; similarly, mixtures of magnesium and calcium carbonates show a deviation for *dolomite*, $MgCO_3.CaCO_3$; and potassium chloride and cupric chloride—$CuCl_2.2H_2O$—form $2KCl.CuCl_2.2H_2O$.

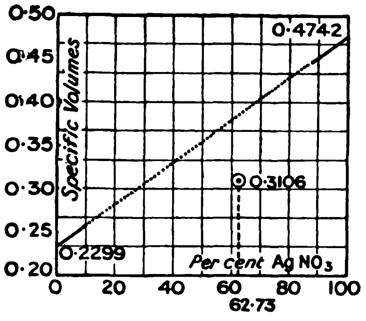


FIG. 93.—Specific Volumes of Mixtures of Silver and Potassium Nitrates.

Overgrowths.—In 1816 J. L. Gay Lussac[24] found that a crystal of alum continues to grow when placed in a solution of another alum. If a crystal of dark violet chromium alum be placed in a saturated solution of ordinary potassium alum, a transparent colourless overgrowth—*lame de superposition*—of potassium alum is deposited as a crust over the dark-coloured chromium alum as a nucleus. Similarly, a crystal of colourless zinc sulphate—$ZnSO_4.7H_2O$—can be coated with an overgrowth of green nickel sulphate—$NiSO_4.7H_2O$—and *vice versa*; crystals of sodium nitrate grow on Iceland spar; and a pale amethyst triclinic crystal of manganese sulphate—$MnSO_4.5H_2O$—can be coated with blue copper sulphate—$CuSO_4.5H_2O$—and *vice versa*. The parallel overgrowths formed in this way have been called **episomorphs.** C. von Hauer grew episomorphs of magnesium sulphate on magnesium chromate or nickel sulphate; of potassium magnesium sulphate on the corresponding cobalt and nickel salts. In nature also episomorphs of potash and soda felspars are common. H. Kopp (1873) stated that this power of forming overgrowths, as well as the power of forming mixed crystals, enables isomorphism to be detected even when no particulars about the crystalline form or about the chemical composition are available. There are some exceptions to the test for isomorphism—trigonal potassium sulphate can be coated with a layer of hexagonal potassium sodium sulphate—$KNaSO_4$; etc.

Isomorphous substances were found by F. M. Jäger and H. Haga [25] to yield similar radiograms although the relative intensities of the spots were often different. C. Viola concluded that mixed crystals of magnesium and zinc sulphate are formed in layers composed alternately of each salt, and therefore differ radically from solid solutions. L. Vegard and H. Schjelderup have also examined the X-ray spectra of mixed crystals of potassium chloride and bromide, and of potassium and ammonium bromide. They found that the crystals behaved as single entities and there was no indication that the crystals were composed of thin homogeneous laminæ. G. Tammann examined the effect of reagents which attack one of the components of binary mixed crystals of gold and copper, and gold and silver. The action is not proportional to the amount of the soluble constituent; indeed, there are limits of composition between which the resistance to attack is very great.

Strictly speaking, all substances with a similar crystalline form are isomorphous. The similarity of external geometrical form is *primâ facie* evidence of the similarity of internal structure, so that those crystalline substances are isomorphous whose structure is analogous (E. Mitscherlich). If the molecular volumes are sufficiently close, isomorphous substances usually form (i) homogeneous mixed crystals (J. W. Retgers); (ii) they form parallel overgrowths on each other (H. Kopp); (iii) they are mutually active in inducing crystallization when a supersaturated solution of the one is inoculated with a small fragment of the other; and (iv) are generally of analogous chemical constitution. None of these tests is an infallible criterion, and here, as is so often the case, a conclusion can be drawn only after carefully balancing the available circumstantial evidence. C. Hlawatsch recognizes degrees of isomorphism, and he has discussed the nature of isomorphism, and classified substances according to their degree of isomorphism on the lines of the following scheme:

(1) The substances exhibit no chemical analogy, but show similarities in certain zones which frequently grow parallel. (2) The substances show analogies in their angles, but do not exhibit the same cleavages or habit. This may be termed isogonism. (3) The substances form mixed crystals, but have not analogous structure. (4) The last case is not to be confused with that presented by isopolymorphous substances when the two modifications possess very different stability. (5) The substances show like structure expressed, not merely by similarity of form, but by like cleavage, twinning, and habit. (6) The substances have similar crystal structure, and may form mixed crystals, but do not belong to the same crystal sub-class. (7) The substances possess similar structure with identical symmetry, and form mixed crystals, but are not chemically analogous. (8) The substances show chemical analogy in addition to the other characters. (9) Lastly, they possess chemical analogy, form mixed crystals, have similar structure, and angular relations which are functions of the atomic weights of the interchangeable elements.

According to G. Tammann (1907), chemically analogous elements are usually isomorphous. Elements in the same groups in periodic system usually form mixed crystals and not compounds, while many elements not in the same group but chemically similar also form mixed crystals. In binary alloys, elements of high melting point usually form mixed crystals with those of low melting point. A. Arzruni, in his *Die Beziehungen zwischen Krystallform und chemischer Zusammensetzung* (Braunschweig, 1898), arranges sixty-eight of the elements in ten isomorphous series (*isomorphe Reihen*):

Series I.—H, K, Rb, Cs, NH_4, Tl, Na, Li, Ag. *Series II.*—Be, Zn, Cd, Mg, Mn, Fe, Os, Ru, Ni, Pd, Co, Pt, Cu, Ca, Sr, Ba, Pb. *Series III.*—La, Ce, Di, Y, Er. *Series IV.*—Al, Fe, Cr, Co, Mn, Ir, Rh, Ga, In (Ti). *Series V.*—Cu, Hg, Pb, Ag, Au. *Series VI.*—Si, Ti, Ge, Zr, Sn, Pb, Th, Mo, Mn, U, Ru, Rh, Ir, Os, Pd, Pt, Te (?). *Series VII.*—N, P, V, As, Sb, Bi. *Series VIII.*—Nb, Ta. *Series IX.*—S, Se, Cr, Mn, Mo, N, Te (?), As, Sb. *Series X.*—Fl, Cl, Br, I, Mn, Cy.

A given element may appear in different isomorphous series. In illustration, manganese, in its different states of oxidation, belongs to different classes. There are also certain regularities exhibited by the members of a sub-group in Mendeléeff's periodic arrangement.

There is undoubtedly a profound connection between the similarity of crystalline form and the similarity of chemical structure. The thousand and one known cases typified by the isomorphism of potassium sulphate and selenate were supposed to be a result of the chemical similarity of the replaceable elements, and isomorphous replaceability was found to be a periodic function of the elements since the elements belonging to the same sub-group in the periodic system usually gave isomorphous compounds. T. V. Barker[26] has compiled a number of examples of what he calls "unusual types of isomorphism," in which there is no similarity of valency structure. The following are taken from T. V. Barker's list, where the number of known analogues of any particular compound is indicated in brackets:

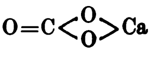
Monoclinic system.	$a:b:c$	β
$CuTiF_6.4H_2O$ (2)	0·7471 : 1 : 0·5564 ;	104° 9′
$CuCbOF_5.4H_2O$ (1)	0·7627 : 1 : 0·5629 ;	103° 20′
$CuWO_3F_4.4H_2O$ (1)	0·7648 : 1 : 0·5629 ;	103° 14′
K_3HSnF_8 (1)	0·6277 : 1 : 0·4928 ;	93° 0′
K_3HCbOF_7 (0)	0·6279 : 1 : 0·4900 ;	93° 14′
$MnCl_2.4H_2O$ (1)	1·1525 : 1 : 0·6445 ;	99° 25′
$BeNa_2F_4$ (0)	1·9913 : 1 : 0·6929 ;	99° 20′
$(NH_4)_2SeO_4$ (2)	1·8900 : 1 : 1·1987 ;	115° 29′
Cs_2HgI_4 (0)	1·3155 : 1 : 0·9260 ;	110° 4′

Rhombic system.	$a:b:c$
$K_2SnCl_4.2H_2O$ (3)	0·6852 : 1 : 0·7586
$K_2FeCl_5.H_2O$ (4)	0·6911 : 1 : 0·7178

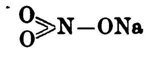
Rhombic system.	$a:b:c$
$KClO_4$ (8)	0·7817 : 1 : 1·2792
$BaSO_4$ (5)	0·8152 : 1 : 1·3136
KBF_4 (1)	0·7898 : 1 : 1·2830
K_2SO_4 (15)	0·5727 : 1 : 0·7418
K_2BeF_4 (4)	0·5708 : 1 : 0·7395
$[N(CH_3)_4]_2HgCl_4$ (1)	0·5766 : 1 : 0·7893

Tetragonal system.	$a:c$
Xenotime, YPO_4 (0)	1 : 0·6177
Zircon, $ZrSiO_4$ (1)	1 : 0·6400
Cassiterite, SnO_2 or $SnSnO_2$ (4)	1 : 0·6726
KIO_4 (3)	1 : 1·5534
$CaWO_4$ (7)	1 : 1·5268
$KOsO_3N$ (1)	1 : 1·6319
$KRuO_4$ (0)	1 : 1·6340

Rhombic crystals of aragonite, $CaCO_3$, and nitre, KNO_3, have axial ratios respectively $a : b : c = 0·622 : 1 : 0·721$ and $0·591 : 1 : 0·701$; both salts have a similar crystalline form but a very different chemical constitution. Similarly with rhombohedral calcite, $CaCO_3$, and sodium nitrate, $NaNO_3$, with the respective rhombohedral angles of 74° 55′ and 73° 27′, and axial ratios $a : c = 1 : 0·854$ and $1 : 0·8297$. The constitutional formulæ of calcium carbonate (calcite) and sodium nitrate are represented respectively by



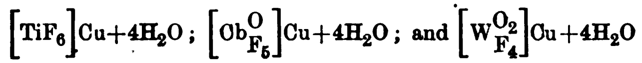
$$O{=}C{<}^{O}_{O}{>}Ca$$



$$^{O}_{O}{\geqslant}N{-}ONa$$

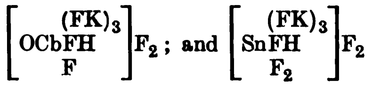
so that if these formulæ really indicate internal structures the observed isomorphism must be due to some obscure accidental cause. The facts indicated a similarity in crystal structure; the valency theory indicated complete dissimilarity. As a result, some denied the apparent isomorphism of these compounds, and narrowed the definition of isomorphism so that a special name **homomorphism** or **isogonism** was devised for the phenomena presented by substances which differ in chemical constitution, but have a similar crystalline form. Attempts to evade the difficulty presented by calcite and sodium nitrate where the total sum of the valencies is in case twelve, by assuming that the sexavalent groups CaC and NaN replace each other isomorphously. The explanation is futile, because it fails to account for the replaceability of the alkali metals by the ammonium radicle, where the valency summations are respectively one and nine. Hence, adds T. V. Barker, "the equality of valency summation has nothing to do with isomorphism."

The X-ray spectrum has enabled W. L. Bragg (1914) to show a close *structural* relationship between the crystals of calcium carbonate and potassium nitrate, which are not considered to be isomorphous. Tetragonal zircon, $ZrSiO_4$, and thorite, $ThSiO_4$, are isomorphous with rutile, TiO_2, and cassiterite, SnO_2. The difference in structure is not so apparent if the constitutions be represented: ZrO_2SiO_2, ThO_2SiO_2, $(TiO)_2$. In virtue of isogonism, the supposed relations which have been traced between chemical composition and crystalline form are often quite accidental. In the triclinic system, isogonism is usually an indication of isomorphism, but its significance becomes less and less as the crystals increase in symmetry. T. V. Barker claims that it is no longer advisable to limit the term isomorphism to cases of chemical and crystal symmetry by interpreting the chemical similarity in terms of the older valency hypothesis. It is true that the dissimilarity in the constitution of these substances with similar crystals is so great that it might be hazarded that "isomorphism may be totally independent of chemical structure;" but this view is untenable, for it is the valency structure which is at fault. If the constitution of these compounds be interpreted on A. Werner's co-ordination structures, there are indications that the compounds with apparently dissimilar structure will prove to have analogous structures. For example, the molecular formulæ of the first three compounds in T. V. Barker's list are not very similar, but when expressed according to A. Werner's system, the case is somewhat different:



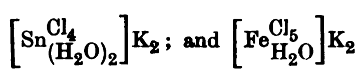
$$\left[TiF_6\right]Cu+4H_2O;\ \left[Cb\overset{O}{\underset{F_5}{}}\right]Cu+4H_2O;\ \text{and}\ \left[W\overset{O_2}{\underset{F_4}{}}\right]Cu+4H_2O$$

Again, J. C. G. de Marignac's compounds K_3HSnF_8 and K_3HCbOF_7 appear closely related when represented by A. Werner's formulæ:



$$\left[\begin{matrix}(FK)_3\\ OCbFH\\ F\end{matrix}\right]F_2;\ \text{and}\ \left[\begin{matrix}(FK)_3\\ SnFH\\ F_2\end{matrix}\right]F_2$$

There is no analogy in the chemical formulæ of the compounds $2KCl.SnCl_2.2H_2O$ and $2KCl.FeCl_3.H_2O$, either in this molecular form or when expressed by the complex salt formulæ $K_2SnCl_4.2H_2O$ and $K_2FeCl_5.H_2O$. The co-ordination formulæ, however, show a close analogy:



$$\left[Sn\overset{Cl_4}{\underset{(H_2O)_2}{}}\right]K_2;\ \text{and}\ \left[Fe\overset{Cl_5}{\underset{H_2O}{}}\right]K_2$$

Again, $[Mn(H_2O)_4]K_2$ and $[BeF_4]Na_2$ are similar if it be assumed that the molecules of water which are co-ordinated can be replaced isomorphously by halogen atoms. The isomorphism of $ZnI_2.4NH_3$ with potassium beryllium fluoride leads to the assumption that the internal structures are similar in this sense: $[Zn(NH_3)_4]I_2$ and $[BeF_4]K_2$, where the positive ion of one compound is analogous with the negative ion of the other. A. Werner also represented $KOsO_3N$ and KBF_4 respectively by the co-ordination formulæ $[OsO_3N]K$ and $[BF_4]K$. Hence, adds T. V. Barker, co-ordination evidently supplies a medium in which analogy of chemical composition in isomorphous compounds formerly classed as homomorphic or isogonic, comes strongly into the foreground.

Isodimorphism—In 1829, J. F. W. Johnston[27] drew attention to the fact that a plumbiferous calcite, which he named *plumbocalcite*, and which not only contained calcium carbonate but also the lead carbonate. Hence, the latter must crystallize in two forms, so that in addition to rhombic cerussite, there must also be a rhombohedral form of lead carbonate which can crystallize with the corresponding form of calcium carbonate. Hence, both lead and calcium carbonate were called *isobimorphs*. Such a form of lead carbonate has not yet been discovered, but J. F. W. Johnston's reasoning was sound. Some years later M. L. Frankenheim made a similar discovery with respect to calcium carbonate and potassium nitrate. Many examples are now known in which there are two independent series of isomorphous salts, and the phenomenon is called **isodimorphism.** The pyrite and marcasite families of minerals form two independent series of isomorphous crystals. The following were compiled by J. P. Iddings (1906):

	Cubic.	Rhombic.
FeS_2	pyrite	marcasite
$CoAs_2$	smaltite	saffrolite
$NiAs_2$	chloanthite	rammelsbergite
$(Co, Fe)(S, As)_2$	cobaltite	glaucodote
$NiS_2.Ni(Sb, As)_2$	corynite	wolfachite

Each of the sulphates $RSO_4.7H_2O$ (where R may be Mg, Zn, Ni, Co, Fe, Mn) is dimorphous, forming rhombic and also monoclinic crystals. The rhombic crystals of all the salts form one isomorphous series, and the monoclinic crystals of all the salts form another isomorphous series. The isodimorphism is here limited to certain proportions of the constituents. For example, mixtures of iron and magnesium sulphates give homogeneous *monoclinic* mixed crystals if less than 54 per cent. of magnesium sulphate, $MgSO_4.7H_2O$, be present, and *rhombic* mixed crystals if more than 81 per cent. be present. The specific volume curve of the mixed crystals does not therefore lie in one straight line. This is illustrated by J. W. Retgers' diagram, Fig. 94.

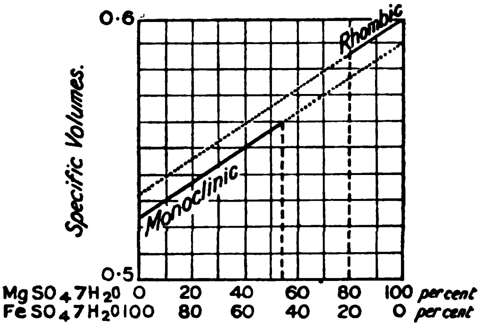


FIG. 94.—Specific Volumes of Mixed Crystals of Magnesium and Ferrous Sulphates—Limited Isomorphism.

Similarly, a mixed solution of silver and sodium chlorates gives mixed cubic crystals if the sodium chlorate be in excess, and mixed tetragonal crystals if the silver chlorate be in excess. J. W. Retgers found that copper sulphate solutions crystallizing in the presence of a small proportion of zinc sulphate (0 to 7·98 per cent.) furnishes *triclinic* mixed crystals of $CuSO_4.5H_2O$ and $ZnSO_4.5H_2O$; and if a larger proportion of zinc sulphate be present, 65·59 to 83·35 per cent., *monoclinic* crystals of a mixture of $CuSO_4.7H_2O$ and $ZnSO_4.7H_2O$; while if a relatively large proportion of zinc sulphate, 97·68 to 100 per cent., be present, *rhombic* crystals of a mixture of $CuSO_4.7H_2O$ and $ZnSO_4.7H_2O$ are formed. Similar results are obtained with mixtures of copper and magnesium sulphates. H. W. Foote (1902) has shown that *tetragonal* beryllium sulphate, $BeSO_4.4H_2O$. forms mixed tetragonal crystals with beryllium selenate, $BeSeO_4.4H_2O$, provided the molecular proportions of the respective salts in solution does not exceed 7·33 : 1; while if the solution contains a less proportion of the sulphate, a series of *rhombic* crystals can be prepared when the molecular proportions of the beryllium sulphate to selenate lie between 4 : 1 and pure beryllium selenate.

The composition of mixed crystals of one salt with a maximum proportion of the other is called the *mixing limit*. Thus, tetragonal mixed crystals of beryllium sulphate and selenate have reached the mixing limit when their composition has $BeSO_4.4H_2O : BeSeO_4.4H_2O = 7{\cdot}33 : 1$. J. H. van't Hoff (1898) suggested an interesting analogy between mixed crystals and ordinary solutions. Pairs of salts which crystallize together are likened to perfectly miscible liquids like alcohol and water, while salts of the second class, whose isomorphism is limited, are likened to partially miscible liquids like aniline and water. The analogy has been pushed still further. At temperatures exceeding 165°, aniline and water mix in all proportions, while below that temperature the two liquids are but partially miscible; hence, it is inferred that unless other changes intervene, salts which are but partially miscible as ordinary temperatures may be perfectly miscible at more elevated temperatures.

According to the phase rule, tetragonal $BeSO_4.4H_2O$ will contain a maximum proportion of $BeSeO_4.4H_2O$ when the solution from which it is deposited is saturated with regard to the mixed crystals of $BeSeO_4.4H_2O$ and $BeSO_4.4H_2O$. In such systems there are four phases—vapour, solution, and two solids—and three components—the two salts and water; the system is accordingly univariant. Accordingly, if one of the possible variables—temperature, pressure, or concentration of phase—be changed, the others must be fixed and unalterable. For instance, if the temperature be fixed, the concentration of each phase and the vapour pressure must be fixed; and if the temperature be changed, another variable must be changed. Hence, the composition of mixed crystals at the mixing limit will change with change of temperature, and this is in agreement with observations.

Two or more compounds which, judged by all analogies, might be expected to be isomorphous may exhibit pronounced differences in crystalline form; but, by suitably altering the conditions, they may furnish a second form, so that the isomorphism of the series is established. Monoclinic felspar—orthoclase—usually contains some sodium; while triclinic soda felspar—albite—contains some potassium. Hence P. Groth (1874) [28] inferred that this is a case of isodimorphism, and that two pure varieties—monoclinic and triclinic soda and potash felspars—should exist. The prediction was verified two years later by A. des Cloizeaux's discovery of microcline, the triclinic form of potash felspar; and later, by P. Barbier discovery of barbierite, the monoclinic form of albite. Sodium phosphate forms two distinct crystals—rhombic and monoclinic. The arsenate appears in only one of these forms. Hence it is inferred that a monoclinic sodium arsenate isomorphous with rhombic sodium phosphate remains to be discovered.

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§ 11. The Rectification of Atomic Weights by Isomorphism

When one body is isomorphous with another whose molecule contains a known number of atoms, then the number of atoms per molecule of the other body is also known because isomorphism is a mechanical consequence of the identity of atomic structure.—J. J. BERZELIUS (1833).

While perhaps not accepting J. J. Berzelius' dictum without modifying the meaning of "number of atoms" to allow for cases of isomorphism where a radicle like NH_4 containing five atoms can take the place of one atom of the alkali metals in some isomorphous salts, yet J. J. Berzelius' statement of the law of isomorphism can be used as a control in deducing the chemical composition of a salt; and also in atomic weight determinations for deciding between two numbers which are multiples of a common factor. The method is restricted to crystalline compounds; and it is only applicable in conjunction with other methods of atomic weight determinations, since at least one member of the isomorphous series must be known.

E. Mitscherlich deduced the number 79 for the atomic weight of selenium by this method, and he also gave selenious and selenic acids formulæ corresponding with sulphurous and sulphuric acids respectively, on account of the isomorphism of the sulphates and the selenates. The analyses of potassium sulphate and of potassium selenate gave:

	Potassium.	Oxygen.	Sulphur.	Selenium.	Total.
Potassium sulphate . .	44·83	36·78	18·39	—	—100·00
Potassium selenate . .	44·83	36·78	—	45·40	—127·01

Assuming that the molecule of potassium sulphate contains one atom of sulphur; that the molecule of potassium selenate contains the same number of atoms; and that the atomic weight of sulphur is 32, we have:

$$\text{Atomic weight S} : \text{Atomic weight Se} = 18·39 : 45·40,$$

Hence, 32 : atomic weight Se=18·39 : 35·34; consequently, the atomic weight of selenium is 79·00. About 1836 the atomic weight of copper was supposed to be 63·4, and of silver, 216·6. The analysis of the native sulphides of these elements were accordingly represented by the formulæ Cu_2S and AgS. But J. B. A. Dumas (1837) pointed out that the two minerals are isomorphous, and various mixed sulphides of the two elements are known by the general term, Fahlerz. Hence the constitution of the two sulphides is probably the same; assuming the formula of the one to be Cu_2S, that of the other will probably be Ag_2S, and the atomic weight of silver 108·3, not 216·6. This result agrees with evidence deduced from other independent sources. More exact determinations of the atomic weight of silver make this element 107·9; but this does not affect the principle of the argument.

EXAMPLE.—Analyses of alumina show that Al : O=18·1 : 16; the equivalent of aluminium in 9·03; hence the formula of alumina might be:

	AlO	Al_2O_3	AlO_2	AlO_3 . . .
Ratio . . . O : Al . . .	16 : 18·1	48 : 27·1	32 : 36·2	48 : 54·2, . . .

that is, the atomic weight of aluminium might be 18·1, 27·1, 36·2, 54·2 . . . There is nothing in the composition of the oxide to show which of these numbers should be selected. It is known, however, that ferric oxide—Fe_2O_3—forms a series of iron alums isomorphous with the aluminium alums; hence, it is inferred that the constitution of aluminium oxide is Al_2O_3—like that of ferric oxide—and that the atomic weight of aluminium is 27·1.

§ 12. The Formulæ of Minerals, and of Isomorphous Mixed Salts

Whether and when formulæ can be employed for minerals must be learned from faithful analyses.—T. BERGMANN (1779).

We can scarcely doubt that there is a fixed proportion of elements in each mineral substance, which constitutes its true nature, so that what exceeds a given limit should be to that degree regarded as accidental and foreign.—R. J. HAÜY (1801).

A great many minerals can be synthesized in the laboratory. The chemist can then use fairly pure materials and obtain fairly pure products. On the contrary, nature, in her great laboratory, has rarely dealt with pure materials, and accordingly, her products—the minerals—are usually contaminated with much impurity. The determination of the formulæ of minerals is exceptionally difficult mainly because (1) the molecular weights can seldom be determined, and the formulæ are therefore nearly always empirical; (2) the material available for analysis is more or less impure; (3) members of certain isomorphous groups of elements—iron, aluminium, chromium, etc.; calcium, magnesium, iron, manganese, etc.; sodium, potassium, lithium, etc.—can replace one another in every conceivable proportion. Usually the crystalline form as well as the analysis, is necessary for establishing the individuality of any mineral. Thus, H. A. Miers (1902) has said: It is necessary to employ at least two properties, namely, the chemical composition and the crystalline form; these two when completely known are necessary and sufficient for the definition and determination of any mineral. Colour, structure, state of aggregation, and minor details of chemical composition are used to distinguish subordinate varieties of the main types.

The ultimate composition of any native calcium carbonates is exceedingly complex. The same remark is more or less true for most native minerals; at least chemical formulæ which rigorously followed the analyses would be very complex. **The formulæ for minerals are commonly represented as if pure minerals occurred in nature.** Ideally pure minerals are seldom found native, and accordingly the standard formulæ represent idealized or imaginary minerals to which real minerals approximate more or less closely. The secondary constituents present in but small quantities are usually ignored and the main constituents are alone included in the formulæ. For example, the analyses of a sample of *limestone* from Buxton furnished:

CaO	MgO	K_2O	Na_2O	CO_2	Fe_2O_3 and Al_2O_3	SiO_2
54·75	0·31	0·25	0·24	43·78	0·26	0·88

Neglecting constituents less than one per cent., the remaining CaO and CO_2 are in the proportions needed for $CaO.CO_2$, or $CaCO_3$. The sample here selected was fairly pure and clean; it contained 98·5 per cent. of calcium carbonate. In the case of less pure minerals there is sometimes a doubt as to what is the best representative formula, and the identification of the mineral is then based on its external or physical properties rather than on its ultimate composition, for it has to be assumed that the deviations are due to admixed impurities in order to avoid conflict with the constant composition law. The difficulty is so real that many mineralogists define a mineral species as a natural inorganic substance whose chemical and physical properties are constant only within certain limits.

EXAMPLES.—(1) Clean crystals of *cerussite* from Tsumeb (S.W. Africa) furnished H. Dubigk (1913) on analysis: PbO, 83·27; CO_2, 16·64; insoluble matter, 0·24 per cent. Show that the best representative formula is $PbCO_3$.

(2) J. T. Bell (1892) analysed a sample of *cuproplumbite*, and found: copper, 61·32 per cent.; lead, 18·97; sulphur, 17·77; and silica (SiO_2), 1·58 per cent. Show that this analysis agrees with the formula $5Cu_2S.PbS$, assuming that the copper occurs in the mineral in the cuprous condition.

(3) A sample of *hodgkinsonite* from New Jersey (U.S.A.) furnished C. Palache and W. T. Schaller (1913) with: SiO_2, 19·86; MnO, 20·68; ZnO, 52·93; CaO, 0·93; MgO, 0·04; H_2O, 5·77 per cent. Show that $MnO.2ZnO.SiO_2.H_2O$ best represents the analytical data.

(4) A *marl* from South Lincolnshire furnished on analysis: CaO, 42·6; MgO, 7·9; CO_2, 41·6; K_2O, 0·3; Al_2O_3, 0·8; Fe_2O_3, 0·5; SiO_2, 5·1; H_2O, 0·8 per cent. Here the water, potash, alumina, ferric oxide appear to be of secondary importance. Divide the weights of each of the remaining constituents by the respective molecular weights, and reduce to the nearest whole number. There remains: $9CaO.2MgO.11CO_2,SiO$, or $9CaCO_3.2MgCO_3.SiO_2$. The substance is thus considered to be a mixture of calcium and magnesium carbonates with silica, and other impurities.

Minerals with isomorphous groups of elements.—In minerals, the members of an isomorphous series of bases appear to be replaceable one with another to an undetermined extent, while the type of mineral or the crystalline form remains the same. For example, in lime garnet, $3CaO.Al_2O_3.3SiO_2$, a certain proportion of the lime, CaO, may be replaced by ferrous oxide, FeO, and by magnesia, MgO, while a certain proportion of the alumina, Al_2O_3, by ferric oxide, Fe_2O_3. If the composition of the mineral is to be represented by a simple formula of the garnet type, the sum of the lime, magnesia, and ferrous oxide and not their individual proportions must be taken to represent the bases, and the sum of the alumina and ferric oxide must be taken as one sesquioxide. An analyses will then be represented by the formula, $(Ca, Mg, Fe)O.(Al, Fe)_2O_3.3SiO_2$; or more generally $R''O.R_2'''O_3.3SiO_2$.

EXAMPLE.—The analysis of a sample of *siderite* furnished :

CO_2	FeO	MnO	MgO	CaO	
38·5	55·6	2·8	1·8	1·0	Total, 99·7.

The basic elements belong to the same isomorphous group. To find if the mineral is of the type $RO.CO_2$, where R may represent Fe, Mn, Mg, or Ca, it is usual to first calculate the percentage amount of oxygen in the acids and bases. This gives

Acidic oxygen in	Basic oxygen in				
CO_2	FeO	MnO	MgO	CaO	
28·0	12·3	0·6	0·7	0·3	Total, 13·9.

There is thus 13·9 per cent. of oxygen in the basic radicles and 28·0 in the acidic radicles. This is very nearly in the ratio 1·2 required by the general formula $RO.CO_2$. The formula for this type of mineral may therefore be written, $(Fe, Mn, Mg, Ca)CO_3$; or $(Fe, Mn, Mg, Ca)O.CO_2$; or $RO.CO_2$; or RCO_3.

Instead of proceeding in this way, the amounts of the isomorphous bases CaO, MgO, MnO, which can be replaced by the equivalent amounts of the isomorphous FeO, can be calculated. Thus, what amount x of FeO is equivalent to 2·8 of MnO? The molecular weight of FeO is 72, and of MnO 71, consequently the proportion $71 : 72 = 2·8 : x$ gives nearly $x = 2·8$. By treating the MgO and CaO in a similar way, 3·2 and 1·3 are obtained respectively. The basic radicles are thus equivalent to $55·6 + 2·8 + 3·2 + 1·3 = 62$ of FeO. The composition of the idealized siderite is thus FeO, 63 per cent., CO_2, 38·5 per cent. Converting these numbers into molecular ratios in the usual manner, the formula of the idealized siderite becomes $FeCO_3$.

Consequently, while mixed crystals or solid solutions are not accepted as chemical units, individuals, or compounds, in mineralogy, those mixed crystals which give rise to *known minerals* are regarded as mineralogical individuals ; and mineralogy merges into chemistry when all the possible products of isomorphous crystallization are taken into account whether they occur in nature or are known solely as laboratory products. The so-called earthy and non-crystalline minerals are regarded as bearing the same relation to possible crystalline minerals as an amorphous precipitate of, say, barium sulphate bears to the mineral barytes.

§ 13. Index of Refraction and Dispersion

The physical character of any chemical compound, and its composition are dependent each on the other, and present two aspects of the same problem, which can never be solved but by a consideration of both.—T. S. HUNT (1891).

When a ray of light travels from one medium to another of different density, it is refracted, bent, or deflected towards or away from the vertical according as the density of the second medium is greater or less than the first. Between 1620 and 1625, W. Snell discovered the law—*the law of sines*—which determines the angle of deflection. If a ray of light, IO, Fig. 95, enters the denser medium at O, not normal to the surface, it travels through the new medium along the path OR, such that if NON' is perpendicular or normal to the surface, and i the angle which the incident ray makes with the normal, and r the angle which the deflected or refracted ray also makes with the normal, the ratio of the velocities of the light in the two media is proportional to the ratio of the sines of the angles of incidence i and refraction r, and *the ratio of the sine of the angle of incidence to the sine of the angle of reflection has always the same numerical value* ; that is,

$$\frac{\text{Velocity in rarer medium, } V_1}{\text{Velocity in denser medium, } V_2} = \frac{\sin i}{\sin r} = \text{Constant} \quad . \quad . \quad (1)$$

The constant is usually symbolized by μ or n. This ratio, sin i/sin r, is called the **index of refraction.** The index of refraction can also be regarded as a number which expresses the ratio of the velocity of light in vacuo to its velocity in the medium, and the index of refraction less unity, $\mu-1$, expresses the fractional shortening of the velocity which occurs when light passes through a transparent substance. For instance, the refractive index of air is 1·000292 at 0° and 760 mm. This means that while passing through air of standard temperature and pressure, light is retarded nearly three-ten-thousandths of its velocity in vacuo. The magnitude $(\mu-1)\times10^6$ is sometimes called the *refractivity* of the substance.

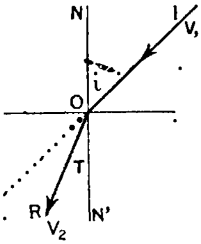

Fig. 95.

The determination of the index of refraction involves fundamentally the measurement of these two angles, and the intruments used for this purpose are called refractometers, etc. A ray of white light is *spread out* or *dispersed* into a number of coloured rays when it passes from one medium to another ; and, in consequence, a definite ray of light, corresponding with a definite part of the spectrum, is used for the measurement of indices of refraction, and two such points are used for the measurement of the dispersion. The index of refraction varies with the wave-length of the particular ray so that the index of refraction with rays from different parts of the spectrum is different. This is illustrated diagrammatically in Fig. 96, which shows how the rays at the violet V-end of the spectrum are refracted more than those at the red R-end. The earlier observations of the indices of refraction were not very precise, for they were referred to a part of the spectrum having a particular colour. Each colour occupies a certain range in the spectrum whose boundaries are not well defined, since two independent observations with the same coloured ray may really refer to different parts of the spectrum. The more conspicuous lines A, D, F, and H of the solar spectrum, or the α-, β-, and γ-lines of the hydrogen spectrum are in use, and they are recorded respectively as μ_A, μ_D, μ_F, μ_H, μ_α, μ_β, and μ_γ. The wave-lengths of the chief Fraunhofer lines in Angström units, are

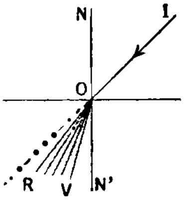

Fig. 96.

A	B	C	D	E	F	G	h	H
7677	6867	6563	5893	5270	4861	4841	4103	3969
K	—	H_α	Na	—	H_β	$H\gamma$	H_δ	—
Red			Yellow	Green	Blue			

The index of refraction for sodium light is a characteristic constant, *e.g.*

Cryolite.	Potash alum.	Halite.	Barytes.	Xenotime.	Strengite.	Diamond.
1·34	1·46	1·54	1·64	1·72	1·81	2·42

The index of refraction of crystalline substances may vary with the direction in which the ray of light is propagated ; it may also vary with temperature. J. L. C. Schroeder van der Kolk, in his *Tabellen zur mikroskopischen Bestimmung der Mineralien nach ihrem Brechungsindex* (Wiesbaden, 1906), has arranged a long list of minerals in the order of the refractive indices of their crystals with the idea of facilitating the rapid identification of small fragments of the mineral from measurements of their refractive index. In some cases, the method needs supplementing by other tests because a very limited number of minerals have indices of refraction so nearly alike, and within the limits of experimental error, that they cannot be distinguished with certainty.

The relation between the index of refraction and density.—As a rule, substances with the greatest density have the greatest index of refraction, but there are a few exceptions—*e.g.* methyl iodide has a density 2·258 and an index of refraction 1·524; while quinoline has a density 1·095, and an index of refraction 1·609. Isaac Newton[1] argued from the corpuscular theory of light:

> If light be swifter in bodies than in vacuo in the proportion of the sines which measure the refraction of the bodies, the forces of the bodies to refract light are very nearly proportional to the densities of the same bodies excepting that unctuous and sulphurous bodies refract more than others of the same density.

Newton then demonstrated that in spite of differences in density, D, the ratio $(\mu^2-1)/D$ is approximately constant; P. S. de Laplace (1805) put Newton's proof on a sounder theoretical basis.

> If the molecular force, like gravitation, is proportional to the mass, the force exerted by a body on a corpuscle of light near its surface will be proportional to the density of the substance when, unlike gravitation, the molecular force is sensible at insensible distances, and insensible at sensible distances. P. S. de Laplace then showed how the change in the velocity of the light corpuscles occurs only at the superficial transitional layer between the æther and the particles of matter; and he also showed how this change can be expressed as a definite integral which reduces to μ^2-1, and which is proportional to the density D, such that $(\mu^2-1)/D$ is a constant.

Serious experimental work on the relation between the index of refraction and the density of a substance was undertaken by J. P. Biot and F. J. D. Arago in 1806 and by P. L. Dulong in 1826, in order to test Newton's formula $(\mu^2-1)/D=$constant. As a result the formula was found to be an accurate description of the relation between the index of refraction and density of gases. The agreement between theory and experiment did not prove the truth of the corpuscular theory of light, for that hypothesis was soon afterwards abandoned in favour of the undulatory theory; but of course the coincidence still remained as an empirical fact.

In 1858, J. H. Gladstone and T. P. Dale[2] tried how Newton's formula held for substances other than gases, and found the empirical rule

$$\frac{\mu-1}{D}=\text{Constant}$$

to be much more nearly in accord with their observations than the older formula. This expression had been found by D. Beer, in 1853, to hold good for gases. Meanwhile, in 1880, L. Lorenz of Copenhagen and H. A. Lorentz of Leyden independently deduced the relation:

$$\frac{\mu^2-1}{\mu^2+2}\cdot\frac{1}{D}=\text{Constant; or }\frac{\mu+1}{\mu^2+2}\cdot\frac{\mu-1}{D}=\text{Constant}$$

H. A. Lorentz developed the expression from the electromagnetic theory of light, and also from the electron theory. L. Lorenz worked from the undulatory theory of light.

> L. Lorenz assumed that the body is isotropic and consists of spherical molecules between which light is propagated with the same velocity as in free space. He further assumed that in the mixed discontinuous medium—æther and molecules—the light may be regarded as if it were propagated with a definite mean wave-length and mean velocity, and with a periodically varying amplitude of vibration. As a matter of fact the wave-length of the light in a molecule may be much smaller than it is in the æther. Hence L. Lorenz really replaced the actual discontinuous medium by a hypothetical mean medium, a method which is not justifiable *a priori*.

All three expressions hold fairly well for gases at ordinary pressures because when μ is nearly unity, as is the case with gases, $(\mu+1)/(\mu^2+2)$ is nearly $\frac{2}{3}$; and for gases,

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therefore, H. A. Lorentz and L. Lorenz's expression is nearly equivalent to J. H. Gladstone and T. P. Dale's formula multiplied by $\frac{2}{3}$; and to twice I. Newton's formula. As a result of numerous comparative experiments on liquids and solids, it has been found that neither J. H. Gladstone and T. P. Dale's nor H. A. Lorentz and L. Lorenz's formula is entirely in accord with all the facts. Each formula has its own special advantages, and each breaks down under quite different experimental conditions. Many other formulæ have been proposed—*e.g.* by E. Ketteler (1888) [3] and W. F. Edwards (1894)—but after much theoretical and mathematical work, no formula yet proposed has been proved entirely in accord with observations. This probably means that the simplifying assumptions, used in deducing the formulæ, want revising.

Nomenclature.—The ratio $(\mu-1)/D$ or $(\mu^2-1)/(\mu^2+2)D$ for an element or compound is called the specific refractory power or the **specific refraction** of the substance. If the index of a substance is 1·501, and the specific gravity 0·880, the specific refraction by H. A. Lorentz and L. Lorenz's formula is $(1{\cdot}501^2-1)/(1{\cdot}501^2+2)0{\cdot}880=0{\cdot}337$; and by Gladstone and Dale's formula $(1{\cdot}501-1)\div0{\cdot}880=0{\cdot}57$. The product of the specific refraction and the molecular weight of a compound is called the **molecular refraction**, and the product of the atomic weight and the specific refraction of an element is called the **atomic refraction** of the element. In measuring the index of refraction, light of a definite wave-length is employed, and the difference between the indices of refraction of a substance for light of two definite wave-lengths—say the red (?) ray and the blue (?) ray of the hydrogen flame; or the *C* and *D* lines of the solar spectrum—is called the **specific dispersion** of the substance, and the difference between the molecular refractions of a substance for light of two definite wave-lengths is called the **molecular dispersion**; and similarly, for the **atomic dispersion**, and for the specific dispersion. The dispersive power was represented by J. H. Gladstone as the ratio of the dispersion and the density—thus, the **specific dispersive power** when multiplied by the molecular weight, furnished the **molecular dispersive power**. Thus, the specific dispersion for the *H* and *A*-rays of the spectrum is $\mu_H-\mu_A$, and the specific dispersive power is $(\mu_H-\mu_A)/D$. The **dispersive power** of a substance has also been defined as the ratio of the specific dispersion of the index of refraction of the mean ray less unity. Thus, this dispersive power is $(\mu_H-\mu_A)/(\mu_F-1)$. The term $\mu-1$ in J. H. Gladstone and T. P. Dale's formula is sometimes called the **refractive energy** of the substance, and $(\mu-1)/D$, the **specific refractive energy.** The term $\mu-1$ is now usually called the **refractivity** of the substance.

The refractivities or refractive indices of gases can be corrected for temperature and pressure either by reference to the equation $pv=RT$, or to one of the many corrected forms [4]—J. D. van der Waals', D. Berthelot's, etc. H. A. Lorentz and L. Lorenz's formula is generally preferred because it has a sounder theoretical foundation; and it is more generally adaptable to the experimental material than J. H. Gladstone and T. P. Dale's—*e.g.* it is valid for a wider interval of temperature, and it is less influenced by the state of aggregation of the substance under examination.

G. Quincke (1883) tested the two rival formulæ by varying the density by hydrostatic pressure, and calculated the values for the density and accordingly also the compressibility, from the observed pressure and the index of refraction. He found H. A. Lorentz and L. Lorenz's formula gave values too small; I. Newton's too large; and with J. H. Gladstone and T. P. Dale's formula the values were sometimes too large and sometimes too small. The mean percentage errors were respectively −14, +17, and ±16. H. Landolt and R. Weegmann [5] found the results indicated in Table IV showing that J. H. Gladstone and T. P. Dale's formula fails signally in bridging the gap in density between liquid and vapour. The general conclusions of G. Quincke's and H. Landolt's comparison of the two rival formulæ are:

(1) When the same specimen of a substance has been examined in the liquid and gaseous state, H. A. Lorentz and L. Lorenz's formula has proved superior in the marked degree.

(2) The effect of increasing the density by hydrostatic pressure fits better with J. H. Gladstone and T. P. Dale's formula than with H. A. Lorentz and L. Lorenz's.

(3) Both formula usually apply well to the change from the liquid to the solid state, but the results are more in favour of J. H. Gladstone and T. P. Dale's formula.

(4) J. H. Gladstone and T. P. Dale's formula gives more accurate results when applied to calculate the index of refraction of a mixture from those of its constituents, for it varied on the average 0·05 per cent.—the deviation in the worst case was 0·16 per cent.; with H. A. Lorentz and L. Lorenz's formula the average deviation was 0·16 per cent., in the worst case 0·6 per cent. Hence, J. H. Gladstone and T. P. Dale's formula gives the better results with chemical optical analysis when it is used, say, to determine the amount of a particular substance dissolved in a solvent from the observed index of refraction and density.

TABLE IV.—COMPARISON OF LORENTZ AND LORENZ'S AND GLADSTONE AND DALE'S FORMULÆ FOR SPECIFIC REFRACTION.

Compound.	$\frac{1}{D}\cdot\frac{\mu^2-1}{\mu^2+2}$			$\frac{\mu-1}{D}$		
	Liquid.		Vapour, 100°	Liquid.		Vapour, 100°
	10°	20°		10°	20°	
Water . . .	0·2062	0·2061	0·2068	0·2068	0·3336	0·3101
Ethyl alcohol .	0·2804	0·2807	0·2825	0·4582	0·4581	0·4237
Ether . . .	0·3026	0·3029	0·3068	0·4935	0·4930	0·4599
Ethyl acetate .	0·2547	0·2549	0·2683	0·4174	0·4172	0·4024
Ethyl iodide . .	0·1557	0·1558	0·1571	0·2663	0·2658	0·2356
Chloroform . .	0·1790	0·1791	0·1796	0·3000	0·2996	0·2694
Carbon disulphide .	0·2805	0·2809	0·2898	0·4977	0·4970	0·4348

(5) The refraction equivalents—*vide infra*—obtained by J. H. Gladstone and T. P. Dale's formula for carbon dioxide, oxygen, hydrogen, nitrogen, and the halogens, hold good for H. A. Lorentz and L. Lorenz's formula; but according to J. W. Brühl, the latter formula is preferable since it gives a smaller percentage error in the calculation of the refraction equivalent of a molecule from those of its atoms.

These facts, said W. Sutherland (1889), ought to furnish logicians with instructive examples in the theory of evidence. H. Dufet (1883)[6] and W. Sutherland (1889) have further shown that a theoretical foundation can be given to the empirical rule of J. H. Gladstone and T. P. Dale.

If V_0 be the velocity of light in vacuo, *i.e.* in free æther; V_1, the velocity in passing through the atoms themselves; and V, the velocity in an atom-strewn medium, then in a unit length of path—since velocity × time = distance traversed—the time occupied in passing through a given medium will be the reciprocal of the respective velocities; and the *loss of time* in the passage of light through the atom-strewn medium, owing to the retardation produced by the atoms, will be proportional to the retardation in passing through an atom, and

$$\frac{1}{V_0}-\frac{1}{V}=kls\left(\frac{1}{V_0}-\frac{1}{V_1}\right)\frac{D}{M}$$

where D/M represents the number of atoms in unit volume; l the mean length of the path through an atom; s the mean sectional area of an atom; and k is the constant of proportion. When multiplied through by V_0, and substituting μ for V_0/V from (1), this relation reduces to $(\mu-1)M/D=kls(N-1)$, where μ denotes the refractive index of the medium, and N that of the substance of the atom itself; M/D, the atomic domain; and the product ls, the average volume of the atom itself. W. Sutherland assumed that the bracketed term on the right is constant, so that the expression reduced to J. H. Gladstone and T. P. Dale's rule, $(\mu-1)/D$=constant. The delay produced by matter is due to the breaking up of the front of the light-wave by the interspersed atoms, and the subsequent loss of time in travelling from atom to atom before the front of the wave recovers its plane form. Assuming that this retardation is proportional to the length of the path, and to a function of the density, say, $a'D+bD^2+\ldots$, then for unit path, $(\mu-1)M/D=kls(N-1)+m(a+bD+\ldots)$; and the specific refraction is $(\mu-1)/D=[kls(N-1)/M+a']+bD$, where the bracketed term is constant, say a.

W. Sutherland's formula for specific refraction resembles J. H. Gladstone and T. P. Dale's specific refraction, but a term bD, proportional to the density, is added to the constant. This furnishes,

$$\frac{\mu-1}{D}=a+bD$$

where a and b are constants to be evaluated from observations of μ and D at two different temperatures. For gases and vapours, the term bD may be neglected on account of the smallness of the term D. W. Sutherland also claims that the revised formula is the best yet advanced, and that it is capable of representing the relation between the index of refraction under all circumstances within the limits of experimental error, where the uncorrected formula of J. H. Gladstone and T. P. Dale fails. Some examples are indicated in Table V.

TABLE V.—W. SUTHERLAND'S FORMULA FOR SPECIFIC REFRACTION.

Compound.	Constant b	Liquid.		Vapour (100°).	
		10° Obs.	20° Obs.	Observed.	Calculated.
Ether . . .	0·044	0·4935	0·4930	0·4599	0·461
Ethyl acetate .	0·017	0·4174	0·4172	0·4024	0·407
Ethyl iodide . .	0·022	0·2663	0·2658	0·2356	0·223
Chloroform . .	0·023	0·3000	0·2996	0·2694	0·265
Carbon disulphide .	0·050	0·4977	0·4970	0·4348	0·435

The agreement between the observed and calculated results in all cases excepting ethyl iodide is good.

E. T. Wherry [7] found that with the refractive indices for the ordinary ω-ray and the extraordinary ϵ-ray of tetragonal crystals are related with the axial ratio so that

$$\frac{\omega^2-1}{\omega^2+2}:\frac{\epsilon^2-1}{\epsilon^2-2}=\frac{c}{a}$$

where the axial ratios are based on the atoms present, and not on the standard axial ratio obtained by taking the most prominent pyramidal form to be (111). There are some disturbing factors with complex compounds, but with the simpler compounds the rule gave good results with a few organic compounds, and minerals of the zircon group. With cassiterite, the two ratios are 0·945 and 0·951; with rutile, 0·926 and 0·911; this is taken to mean that in these minerals the space lattice must have the same number of layers of atoms in the horizontal as in the vertical direction. In zircon and xenotime, the refraction ratios are equal to 3 : 2 times the standard ratio $c:a$, meaning that in the unit cell of these minerals there are three horizontal layers of atoms for every two vertical layers.

The effect of pressure on the refractive index.—The effect of variations of pressure on the index of refraction of gases has been investigated between 0·05 and 200 atm. W. Kaiser [8] found that for pressures between 20 and 760 mm., with sulphur and carbon dioxides, the variation of the index of refraction with pressure, $d\mu/dp$, increases faster than the variation of the density of the gas with changes of pressure; with pressures higher than atmospheric, E. Mascart [9] found the relation $\mu=1+ap+bp^2$ described his results for air, nitrogen, oxygen, carbon monoxide, carbon dioxide, nitric oxide, nitrous oxide, and cyanogen very well.

The effect of pressure on the refractive index of a few liquids (Na light) is as follows:

	Water (20°)	Alcohol (17·5°)	Benzene (20°)	Ether (8°)	Carbon disulphide (20°)
$d\mu/dp$.	0·00001514	0·00004174	0·00005060	0·00006161	0·00006583

The effect of temperature on the refractive index.—The exact relation between the temperature and the refractive index has not been established. J. P. Biot[10] represented his measurements of the refractive index of gases between 0° and 25°, by $\mu=\mu_0-a\theta$, where μ_0 represents the refractive index at 0°, and a is a constant independent of temperature. V. von Lang added another term to Biot's formula for his results between 0° and 100°; thus, for air, he used $\mu=\mu_0-0{\cdot}0_6905\theta+0{\cdot}0_72\theta^2$. E. Mascart used the more complicated expression: $(\mu-1)(1+a\theta)=$constant. If the relation $(\mu-1)D=$constant be valid, then, for ideal gases, at pressure p and p_0 with the corresponding temperatures $\theta°$ and $\theta_0°$,

$$\frac{\mu-1}{p}(1+a\theta)=\frac{\mu_0-1}{p_0}(1+a\theta_0)$$

and hence $\mu-1$ varies inversely as $(1+a\theta)$. He assumed that the temperature coefficient of refraction a, and the ordinary coefficient of thermal expansion a' to be the same. The observed differences showed that a was about 12 or 15 per cent. greater than a'; V. von Lang found the opposite, for a' was greater than a; and J. R. Benoit obtained $a=a'$. Hence G. W. Walker made some careful measurements of the two constants, and found a to be less than a' for air and hydrogen by respectively $0{\cdot}0_47$ and $0{\cdot}0_316$; and a greater than a' for carbon and sulphur dioxides by respectively $0{\cdot}0_49$ and $0{\cdot}0_326$. The influence of temperature on the refractive index of a number of minerals and liquids has been represented by formula of the type $\mu=a+b\theta+c\theta^2+\ldots$ Since changes of temperature are always accompanied by changes of density, it is generally assumed that the velocity of the propagation of light in a body is not affected by variations of temperature except in so far as the density of the substance is simultaneously altered; and the influence of density, D, is given by J. H. Gladstone and T. P. Dale's or L. Lorenz and H. A. Lorentz's formula. H. D. Ayres[11] found both Lorentz and Lorenz's and Gladstone and Dale's formulæ to apply equally well at −189·2° between 10·1 and 149·5 cm. pressure of mercury. He found that the refractivity $\mu-1$ of hydrogen, oxygen, nitrogen, and carbon dioxide varied lineally with the density at temperatures from 0° to −189·0°. K. Scheel compared the calculated values of the density D at −190° with the values D' observed by M. W. Travers and G. Senter, and by A. Bestelmayer and S. Valentiner. Assuming that the density of the gas is unity at 0° and 760 mm., the density D at $\theta°$ were calculated, by K. Scheel, from $(\mu-1)/D=$constant, and the observed densities of hydrogen and nitrogen between 0° and −190° were found to be about 0·4 per cent. greater than the calculated values.

The refractive index at the critical temperature.—P. A. Guye[12] has shown that J. D. van der Waals' constant b is related with the molecular refraction μ, by the expression:

$$b=k\frac{\mu^2-1}{\mu^2+2}\cdot\frac{M}{D}$$

where M denotes the molecular weight, D the density, and k is a constant which, according to I. Traube, is equal to 4·03. With the 35 inorganic compounds examined by P. A. Guye,

$$1{\cdot}8\frac{T_c}{p_c}=\frac{\mu^2-1}{\mu^2+2}\cdot\frac{M}{D}$$

where T_c denotes the absolute critical temperature and p_c the critical pressure, if v_c denotes the critical volume. J. D. van der Waals showed that $\mu_c=3b$, and that $p_cv_c=21{\cdot}76T_c$. This means that **the refraction constants of a substance are**

independent of the pressure, temperature, and state of aggregation, and for all substances at the critical temperature $v_c=1\cdot126$. V. Smith has compared this deduction for the gases and liquids indicated in Table VI.

TABLE VI.—THE CRITICAL VALUES OF μ FOR SOME GASES AND LIQUIDS.

	θ	$\mu_{D}\theta^{\circ}$	T	Critical value of μ	Deviation, per cent.
Gases :					
Oxygen . .	0°	1·000271	−118·8	1·126	0
Ethylene . .	0°	1·000723	13·0	1·124	−0·2
Carbon dioxide .	0°	1·000449	31·35	1·109	−1·5
Sulphur dioxide .	0°	1·000686	156·0	1·128	+0·2
Nitric oxide . .	0°	1·000576	35·4	1·110	−1·4
Liquids :					
Ammonia . .	16·5°	1·325	131·0	1·120	−0·5
Hydrogen chloride .	10·5°	1·254	52·3	1·109	+0·4
Hydrogen bromide .	10·0°	1·325	91·3	1·126	−1·5
Chlorine . .	14·0°	1·367	148·0	1·131	0
Carbon dioxide .	15·5°	1·192	31·35	1·101	−2·2

The effect of dispersion on the refractive index.—The effect of dispersion on the index of refraction μ for rays of wave-length λ can be calculated from A. L. Cauchy's formula,[13] $\mu=a+b\,\lambda^{-2}+c\,\lambda^{-4}+\ldots$, where a, b, c, . . . are constants to be computed from measurements of μ and λ. The constant a is sometimes called A. L. Cauchy's coefficient of refraction ; b, c, . . . are coefficients of dispersion. Several other formula have been proposed—*e.g.* by F. Redtenbacher, and by C. Briot—and they all give quite good results for the visible part of the spectrum, but fail as the invisible red is approached. S. P. Langley found C. Briot's formula gave the best results with the invisible red rays, but even these were not satisfactory. A. L. Cauchy's formula is usually preferred because of its simplicity. It agrees very well with observations for substances of low dispersive power, but not so well with substances of high dispersive power. The relation between the refractivity and the wave-length is then represented by an expression of Cauchy's type :

$$\mu-1=a\left(1+\frac{b}{\lambda^2}\right)$$

where a and b are constants. For mercury, $a=0\cdot001755$, and $b=22\cdot65\times10^{-11}$. It is found that in four cases—helium, argon, krypton, and xenon—where the measurements are available, if the refractivity $\mu-1$ for infinite wave-length λ be plotted against the value of b in this formula, the result is a straight line.[14]

It has been shown, by F. L. Perrot, A. E. H. Tutton, etc.,[15] that the index of refraction and the dispersion of a series of isomorphous crystals usually increase when one element is replaced by another with a greater atomic weight. For example, potassium, rubidium, and cæsium sulphates have respectively the values $D=1\cdot4947$, 1·5113, and 1·5644 ; and for anhydrite, $CaSO_4$, $D=1\cdot57518$; celestine, $SrSO_4$, 1·62367 ; barytes, $BaSO_4$, 1·63717 ; and anglesite, $PbSO_4$, 1·88226.

The relation between the refractive index and chemical composition.—In 1826, P. L. Dulong[16] concluded from his experiments that the specific refraction of a *mixture* of gases is the mean of the specific refractions of the constituents calculated for the partial pressures of the gases in the mixture ; while the specific refraction of a compound is not a mean of those of the component gases, for it is sometimes greater and sometimes less. J. H. Gladstone and T. P. Dale (1863) investigated the effect of chemical constitution on the refractive energies. One of the most important facts developed by this study from a chemical point of view is that the refractive equivalent of an atom is not a constant, but depends upon the way the atom is linked with other atoms. J. H. Gladstone and T. P. Dale said:

> We sought to determine the amount of change in the optical properties which results from a replacement of one element by another, the type remaining the same, . . . in order to attain a knowledge of the action of the individual elements on the rays of light transmitted by them. . . . The general conclusion is that *every liquid has its own specific refractive energy composed of the specific refractive energies of its component elements*, modified by the manner of combination, and which is unaffected by change of temperature, and accompanies it when mixed with other liquids.

The subject was followed up by H. Landolt (1864), J. W. Brühl (1886), etc., and as a result, it was found that the molecular refraction or dispersion of compounds is:

(1) An additive property in that it depends on the number and kind of atoms in the molecule—*e.g.* the atomic refractions and dispersions of hydrogen and chlorine are virtually the same whether they are free, or combined.

(2) It is also a constitutive property in that it depends on the mode of combination of the different elements—*e.g.* the atomic refraction and dispersion of carbon is very different according to the way it is combined—single, double, or triple-bonded carbon atoms have different values. While the atomic refraction of single-bonded carbon and carbonyl, CO, carbons are nearly the same, the atomic dispersion of the one is nearly double that of the other. Similar remarks apply to oxygen, and more particularly to nitrogen.

The refractive indices of the elements gaseous at ordinary temperatures have been measured directly; the opaque metals do not lend themselves to this treatment although the method has been used in case of a few metals which can be beaten into thin enough sheets to permit the passage of light. A. Kundt[17] determined values for half-a-dozen metals in this way; the values for gold, silver, and platinum so determined are respectively 0·58, 0·27, and 1·64. P. Drude also developed a method for measuring the refractive indices of the metals which are based on the angle of reflexion, and accordingly obtained values for the refractive indices of over a dozen metals. The results of A. Kundt and of P. Drude did not agree very well. The molecular refractions of a number of compounds has been measured directly, and values for the constituent elements have been computed on the assumption that the atomic refraction is an additive quality. The indices for a number of inorganic salts have also been estimated from the indices of refraction obtained for their aqueous solutions on the assumption that J. H. Gladstone's additive formula

$$\text{Molecular refraction} = (18n+M)R_1-18nR_2$$

holds good. Here M denotes the molecular weight of the compound; R_1 and R_2 the refraction constants of water and of the solution respectively; and n denotes the number of gram-molecules of water per gram-molecule of salt. After comparing the observational data of a large number of compounds, J. W. Brühl drew up tables of the atomic refractions and dispersions of a number of elements based on constants calculated from observations on the refractive index reduced by Lorentz and Lorenz's formula. Different constants are obtained when J. H. Gladstone and T. P. Dale's formula[18] is used. Table VII contains values of the atomic refraction, $w(\mu^2-1)/(\mu^2+2)D$, compiled by W. A. Roth and F. Eisenhohr in their *Refractometrisches Hilfsbuch* (Leipzig, 1911).

The additive or mixture law.—The molecular refractions of a number of organic compounds were found by H. Landolt to be the sum of the atomic refractions of their constituent atoms when due allowance is made for the modifications in the atomic refractions of elements united in special ways. If a substance of molecular weight M contains n_1 atoms each of atomic refraction R_1; n_2 atoms of atomic refraction R_2; . . . then the molecular refraction is

$$\text{Molecular refraction}=n_1R_1+n_2R_2+ \ . \ . \ . =\Sigma nR$$

The results of this method of investigation have established the proposition that the atoms of the elements have the power of retarding light; and that in some cases this power is not materially changed when the atoms pass from one compound to another; but closer investigation shows that the specific refractive energies of the atoms are greatly modified by the nature of the combination. The relation between the different atoms is an important factor. Thus, J. W. Brühl showed that the refractive effect of oxygen is greater when the oxygen is united to carbon than when it is united to two other elements; and E. Conrady [19] further showed that still a different value for oxygen is obtained with oxygen in the ethers. J. H. Gladstone showed that hydrogen in the weak acids has but 40 per cent. of its value in the strongly ionized acids; M. le Blanc found two distinct values for chlorine; E. Wiedemann found two for sulphur; and seventeen values have been obtained for nitrogen. In some cases, the additive rule is applicable more particularly when the compound contains but a few elements combined in the same way; but in general, the additive mixture law breaks down completely for chemical compounds. It is, however, valid for mere mixtures which exert no chemical action on one another. The observed and calculated values for air, for example, coincide—within the limits of experimental error. The principle has been applied to the technical analysis of gases, and of many solutions. The molecular refraction (and likewise also the molecular dispersion) of compounds calculated in this way may then furnish concordant results; and the results have been used as circumstantial evidence in favour of particular hypotheses about the constitution [20] of the compound under investigation.

TABLE VII.—ATOMIC REFRACTIONS AND DISPERSIONS—$w(\mu^2-1)/(\mu^2+2)$.

	Atomic refraction.				Atomic dispersions.	
	H_α	D	B_β	H_γ	$H_\beta - H_\alpha$	$H_\gamma - H_\alpha$
Carbon	2·413	2·418	2·438	2·466	0·025	0·056
Hydrogen	1·092	1·100	1·115	1·122	0·023	0·029
Carbonyl oxygen	2·189	2·211	2·247	2·257	0·057	0·078
Ether oxygen	1·639	1·643	1·649	1·662	0·012	0·019
Hydroxyl oxygen	1·522	1·525	1·531	1·541	0·006	0·015
Chlorine	5·933	5·967	6·043	6·101	0·107	0·168
Bromine	8·803	8·865	8·999	9·152	0·211	0·340
Iodine	13·757	13·900	14·224	14·521	0·482	0·775
Ethylene bond	1·686	1·733	1·824	1·893	0·138	0·200
Acetylene bond	2·328	2·398	2·506	2·538	0·139	0·171
Nitrogen in primary aliphatic amines	2·309	2·322	2·368	2·397	0·059	0·086
Nitrogen in secondary aliphatic amines	2·475	2·499	2·561	2·603	0·086	0·119
Nitrogen in tertiary aliphatic amines	2·807	2·840	2·940	3·000	0·133	0·186
Nitrite nitrogen	3·054	3·070	3·108	3·129	0·055	0·065
Nitrogen in amides (C−N=C)	3·740	3·776	3·847	3·962	0·139	0·220

EXAMPLES.—(1) Assuming that in benzene, C_6H_6, there are two ethylene linkages, compare the calculated and observed molecular refractions, given the index of refraction is 1·50144 and the density 0·880, and the molecular weight 78. From Table VII $(6\times2{\cdot}365)+(6\times1{\cdot}103)+(3\times1{\cdot}836)=26{\cdot}3$; etc.

(2) Compare the atomic refraction and dispersion of hydroxylamine on the assumption that the formula is H_2N-OH with the observed values 7·23 and 0·19 respectively.

	Atom refraction.	Dispersion.
N in ammonia	2·497	0·072
O in OH group	1·610	0·019
3 H atoms	3·150	0·120
H_2N-OH	7·257	0·211
Found	7·23	0·19

The approximate agreement of the observed and calculated values of the atomic refraction and dispersion is taken to favour the hypothesis that the constitution of hydroxylamine is $H_2=N-OH$. Hydrogen peroxide furnishes another example.

The errors involved in the computation of the refractive equivalents of some of the elements are sometimes as great as 12 per cent.; and when it is remembered that in comparing the observed and calculated refractivities of a compound, the differences seldom exceed 10 per cent., it will be obvious that the errors in the data are as large as the magnitude under observations. In such cases, the process of investigation is of comparatively little value. Many attempts have also been made to establish a relation between the dispersive power of a substance and chemical composition,[21] but the results are not so good as with refractivities, probably because dispersion is more readily influenced by composition than refractivity.

The refractivity of compounds is an additive property for liquids and solids when the refractive constants are determined from the compounds themselves. In gases, this is not true. Out of sixteen gaseous compounds of which the refractivities of the components have been measured in a free state, C. Cuthbertson [22] did not find one to agree with the additive rule—with the nitrogen compounds the deviations varied between 5 and 14 per cent.; with sulphur dioxide the deviation is 18 per cent.; with selenium hexafluoride, 30 per cent.; and with tellurium hexafluoride, 45 per cent. C. Cuthbertson says the failure of the additive rule is not far to seek:

> The true refractive constant of an element is, evidently, the retardation caused by the free gaseous atom. The forces which compel atoms of different elements to combine, and to assume the liquid or solid states, whatever they may be, are evidently very powerful, and it is unreasonable to expect that causes which can modify other attributes of matter in ways and to an extent which we are unable to predict should have no effect, or always the same effect, on its power to retard light. It is therefore to the study of the gaseous refractive indices that it is necessary to turn in the hope of obtaining really accurate information with regard to the optical properties of matter.

TABLE VIII.—REFRACTIVE INDICES OF SOME GASEOUS ELEMENTS (C. CUTHBERTSON).

Element.	$\mu-1=a\left(1+\frac{b}{\lambda^2}\right)$		Refractivity, $(\mu-1)\times10^6$		Empirical ratio.
	a	b	$\lambda=\infty$	$\lambda=5893$	
Hydrogen	$0{\cdot}0_31358$	$6{\cdot}67\times10^{-11}$	135·8	138·4	
Helium	$0{\cdot}0_46956$	$2{\cdot}2\times10^{-11}$	69·56	70·0	1
Neon	0·0001374		—	137·4	2
Argon	$0{\cdot}0_35584$	$5{\cdot}6\times10^{-11}$	558·4	567·4	8
Krypton	$0{\cdot}0_38378$	$6{\cdot}97\times10^{-11}$	837·8	854·6	12
Xenon	$0{\cdot}0_31364$	$610{\cdot}14\times10^{-11}$	1364·6	1404	20
Fluorine	0·000195		—	195	2
Chlorine	0·000768		—	768	8
Bromine	0·001125		—	1125	12
Iodine	0·00192 (violet) 0·00205 (red)		—	—	20
Oxygen	$0{\cdot}0_32663$	$5{\cdot}07\times10^{-11}$	266·3	270·2	2
Sulphur	0·001045	$721{\cdot}2\times10^{-11}$	1046	1111	8
Selenium	0·001565		—	1565	12
Tellurium	0·002495		—	2495	20
Nitrogen	$0{\cdot}0_329061$	$7{\cdot}7\times10^{-11}$	290·6	297·1	2
Phosphorus	0·001162	$15{\cdot}3\times10^{-11}$	1162	1212	8
Arsenic	0·001552		—	1552	12
Zinc	0·002050		—	2050	
Cadmium	0·002675		—	2675	
Mercury	0·001755	$22{\cdot}65\times10^{-11}$	1755	1866	

The refractive indices of gases.—J. P. Biot and F. J. D. Arago[23] measured the refractivities of hydrogen, oxygen, and nitrogen; to these P. L. Dulong added chlorine; F. P. le Roux, iodine, sulphur, phosphorus, arsenic, and mercury; E. Mascart, bromine; W. Ramsay and co-workers, the five inert gases—helium, neon, argon, krypton, and xenon; and C. Cuthbertson and co-workers added selenium, tellurium, zinc, cadmium, and fluorine. The earlier less accurate determinations have also been revised by a number of different workers. The results are indicated in Table VIII. The refractivities of the five mono-atomic gases are almost exactly in the ratios 1 : 2 : 8 : 12 : 20—the last three being as 2 : 3 : 5. A similar ratio obtains with the halogens; and with the other families indicated in the table. There is a 4·7 per cent. error with selenium; a 8·7 per cent. error with tellurium; arsenic has a deviation of about 17 per cent. No simple ratio was observed with the zinc family, for mercury with the highest atomic weight has the lowest refractivity. However, it must be added that some chemists doubt if mercury is rightly placed with the zinc family. The anomalous dispersion of iodine in the red will be noticed. The estimated refraction equivalents of the alkali metals by J. H. Gladstone also fall in line—the values for potassium rubidium and cæsium being respectively 7·85, 12·1, and 19·2. Rearranging the data,

TABLE IX.—REFRACTIVITIES OF THE ELEMENTS.

				He	Li	Be . . .
				70	—	—
	N	O	F	Ne	Na	Mg . . .
	149 × 2	135 × 2	96 × 2	70 × 2	—	—
	P	S	Cl	Ar	K	Ca . . .
	149 × 8	138 × 8	96 × 8	70 × 8	—	—
. . . Ge	As	Se	Br	Kr	Rb	Sr . . .
—	129 × 12	130 × 12	93·8 × 12	70 × 12		—
. . . Sn	Sb	Te	I	X	Cs	Ba . .
—	—	125 × 20	96 × 20	70 × 20	—	—

An examination of the horizontal rows in Table IX shows that refractivity must be closely connected with valency; the elements with the higher atomic weights have the lowest refractivities although the relation between the two is not known. J. H. Gladstone thought that the product of the specific refractivity and the square root of the chemical equivalent is approximately constant—1·3 for the univalent elements, and 1·01 for the bi-, ter-, quadri-, and quinquevalent elements. Improved observational data do not support Gladstone's rule. An increase of valency is accompanied by an increase of refractivity. Only part of the refractivity is concerned with valency, or the non-valent elements would not retard light at all.

According to the electronic hypothesis of matter, the electrons bound within the atoms by quasi-elastic forces, are supposed to be stimulated into oscillatory motions by incident waves of light; the mode of motion is influenced by the orientation of the atoms in the molecules. The same electrons probably also play an important rôle in the union of the atoms to form the molecules. It is now assumed that the retardation of light in passing through a material medium is caused by the expenditure of energy in starting and maintaining the motion of the electrons which form part of the atom. These electrons are supposed to have a natural period of vibration of their own, and the loss of energy and velocity is greatest with rays whose wave-length approaches most nearly to the natural period of vibrations of the constituent electrons—the long red waves, for example, are retarded 1 to 2 per cent. less than the shorter violet waves.

Valency and the refractive index.—According to H. A. Lorentz's theory, the refractivity is directly proportional to the number N of electrons in unit volume of the medium, and inversely as the difference in the frequency of the free vibrations

n_0 of the atoms which are instrumental in effecting refraction, and n that of the incident light; $n\lambda = V$, so that

$$\mu - 1 = \frac{C}{{n_0}^2 - n^2}$$

Calculations show that the numerator of this expression is proportional to N, the number of electrons in unit volume such that $C = \frac{1}{8}\pi^{-2}e^2N/m$, where π denotes the well-known constant, m is the mass, and e the electric charge. Then if v denotes the number of valency bonds associated with an element, P. Drude's theory of dispersion[24] leads to the conclusion that the sum of the valencies contained in the molecules of a compound is proportional to the accepted chemical valencies; or that C is proportional to the positive valency v of the atom, or that C/v is a constant which has the same value for all gases. Thus,

TABLE X.—THE RELATION BETWEEN VALENCY AND THE REFRACTIVE INDEX.

	$C \times 10^{-27}$	v	$\frac{C}{v}$
Hydrogen	1·692	1	1·692
Oxygen	3·397	2	1·699
Phosphorus	7·610	4½	1·691
Nitrogen	5·034	3	1·678
Sulphur	4·808	3	1·603

The results are not so good with the last two elements; but the agreement in all cases is fairly close, giving grounds for the assumption that the number of electrons concerned in dispersion is proportional to the received valency of the element. According to this theory, L. Natanson inferred that the product of v with the term Δ should be independent of the nature of the gas, and be the same for all gases referred to the normal state. Here:

$$\Delta = \frac{3(\mu_1 - \mu_2)\lambda_1^2\lambda_2^2}{2(\mu_1 - 1)(\mu_2 - 1)(\lambda_1^2 - \lambda_2^2)}$$

where μ_1 and μ_2 are the refractive indices corresponding with two different rays of wave-length λ_1 and λ_2 respectively. The mean values of the product $v\Delta$ for hydrogen, oxygen, nitrogen, carbon monoxide, sulphur dioxide, hydrogen disulphide, and carbon monoxide are approximately constant, but deviations occur with some of the hydrocarbons. For example:

	H_2	O_2	N_2	CO_2	SO_2	H_2S	CO
v . . .	2	4	6	8	8	6	4
Δ . . .	7·99	3·87	2·73	2·16	2·23	2·80	3·68
$v\Delta$ . . .	15·98	15·48	16·38	17·28	17·84	16·80	14·72

whereas the values of $v\Delta$ for methane ($v=8$), ethane ($v=14$), ethylene ($v=12$), and acetylene ($v=10$) are respectively 27·95, 25·50, 32·72, and 34·45.

The study of the refractive indices of gases is therefore promising to throw light on the intimate structure of atoms and molecules. The sterility of the enormous amount of work which has been done on the refractivities of liquids and solids, says C. Cuthbertson, proves that in these states of aggregation the causes which obscure the simplicity of the results are too powerful, and that it is vain to hope for much addition to our knowledge in this direction. The little work which has been done on the refractivities of gases has furnished a few simple relations, which by their very simplicity seem to be the outward and visible truth which ought to be pursued by the accumulation of more data.

The relation between the index of refraction and the magnetic rotatory power.—J. H. Gladstone and W. H. Perkin[25] have shown that there is some connection between the rotation of a polarized ray under the influence of magnetization, and the retardation of the rays in passing through a material substance as represented by the index of refraction and dispersion. The three properties are additive in an analogous manner, and a change in the active valency of an element is attended by a parallel change in all three properties. With the halogen acids all three properties exhibit parallel deviations from the normal when measured in solutions of iso-amyl ether, and in water :

TABLE XI.—MAGNETIC ROTATORY POWER OF HYDROCHLORIC ACID.

Hydrochloric acid.	Molecular magnetic rotation.	$M\frac{\mu-1}{D}$	Molecular dispersion.
Free	2·187	11·20	0·54
Aqueous solution . . .	4·412	14·45	1·12
Solution in isoamyl ether . .	2·238	71·36	0·51

The relation between the index of refraction and the dielectric constant.—The numbers in Table XI point to a relationship between electromagnetism and the velocity of light. According to J. C. Maxwell's electromagnetic theory of light,[26] if K and K_1 respectively denote the dielectric constants of two transparent media, and μ the limiting value towards which the index of refraction approaches when the wave-length of the rays become indefinitely large, then $\mu^2=K/K_1$. If one of the two media be air, for which K_1=unity, then $\mu^2=K$, meaning that the specific inductive capacity, or the dielectric constant of any medium relative to air unity, is equal to the square of the index of refraction of that medium when μ^2 is measured for the slowest vibrations of light, and K for the most rapid electrical oscillations ; the agreement between the observed values of K and μ^2 becomes very close, as is illustrated in Table XII.

TABLE XII.—OBSERVED VALUES OF $K=\mu^2$.

Substance.	K	μ^2
Air	1·000590	1·000588
Hydrogen	1·00264	1·000276
Phosphorus	4·20	3·60
Selenium	5·96	6·60
Liquid chlorine	1·87	1·88
Bromine	2·57	3·10
Iodine	4·00	4·00
Carbon disulphide	2·67	2·67

The value of K for water is 80 and μ varies between 1·33 and 1·34; and for alcohol, K=26, and μ varies between 1·36 and 1·37. Hence, as F. Heerwagen showed, there appears no kind of relation between μ and K for water. H. A. Lorentz and L. Lorenz's relation $(\mu^2-1)/(\mu^2+2)D$=constant becomes $(K-1)/(K+2)D$ =constant, when $K=\mu^2$, and L. Boltzmann found the results to be satisfactory. For gases, $(K-1)/D$=constant, and at a constant temperature, therefore, $K-1$ is proportional to the pressure. The results were confirmed by A. Palaz, P. Fuchs, A. Rosa, P. Lededew, and K. Bädeker. F. Linde found that the formula is not applicable to liquid and gaseous carbon dioxide, sulphur dioxide, nitrous oxide, and chlorine. F. Ratz could not use the formula satisfactorily for his experiments on the influence of temperature and pressure on the dielectric constant, while O. Hasenhörl obtained satisfactory results. A. Batschinsky found the formula fails when K is greater than μ^2. R. Millikan, F. Beaulard, and V. Boccara and M. Pandolfi obtained good results with many mixtures. S. Pagliani found that better results are obtained with the formulæ $(K-1)N/KV$=constant; and $(K-1)/K\sqrt{N/M}$=constant, where N denotes the number of atoms in a molecule; M, the molecular weight; and V, the molecular volume.

The experiments of A. P. Cole, L. Arons and H. Rubens, and of A. Ellinger[27] show that for rays of very great wave-length—say 60 to 600 cm. in air—the index of refraction of water is nearly $\mu=9$. Similarly, for alcohol, the index of refraction for waves 209 cm. long in air was 5·24, and the square of this number agrees well with the dielectric constant of alcohol for low-frequency oscillations. This shows that J. C. Maxwell's formula, $\mu^2=K$, is valid for these substances with radiations of great wave-length.

According to J. A. Fleming,[2] substances of simple symmetrical constitution—*e.g.* liquid elemental gases, saturated hydrocarbons, paraffins—follow Maxwell's rule $\mu^2=K$ for light waves; and they have dielectric constants between 2 and 3, and values of μ lying between 1·4 and 1·7, and these values are not much affected by changing the frequency of the incident waves from zero to billions per second. The molecules of which bodies are composed can double the dielectric constant of the intermolecular spaces without changing the qualitative characteristics of the æther—according to Thwing's rule: the dielectric constant of these bodies is nearly 2·6 times their density. Substances made up of molecules with groups of radicles—hydroxyl, nitryl, etc.—do not generally follow Maxwell's rule, and they have dielectric constants which are much more sensitive to changes in frequency—as a rule, increasing the frequency decreases the dielectric constant.

Again, electromagnetic waves travel much more slowly through dielectrics than through empty space; with water, the velocities in space and in the liquid are as 9 : 1 for all electric waves yet produced, while for visible light waves the ratio is nearly 1·3 : 1; for alcohol, the ratio varies from 5 : 1 to 2·5 : 1 in passing from the longest to the shortest waves yet produced electrically, while for visible light rays the ratio is 1·3 : 1. Low temperatures annul the difference in the velocity ratios for long and short waves. For substances like paraffin, hydrocarbons, liquid oxygen, and bodies of simple chemical constitutions there is no marked difference between the velocities of the waves of different wave-length.

J. A. Fleming assumes that there is a slight displacement of the electric charges (electrons) on the atoms in opposite directions when the molecules of inert substances—like the paraffins and saturated hydrocarbons with symmetrical atoms—are subjected to an electric force. This displacement is the same whether the stress has a frequency of some billions per second, as in the case of a ray of light, or 100 per second, as in the case of electrical oscillations; and Maxwell's rule is fulfilled. On the other hand, with unsymmetrical molecules—like water $H^{\bullet}-OH'$—the electric charges are so displaced that the molecules have an electrical moment, and under the influence of an electric force, they are oriented in space like small magnets in a magnetic field. This displacement is over and above the strain due to the charges of the molecule in that it bestows an abnormal value on the dielectric constant. These abnormal values become normal on lowering the temperature because the molecules aggregate into more complex groups which no longer possess an electric moment, and are no longer liable to orientation in the electromagnetic field. Waves of high frequency produce the same result as very low temperatures, because the inertia of the molecules under rapid alternations of electric force (billions per second) prevents the orientation of the molecules.

J. Stefan (1872)[28] drew attention to a simple relation between the index of refraction, μ, of a gas and the mean free path, l, of the molecules such that $(\mu-1)l$=a constant. R. Clausius (1879) developed the idea, on the lines of J. C. Maxwell's theory, and showed that the expression $(K-1)/(K+2)$ represents the ratio of the real volume of the molecules of a substance to the volume they actually occupy *en masse*. The idea was extended by O. F. Mosotti and F. Exner (1885), who developed the idea with respect to the equivalent expression $(\mu^2-1)/(\mu^2+2)$ such that if the molecules have a spherical form, and do not touch, the relation between the specific inductive capacity or the dielectric constant, K, and the space v actually occupied by the molecules $v=(K-1)/(K+2)$, and since, for vibrations of great wave-length, $\mu^2=K$, the spaces occupied by the molecules will be $v=(\mu^2-1)/(\mu^2+2)$. If the true molecular volume be represented by v, and if ΣM represents the sum of the atomic volumes, when A_1, A_2, . . . represent the atomic volumes and n_1, n_2, . . . the number of atoms of each kind respectively present in the molecule, the fraction of unit space actually occupied by the molecule will be $\Sigma nA/V$, and I. Traube assumed this to be proportional to V, that is, to $(\mu^2-1)/(\mu^2+2)$, so that:

$$\Sigma nA=k\frac{\mu^2-1}{\mu^2+2}V\ ;\ \Sigma nA=k\frac{\mu^2-1}{\mu^2+2}\cdot\frac{M}{D}$$

where k is a constant, and $V=M/D$, where M denotes the molecular weight, and D the density. I. Traube obtained a value 3·46 for the constant k for a long series of saturated organic compounds. The constant k decreases with an increase in the number of double linkages in saturated organic compounds.

H. Davies showed that if the absolute volume of unit mass of liquid be v, the volume at absolute zero be v_0—the b of J. D. van der Waals' equation—and if the volume of the liquid at the temperature T° K. be V; then, if $v_0=kV$:

$$\frac{v}{V}=\frac{1}{2akT_c};\ \frac{K-1}{K+2}=\frac{1}{2akT_c}$$

where a denotes the coefficient of cubical expansion. The values of the constant k calculated from this expression for the liquids tried deviate very little from 2·5. Hence, the ratio of the volume at the absolute zero to the real volume occupied by a number of molecules is 2·5. H. Davies also showed that:

$$\frac{K-1}{K+2}\cdot\frac{M}{D}=\frac{Mv_c}{10};\ \text{and}\ \frac{K-1}{K+2}\cdot\frac{M}{D}=2{\cdot}3\frac{T_c}{p_c}$$

observation gave $2{\cdot}43T_c/p_c$, when p_c is measured in atmospheres. P. A. Guye found empirically that the molecular refractive power is $1{\cdot}8T_c/P_c$.

The refractive index of crystals of isomeric compounds.—The specific refraction of isomeric substances has been suggested as a possible method of distinguishing between metamerism and polymerism. With metamers the difference in the specific refraction is small, and said to be less than about 0·5 per cent. The following examples have been cited in illustration:

TABLE XIII.—METAMERS.

TiO_2	Specific gravity D	μ	$\frac{\mu-1}{D}$	Difference.	Percentage deviation.
Anatase . .	3·840	2·5011	0·3909	0·0004	0·1
Brookite . .	4·065	2·5872	0·3905	0·0017	0·4
Rutile . .	4·239	2·6642	0·3926		

With polymers, the difference in the specific refraction is large, say, over one per cent. For example:

TABLE XIV.—POLYMERS.

$CaCO_3$	Specific gravity, D	μ	$\frac{\mu-1}{D}$	Difference.	Percentage deviation.
Calcspar . .	2·713	1·5958	0·2196	0·0068	3·1
Aragonite . .	2·950	1·6277	0·2128		

With the three aluminium silicates there appears both metamerism and polymerism.

TABLE XV.—METAMERS AND POLYMERS.

$AlSiO_5$	Specific gravity, D	μ	$\frac{\mu-1}{D}$	Difference.	Percentage deviation.
Andalusite . .	3·180	1·6357	0·1999	0·0003	0·3
Cyanite . .	3·603	1·7182	0·1883	0·0045	2·3
Sillimanite . .	3·235	1·6613	0·2044		

It will be observed, however, that the molecular structure of none of these examples has been established, and the argument therefore proceeds in a vicious circle.

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CHAPTER XII

THERMODYNAMICS AND THERMOCHEMISTRY

§ 1. Matter and Energy

> All physical science starts from certain postulates. One of them is the objective existence of a real world.—T. H. HUXLEY (1887).
>
> Substance is like a river in continual flow; the energies undergo constant changes and do work in infinite variety. There is hardly anything that stands still or remains still.—MARCUS AURELIUS.

SIDE by side with ponderable matter, capable of being weighed, early science accepted imponderable matter such as electricity, fire, heat, etc.; and, up to the beginning of the nineteenth century, it was generally assumed that heat is a substance which was variously styled caloric, igneous fluid, phlogiston, etc. Indeed, A. L. Lavoisier was influenced by the time-honoured tradition, and in his *Traité élémentaire de chimie* (Paris, 1793), included *lumière* and *calorique* in his *Tableau des substances simples* to be regarded as elements, although he knew quite well that they had no perceptible weight. Even J. Fourier, in his classical *Théorie de la chaleur* (Paris, 1816), regarded heat as a material substance; and J. J. Berzelius, in his *Lehrbuch der Chemie* (Dresden, 1825), classed *Licht- und Wärmestoff* among the *einfache unwägbare Stoffe*.

As a result of Newton's theory of gravitation, it was soon recognized that matter seems to have a property, called *mass*, which shows itself as *weight* under the influence of gravity. Matter also occupies space so that it is always extended in some shape or form; and further, matter is invariably associated with energy. Consequently, matter, as perceived by the senses, possesses certain attributes—weight and form—which appear to be permanent and essential qualities abiding in all known kinds of matter; whereas other properties—*e.g.* colour, odour, etc.—appear to be secondary and accidental attributes which are peculiar to specific forms of matter. This distinction between the primary and secondary qualities of matter was recognized by Democritus, *c.* 350 B.C.; it appeared among the tenets of Albertus Magnus, who in his *De generatione elementorum* said:

> That matter and power are the principles of each body is clear, for having taken away all the accidental forms, we arrive at length at a substantial form which, being abstracted *per intellectum*, there remains a something very occult which is *prima materia*.

The idea was further emphasized by J. Locke in 1689. Matter may also be found under different conditions of temperature, electrification, motion, etc.; and daily experience teaches us that changes are continually taking place in the conditions of bodies around us. Change of position, change of motion, of temperature, volume, and chemical combination are but few of the myriad changes associated with bodies in general.

The forms of energy.—There are many different forms of energy—electrical, chemical, mechanical, thermal, and actinic—and by suitable means these can be mutually converted one into the other; *e.g.* the galvanic battery converts chemical into electrical energy, and the dynamo converts mechanical into electrical energy. Much of the motive power used in the industrial arts is derived from the chemical action between coal and oxygen in the furnace of a steam engine. Heat and light are also well-known concomitants of chemical action. Hence, it is inferred that heat, electricity, mechanical motion, light, and chemical action are all different forms of one distinct entity—energy. The different forms of energy are supposed to be the external aspects of one single basic form of energy, which, in the words of S. A. Reeve (1909), we may never hope to comprehend. Examples of the mutual identity of the different forms of energy multiply daily in familiar experience. The idea was dimly foreshadowed in the seventeenth century by F. Bacon in his essay *De forma calidi* (1627), which was offered as a model of method for investigating nature. Here Bacon argued that the facts could be satisfactorily explained only by assuming that heat is a kind of motion among the particles of a body; heat and mechanical motion are mutually convertible. The same idea was accepted by R. Hooke (1667), Isaac Newton (1675), R. Descartes (1677), R. Boyle (1680), J. Locke (1689), and others.[1] The same idea was emphasized by Count Rumford[2] who, in *An inquiry concerning the weight of heat* (1798), proved that heat could not be a material substance because unlimited quantities can be developed by friction, and concluded that heat must be motion. H. Davy, likewise, in 1812 showed that ice can be liquefied by friction, and the resulting liquid contains a far greater amount of heat than the ice, and he concluded:

> The immediate cause of the phenomena of heat is motion, and the laws of its communication are precisely the same as the laws of the communication of motion.

The later work of J. P. Joule (1846–9) and others has fixed the generalization that **any one form of energy can be transformed, wholly or partially, directly or by intermediate steps, into any other form.** This is the so-called **law of transformation of energy.** All types of machinery are devices for transforming energy from one form into another; and all phenomena in the material world can be represented as transformation of energy. Industrial operations usually involve the expenditure of considerable amounts of energy. For instance, *mechanical energy* is expended in crushing and grinding rocks, rolling metals, transporting materials, etc.; *thermal energy* is expended in the steam engine, and used for melting metals, burning lime and cement, bricks and pottery, etc.; *electrical energy* for illumination, electroplating, refining metals, production of aluminium, etc.; *light energy* for illumination and photography; *chemical energy* in the manufacture of chemical compounds, explosives for blasting and warfare, driving gas engines, etc.

Energy and work.—As a first approximation, every change in the condition of the various bodies around us is supposed to be due to the action of what T. Young (1807)[3] called *energy*. In other words, energy is regarded as an operative physical agent which has the power of changing the condition of bodies. Whenever a body is changing its condition, there energy is in action. Energy is the cause, change of condition the effect. The action of energy may be resisted. Change can take place only when the restraint is withdrawn or overcome. The action by which energy produces a tendency to change is called a **force.** The word *tendency* here means that the change will take place the moment the restraining influence is withdrawn. Force is thus supposed to be an imaginary intermediate link between the physical cause of a phenomenon and the resulting effect. Force is thus a manifestation of energy. Whenever resistance is overcome, energy must be expended. Hence, energy is sometimes defined as "the power to overcome resistance." Work is said to be performed whenever change takes place in opposition to a force opposing that change. Work is a manifestation of the transfer or transformation of energy. The work is done at the expense of the energy, and the amount of work is equivalent to the quantity of energy transferred. The work performed is equal to the energy expended, and just as quantity of matter is measured by weight so quantity of energy is measured by work. Consequently, energy is sometimes defined as the capacity for doing work; or, as W. Ostwald (1892)[4] puts it: *Wir werden allgemein Energie als Arbeit, oder alles, was aus Arbeit entsteht und sich in Arbeit umwandeln lässt, definiren*—energy is work and all else that can be produced from or converted into work. Not all energy is capable of doing work. There are two kinds of availability of energy for work; energy appears as if it were on two planes, a higher and a lower. The work value is a measure of the availability of energy on the higher plane; the work value of energy on the lower plane is nil. Consequently, the definition of energy as capacity for work, is valid only when it refers to a particular form of energy which is in a condition to do work; it is not a definition of energy.

Two factors are involved during the expenditure of energy in doing work: (1) The *magnitude* of the resistance; and (2) the *extent* to which the resistance is overcome. Thus, when a particle moves a certain distance s by the application of a force F the amount of energy expended is measured by the work done, and is equal to the product Fs; if a gas suffers a change in volume dv, when subjected to a steady pressure p, the work dW done during the change in volume, or the energy expended during the operation, is equivalent to the product $p.dv$. This latter problem is so important to the chemist in studying the energy changes which occur during chemical reactions in which the volume of the end-products is different from that of the initial-products, that it must be considered in more detail.

The work done by a gas when it changes its volume without changing its temperature.—Imagine a gas occupying a volume v_1, confined in a cylinder, Fig. 1, fitted with a piston to move up and down without friction; and let the constant pressure p press the piston downwards. Let the gas expand from a volume v_1 to a volume v_2 when the work performed will be equivalent to $p(v_1-v_2)$. This expression is a convenient approximation, for it can be rigorously true only when the change in volume is very small because the pressure of the atmosphere on the expanding gas does not remain quite constant, but changes slightly as the volume increases. Hence, the very small amount of work dW done when the gas suffers an indefinitely small change of volume dv, is $dW=p.dv$. With an ideal gas, $p=RT/v$; and when the expression $dW=RT(dv/v)$, obtained by substituting this value of p in pdv, is integrated for a change in volume from v_1 to v_2, the work of expansion W (temperature constant) is $W=RT \log (v_2/v_1)$, or $W=RT \log (p_1/p_2)$. The second expression represents the work done during the expansion of a gas from a pressure p_1 to a pressure p_2; and it is obviously derived by substituting for v_1 and v_2 from the relation $p_1v_1=p_2v_2$; or $v_2/v_1=p_1/p_2$. Remember also that natural logarithms are supposed to be used; if ordinary logarithms are employed, the terms on the right must be multiplied by 2·3026. The same expression also represents the work required to concentrate a solution with a vapour pressure p_1 to one with a vapour pressure p_2.

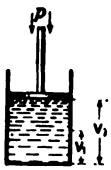

FIG. 1.

This shows that the maximum work performed by an ideal gas in increasing its volume from v_1 to v_2 is either

$$W=RT \log \frac{v_2}{v_1}; \quad \text{or,} \quad W=RT \log \frac{p_1}{p_2}$$

Otherwise expressed, the maximum work performed by an ideal gas under the given conditions is (i) dependent only on the initial and final volumes or pressures, but is independent of their absolute magnitudes; (ii) proportional to the absolute temperature; and (iii) the same magnitude for all gases which obey the ideal gas laws. The values for the constant R are indicated in Table I.—*e.g.* if the pressures are expressed in atmospheres, and volumes in litres, R is 0·0827, and the results are in litre-atmospheres.

EXAMPLES.—(1) A unit mass of gas, at 20°, is allowed to expand at a constant temperature from a pressure of 10 atm. until its pressure is one atm. The work of expansion is $2{\cdot}3026 \times 2 \times (273+20) \times \log_{10}10$ gram-cals., when $R=2$.

(2) One gram of liquid water (volume 1·043 c.c.) at 100° changes to vapour (volume 1660 c.c.) at 100° against atmospheric pressure, show that the work of expansion is equivalent to 168 joules, nearly, given $R=8{\cdot}31$.

Energy and matter are inseparable.—Our knowledge of the material world can be conveniently described in terms of two entities or abstractions: 1. Energy; 2. Matter. It is sometimes advantageous to keep these two concepts distinct; although energy and matter are separable only in thought, in reality they are indissolubly joined together. Energy is not matter, nor matter energy.[5] There can be no matter without energy, nor energy without matter. To summarize, matter is a term grouping together entities which possess certain properties in common; energy likewise is a term grouping together certain phenomena which, like matter, have many forms; and sometimes a third term, æther, is used for grouping together certain relations between matter and energy.

At first sight, common sense and science seem to support the supposition that there is a real universe existing in all its completeness quite independent of all relation to the intelligence; and that observations are made on real things which are apprehended or perceived as existing fully formed and complete in themselves. According to **the energetic hypothesis of matter,** the *objective* reality of matter is a derived idea, for the existence of matter as something external to ourselves is assumed in order to explain certain *subjective* sensations; consequently, our knowledge of the material world is founded upon our perceptions, which are in turn based upon the evidence of our senses. We do not see material objects directly, but rather experience a sensation presumably due to the formation of a picture of the object upon the retina, and which is possibly a chemical effect induced by energy radiated from the object on to the retina. Again, the mechanical energy of vibrating air may produce sensations in the auditory organs; and the mechanical energy of pressure or tension may produce sensations in the organs of touch. In this way, it can be shown that all our perceptions of the material world are derived from sensations produced by manifestations of various forms of energy. Take away the manifestations of energy, and nothing remains, since a body without a quality is indistinguishable from nothing. In this sense, the objective reality of matter can be regarded as an hypothesis, postulated to explain our subjective sensations. W. Ostwald accordingly emphasized the old idea that matter is a redundant hypothesis, a creature of the imagination designed as a carrier or vehicle of energy; and that the only things we really know are manifestations of energy. Energy and only energy is the thing in itself; energy is the real substratum of the physical and chemical world. In his *Studien zur Energetik*, W. Ostwald (1892)[6] thus describes his conversion to the energy hypothesis:

> The more intimately acquainted I became with the properties of energy, the clearer became the proof that matter is nothing but a complex of different factors of energy which possess the property of being reciprocally proportioned. The traditional fundamental properties of matter show themselves as modes of expression or factors of energy.

G. F. Fitzgerald (1896), M. Planck (1896), and L. Boltzmann (1896)[7] and others have challenged the validity of the energetic view as an elemental hypothesis which cannot be reduced to simpler terms, for kinetic energy is defined as the product of half the mass m of a moving body into the square of its velocity V, or $\frac{1}{2}mV^2$, but mass is defined in terms of kinetic energy, and the definitions thus proceed in a circle.

It is best, however, to leave the metaphysical chemist to deal with matter defined as the unknown cause of known sensations, and answer for himself such questions as: What is matter in and by itself? What is the thing matter *per se?* Whether it is better to regard matter as a passive vehicle for energy, or a particular form of energy having no existence apart from energy? The working chemist finds it convenient to assume that all sensible objects occupying space have a material substratum which accompanies these objects in their motions from place to place; and he defines: **Matter is that which possesses weight and occupies space.** Matter is thus a convenient word for grouping together those things which have the common property of weight and form. Air, water, glass, copper, etc., are forms of matter; heat, light, electricity, and magnetism are forms of non-matter—energy; colour, odour, etc., are specific properties of particular forms of matter.

Energy, like matter, is indestructible.—Whenever it has been possible to make accurate measurements, it has been found that any quantity of one form of energy is made to disappear, an equivalent quantity of another form, or forms of energy, appears. L. A. Colding, in his *Thesis on Energy* (Copenhagen, 1843),[8] said:

> Energy is imperishable and immortal, and therefore wherever and whenever energy seems to vanish in performing certain mechanical, or other work, it merely undergoes a transformation, and re-appears in a new form, but the total quantity of energy still abides.

This is the quantitative aspect of the mutual transformability of the different forms of energy. No gain or loss of energy has ever been observed in an isolated system. This is the famous **law of conservation or persistence of energy,** which appears to have been foreshadowed by R. Descartes and the Cartesian school as the law of the indestructibility of momentum or motion; and by G. W. von Leibniz as the law of conservation of *vis viva*, or force as it was then called. The perdurability of energy was also foreshadowed by Isaac Newton in 1687,[9] and by F. Mohr in 1837, although, as E. Mach[10] has shown, almost all eminent investigators had a more or less confused idea of it; and, since the time of S. Stevinus (1605), and G. Galilei in the seventeenth century, it has served as the foundation of the most important extensions of the physical sciences; and adds:

> This theorem is usually considered to be the flower of the mechanical world,—the highest and most general theorem of natural science, to which the thought of many centuries has led.

Action and reaction, said Isaac Newton, are equal and opposite; and further,

> If the activity of an agent be measured by the product of the force into its velocity, and if similarly the counter-activity of the resistance be measured by the velocities of its several parts, whether these arise from friction, adhesion, weight, or acceleration, etc., then activity and counter-activity in all combinations of machines will be equal and opposite.

The same principle was recognized to be of universal application by J. R. Mayer, in a memoir: *Bemerkungen über Kräfte der unbelebten Natur* (1842),[11] which was rejected as eminently heretical by some of the supremely orthodox journals at that time. This work was followed by that of W. R. Grove, *On the correlation of the physical forces* (London, 1843), and almost simultaneously by that of J. P. Joule,[12] in a paper, *On the calorific effects of magneto-electricity, and on the mechanical equivalent of heat*, and by that of H. von Helmholtz, *Ueber die Erhaltung der Kraft* (1847). In the writings of the brilliant N. L. S. Carnot, published after his death in 1832, there occur these remarkable words:

> Heat is simply motive power or motion which has changed its form, for it is but a movement amongst the particles of a body. Whenever motive power is destroyed, an equivalent quantity of heat is produced; and reciprocally whenever heat is destroyed, motive power is developed. It is therefore possible to establish the *thèse générale* that motive power is a quantity which is invariable in nature; that is, to speak correctly, motive power is a quantity which can neither be produced nor destroyed. True enough, it may change its form, or produce sometimes one kind of motion, and sometimes another, but it is never annihilated.

Hence, in all chemical changes, two entities—matter and energy—remain quantitatively the same, but qualitatively different. "The transactions of the material universe," said J. C. Maxwell, in that inimitable work *Matter and Motion* (London, 1894), "appear to be conducted, as it were, on a system of credit. Each transaction consists of a transfer of so much credit or energy from one body to another. The act of transfer or payment we call work." H. St C. Deville, in his *Leçons sur la dissociation* (Paris, 1864), emphasized the same idea a little differently. He said:

> All the labours and all the tendencies of modern science lead to the identification of all the forces which come into play in physical and chemical phenomena; all the numerical relations which have been obtained, establish their equivalence in the most rigorous manner.

Quantitative relation between the different forms of energy.—Energy in all its forms can be expressed in terms of one basal unit the **erg**; an erg is equivalent to a force of one **dyne** acting through one centimetre; that is, a dyne acting through one cm. generates one erg of energy. A dyne is that force which acting for one second on one gram produces a velocity of one cm. per second. The dyne is also equivalent to a weight of one gram divided by g, the **acceleration of gravity** in cm. per sec. per sec.—where $g=980{\cdot}665$ cm. per sec. per sec. at latitude 45° and sea-level. A pressure of one atmosphere equals 1,013,000 dynes per sq. cm. Weights considered as forces can be expressed and measured in terms of the dyne. The gravitational unit of energy or work is the weight of 1 gram through 1 cm., and this is equal to g dynes per cm.—that is, to g ergs. For a latitude 45° at sea-level, g is 980·617 dynes per cm. For a latitude λ, and height h metres above sea-level, Helmert's formula is $g=980{\cdot}617-2{\cdot}593\cos 2\lambda-0{\cdot}0003086h$.

The principle of the mutual convertibility of the different forms of energy assumes that there are measurable relations between the different forms, and that the modes of measurement are homologous. The possibility of measuring energy when converted from one form into another is dependent on an equation showing in what ratio the transformation has been accomplished. The ratio between heat and mechanical energy was worked out in a fairly satisfactory way by J. P. Joule in 1846–9, when he found that " 772 lbs. falling one foot would heat a pound of water 1° ; " and he called this ratio **the mechanical equivalent of heat.** Later, more exact determinations of this constant give a rather higher number than that found by J. P. Joule ;[13] the best available data range from $4{\cdot}181$ to $4{\cdot}192\times10^7$ ergs per gram-calorie at 15° ; and the best representative value is taken to be **$4{\cdot}182\times10^7$ ergs per gram-calorie at 15°.** If a **calorie** be defined as the amount of heat required to raise the temperature of one gram of water at 15° one degree, then 42·670 grams falling one centimetre will generate one calorie. Hence a calorie is equivalent to 42,670 gram-centimetres of energy. Another ratio commonly employed is the so-called **joule,** such that one joule is equivalent to 10,198 gram-centimetres of mechanical energy. Hence,

1 calorie=4·182 joules ; 1 joule=0·2423 calorie

Table I summarizes the quantitative relationship between the different forms of energy, and is convenient for reference.

TABLE I.—NUMERICAL EQUIVALENTS OF SOME FORMS OF ENERGY.

One	Gram-calorie.	Gram-centimetre.	Watt-hour.	Erg.	Litre-atmosphere.	Joule.
Gram-calorie .	1	42670	$11{\cdot}62\times10^{4}$	$41{\cdot}86\times10^{6}$	$41{\cdot}33\times10^{-3}$	4·186
Gram-cm. .	$23{\cdot}41\times10^{-6}$	1	$27{\cdot}24\times10^{9}$	80·6	$96{\cdot}77\times10^{-8}$	$98{\cdot}06\times10^{-6}$
Watt-hour .	860·3	$3{\cdot}670\times10^{7}$	1	36×10^{9}	35·53	3600
Erg . .	$24{\cdot}23\times10^{-9}$	0·00101980	$27{\cdot}78\times10^{-12}$	1	$98{\cdot}70^{-11}$	10^{-7}
Litre-atm. .	24·54	$10{\cdot}332\times10^{4}$	$28{\cdot}15\times10^{-3}$	$10{\cdot}13\times10^{8}$	1	101·3
Joule . .	0·2423	10198	$27{\cdot}78\times10^{-5}$	10^{7}	0·00987	1
Gas constant, R	1·9885	847	—	$8{\cdot}31\times10^{7}$	0·08207	8·316

The index notation is used for representing small or large magnitudes as powers of 10. Thus $10^1=10$, and $10^{-1}=\frac{1}{10}$th, or 0·1 ; $10^2=100$, and $10^{-2}=\frac{1}{100}$th, or 0·01 ; $10^3=1000$, and $10^{-3}=\frac{1}{1000}$th, or 0·001. The positive index, therefore, represents the same number of cyphers as the index number, and the negative index one cypher less after the decimal point than the index number.

Perpetual motion.—The law of persistence of energy is sometimes called **the first law of thermodynamics,** or **the first law of energetics,** and it can be expressed another way. No machine can generate energy or do work of itself without consuming at least an equal quantity of pre-existing energy. Energy cannot be produced from nothing, something must be consumed. A machine can do no work without the aid of an external driving force—energy. It is impossible to construct a machine which will do work without parting with energy ; when all the energy is consumed, the machine can do no more work until more energy is supplied from without. This revised statement of the law of persistence of energy is called **the law of excluded perpetual motion.** This law does not mean that perpetual motion is theoretically impossible, but it does mean that work cannot be done without a supply of compensating energy, for no work can be performed without a loss of motion or the expenditure of energy. Isaac Newton's first law really postulates perpetual motion as the normal state of a body moving without constraint in a frictionless medium. Perpetual motion implies a sustaining and propelling source of energy in order to compensate the losses necessarily entailed in overcoming friction, etc. No system can furnish an inexhaustible supply of energy. Neither gravitation nor magnetism can supply energy which will make good its own loss.

Even as early as 1269, P. Peregrinus alluded to the quest for the *perpetuum mobile* as a pursuit where many had " wandered about wearied with manifold toil." In all times, recent and modern, sanguine seekers after perpetual motion have attempted to circumvent the law of the conservation of energy. C. E. Benham has said that " the playful way in which nature presents us with phenomena sometimes seems as if they has been cunningly devised to lure and entrap the human mind into a belief in the possibility of achieving this unattainable result." The impossibility of perpetual motion seems to contradict the one phenomenon which is universal and constant and which is more striking than any other. From the incessant movements of celestial spheres down to the congeries of rapidly vibrating atoms and electrons in every created thing, everything appears to be in perpetual motion. It is therefore inferred that the apparent perpetuity of the movement is illusory ; that these movements represent but an intermediate stage in a vast universe which is slowly sinking into a state of final quiescence, when all motion will cease to be. It must be candidly confessed that we can offer no real proof of the truth of this law, other than the uncontradicted experience of mankind with finite systems which admit of observation.[14] It is obviously not sound reasoning to infer that because a phenomenon always has been, it will therefore always be. Knowledge which has appeared to be certain for hundreds of years may suddenly prove to be gross ignorance. We assume that if perpetual motion has been possible it would have been discovered long ago. Of course a similar argument might have been used in 1890 against the existence of a gas like argon in the atmosphere, and the " uncontradicted experience " would have been contradicted four years later. Consequently, evidence of this kind can never attain certainty, and we can only say that the wider the uncontradicted experience, the stronger is its testimony that the empirical law is valid, and the less likely is the necessity to arise for a thorough revision of the fundamental statement. The search for a perpetual motion through centuries of laborious work has been fruitless. It has brought nothing but failure. So great is our faith in the truth of this unproved law that a demonstration showing that any supposed process would involve a perpetual motion or the creation or destruction of energy, is considered sufficient proof that the supposed process is impossible. We assume with M. Faraday (1857) : " No hypothesis should be admitted nor any assertion of fact credited that denies this principle. No view should be incompatible or inconsistent with it." Most scientific societies would refuse to consider seriously papers which violated the assumed law of excluded perpetual motion.

Algebraic statement of the law of conservation of energy or the first law of energetics.—According to the principle of the conservation of energy, if an amount of work W be performed by a body against external forces (say, atmospheric pressure), when q units of heat are absorbed by the system, the change in the internal energy dU which the system suffers in consequence of the isothermal change will be :

$$\underset{\text{internal energy.}}{\overset{\text{Decrease of}}{dU}} = \underset{\text{absorbed.}}{\overset{\text{Heat}}{(+q)}} \quad \underset{\text{performed.}}{\overset{\text{Work}}{-W}}$$

in words, the changes in the internal energy U, which a system suffers in consequence of an isothermal change, is equivalent to the amount of heat absorbed less the external work W done by the system.

In 1862, R. Clausius[15] drew a clear distinction between the external and internal work which a body can do when it changes its state. The term **external work,** W, refers to work due to the action of external forces on the system, *e.g.* (i) Expansion against an external pressure (usually atmospheric); (ii) Resistance to changing its form (*i.e.* distortion); (iii) Changes in surface area against capillary forces; and (iv) Electric or magnetic forces when a body is moved from a high to a lower potential. The term **internal energy or work,** U, includes: (i) The increased kinetic energy of the molecules which causes a rise of temperature; (ii) Intermolecular work done by or against molecular forces when the volume, cohesion, or elasticity is changed; (iii) Intramolecular vibrations, *i.e.* atomic vibrations within the molecule; and (iv) Chemical work as when a body changes its state, etc.

From the energetic point of view, the heat q is conventionally *positive* if the system *absorbs* heat; and *negative* if the system evolves heat; if the external work W be done *by* the system, W will be *negative*, and *positive* if done *on* the system; the internal energy, U, is *negative* when *U diminishes*, and *positive* when U increases. If the system does no external work, as occurs when a chemical reaction takes place in a calorimetric bomb, $W=0$, and $U=q$, meaning that in an isothermal change the system will gain an amount of internal energy equivalent to the amount of heat absorbed. In most calorimetric work, the pressure, not the volume, is constant, and if v_1 and v_2 respectively denote the initial and final volumes under a constant pressure p, and U_1 and U_2 the initial and final energies of the system, the preceding equation can be written:

$$U_2-U_1=q-p(v_2-v_1)\text{ ; or, }q=(U_2+pv_2)-(U_1+pv_1)$$

Hence, the heat absorbed in the reaction depends on the initial and final states of the system. In the more general case, if $v_1, v_1' \ldots$ represent the volumes of the substances consumed in a reaction under the respective pressures $p_1, p_1' \ldots$, $v_2, v_2' \ldots$, and $p_2, p_2' \ldots$, the corresponding values for the substances produced on the reaction, then, if U_1 represents the internal energy of the substances destroyed in the reaction, and U_2 that of the substances produced,

$$U_2-U_1=q-\{(p_2v_2+p_2'v_2'+\ldots)-(p_1v_1+p_1'v_1'+)\}$$

which may be more conveniently symbolized, $U_2-U_1=q-(\Sigma p_2v_2-\Sigma p_1v_1)$. Where q denotes the thermal value of a reaction at ordinary atmospheric pressures, the symbol Q may be used in place of q, and

$$Q=(U_2+\Sigma p_2v_2)-(U_1+\Sigma p_1v_1)\text{ ; or }Q=U+\Sigma pv$$

The magnitude $U+\Sigma pv$ is called the heat content of a given system.

EXAMPLES.—(1) If one gram of liquid water, whose volume is 1·043 c.c. at 100°, be converted into vapour occupying 1661 c.c. at 100°, against atmospheric pressure in consequence of the absorption of 537 cals. (heat of vaporization), show that the increased internal energy in consequence of the vaporization will be 2087 joules. The external work of expansion is 168 joules; and $537\times4{\cdot}2=2255$ joules is equivalent to 537 cals. Hence, $U=168$ less $2255=-2087$ joules. If the vaporization could be made to take place without an increase in volume, no external work would be done, and the increase in internal energy would be equivalent to 2255 joules.

(2) If a zinc rod be immersed in a solution of copper sulphate a reaction symbolized $Zn+CuSO_4=ZnSO_4+Cu$ occurs, and the transformation of chemical energy generates a calories of thermal energy; no external work is done, so that $W=U$. If the system be so arranged that the chemical energy is transformed into electrical energy—say, by placing a zinc rod in a solution of zinc sulphate contained in a porous pot immersed in a solution in which a copper rod is partly immersed, and connecting the exposed parts of the two rods by wire—b calories of thermal energy are at the same time evolved. Then U, the electrical energy produced, will be equivalent to $b-a$ cals.

Relation between the laws of conservation of energy and of matter.—In 1902, Lord Rayleigh[16] showed that if a real change in weight could be demonstrated during a chemical reaction, perpetual motion would be possible. In the reversible chemical action $A \rightleftharpoons B$, let the system in the state A be initially at a low level, and then raised (in vacuo) to a higher level when the system is transformed into the state B. Then let the system be returned to the lower level and transformed into the state A. The temperature is maintained constant during the whole of the operations. The reversed chemical reactions compensate one another and there is no gain or loss of energy; the operations of raising and lowering the two systems do not compensate one another unless the weights of the system in the two states A and B are the same. If the weights be different, the cycle of operations can be so executed that work is gained, and perpetual motion becomes possible. Hence, unless something has been overlooked, there cannot be a difference in the weights of a system in the two states A and B. In spite of this demonstration, attempts are not infrequently made to show that chemical changes involve a real loss of weight too small to be detected by the balance.

Kinetic and potential energy.—There is an important difference between a stone lying on the ground and a similar stone lying on the table. Both appear alike to be motionless, yet the latter possesses more available energy than the former. For example, the stone on the table, in descending to the ground, could be made to transfer its energy to the mechanism of a clock, and do work. The available energy would thus be transformed into mechanical motion. For the same reason, a wound watch spring possesses more available energy than a similar spring not wound up. Thus available energy may be conventionally regarded as active (*i.e.* kinetic) or passive (*i.e.* latent or potential). When a marble is rolling along the ground, it has the power, in virtue of that motion, to change the state of another marble with which it might collide. A body, therefore, might possess energy in virtue of its motion. This energy is said to be in a *kinetic* or active condition. In 1686, G. W. von Leibniz, in a memorable controversy with R. Descartes, established the proposition that the *vis viva*—the living energy—or, as it is now called, the available **kinetic energy** K, of a body of mass m moving with a velocity V, is $K=\frac{1}{2}mV^2$. This energy may be transformed into heat when the motion of the body is arrested. In contrast with this, it is sometimes convenient to use the term **potential energy,** suggested by W. J. M. Rankine in 1853, for the available energy which is potential to, possible to, or latent in a body in virtue of its condition with respect to surrounding objects; in G. W. von Leibniz's terminology this would be the *vis mortua* of the system. The distinction between potential and kinetic energy was recognized by Aristotle (*c.* 320 B.C.), and he called the former ἐν δύναμει (dynamic) and the latter ἐν ἐνεργεία (energetic); and in 1803, N. L. S. Carnot called potential energy the *force vive latente.*

When a stone is lifted above the ground, the energy expended and the work done depend upon the weight w of the stone, and the height h to which the stone has been lifted. Consequently, the available potential energy E of the stone will be $E=wh$. The meaning is that a measurable quantity of energy is stored up or rendered passive in some way, and that this same amount of energy can be recovered. For instance, when the stone returns to the ground, it will in falling acquire an equivalent amount of kinetic energy. Kinetic and potential energy are here referred to the earth as constant, for obviously the suspended stone would have no available potential energy if it could never fall. Again, water in an elevated position can do work, in virtue of the law that all liquids will flow to the lowest level that circumstances will permit. Consequently, water at the top of a hill possesses potential energy. A bent spring, a raised hammer, compressed air, and a piece of iron in the vicinity of a magnet, all possess potential energy. Substances which in virtue of their relative condition, or the motions of their constituent molecules, are capable of entering into chemical actions, are also said to possess potential energy. Such are gunpowder, a mixture of metallic zinc and sulphuric acid, etc. The light, heat, sound, and mechanical motion which attend the explosion of gun-cotton are equivalent to the chemical energy stored in the explosive.

For convenience, the different forms of energy are usually classified as mechanical and kinetic energy; potential energy involving stress or strain; thermal energy; actinic and radiant energy; electric energy; magnetic energy; and chemical energy. Each of these, in turn, can be regarded either as energy of tension, or energy of motion.

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§ 2. Thermochemistry

Heat and cold are nature's two hands by which she chiefly worketh.—FRANCIS BACON (1627).

Sine igni nihil operamur.—C. GLASER (1663).

It has been shown that matter, as we know it, can be resolved into two abstractions—matter and energy. Neither exists alone. We have no acquaintance with the one apart from the other. Isolated, matter and energy are pure abstractions. Each one completes and presupposes the other. The element phosphorus, for instance, can be regarded as a form of matter which is always associated with a certain amount of free or available energy, because it is able to do chemical work, and we cannot conceive of energy coming from nothing. We cannot answer: How much energy is associated with the phosphorus? The actual amount available possibly depends upon the nature of the substance with which it is brought in contact. Similarly with oxygen. When these two elements—oxygen and phosphorus—are brought in contact, under the right conditions for the degradation of energy, chemical action sets in, and the chemical energy is degraded or transformed into heat or light. The resulting compound—phosphorus pentoxide—still contains some chemical energy, for if it be mixed with water, a great amount of heat is developed, chemical energy is degraded, and phosphoric acid results. The phosphoric acid still contains chemical energy because more energy is degraded in the form of heat when the phosphoric acid is brought into contact with sodium hydroxide. **Every chemical reaction involves a change both in the form of the matter and in the form of the energy of the system.**

Modern chemistry would make C. Glaser's old motto read: Without available energy nothing can change. What is generally understood by descriptive material or chemistry deals with matter, not with energy. Chemistry proper is essentially concerned with both energy and matter; and hence, it can no longer leave the development of the energy concept, as was formerly done, exclusively to physics and mechanics. The fundamental part played by energy in determining the nature and character of chemical processes was for a long time obscured by the erroneous notion that all forms of energy are but forms of mechanical energy. This idea was perhaps the illicit consequence of man's early familiarity with mechanical energy. First impressions are obstinately persistent. It was not easy for man to realize that mechanical energy is but one phase of a much wider and more comprehensive concept which includes all the other different forms of energy. It has been as difficult for the chemists to recognize that energy is an entity with which he has to deal, as it was for the alchemists to realize that gases and vapours are of material importance in the study of chemical changes.

The law of Lavoisier and Laplace.—The free or available chemical energy of different substances is usually degraded in the form of heat during chemical action. The system gets hotter because heat is evolved by the reacting substances —such reactions are said to be *exothermic or thermopositive reactions* in contrast with *endothermic or thermonegative reactions* which consume heat and thus cause the system to become cooler. That branch of chemistry which deals with the relation between thermal and chemical energy is called **thermochemistry.** The heat evolved during a chemical reaction is proportional to the quantity of the reacting substance, and as a convenient standard, the amount of heat given out at constant volume and temperature per gram-molecule of the reacting substance is called **the heat of the reaction**; this heat Q is wrongly supposed to be a measure of the decrease in the internal energy of the substance. Experiment shows that a definite chemical process generates a definite amount of heat. Every compound has a definite heat of formation, which is numerically equal to the heat required for the decomposition of the compound back into its elements, but of opposite sign. Action and reaction, says Newton's third law, are equal and opposite. This is obviously a corollary of the law of the conservation of energy. If it were not so, heat would be gained or lost when a compound is formed and then decomposed back into its original constituents. Such a result is at variance with the principle of the persistence or conservation of energy. The fact that **every compound has a definite heat of formation which is numerically equivalent to its heat of decomposition but of opposite sign,** is sometimes called the **law of Lavoisier and Laplace,** because A. L. Lavoisier and P. S. de Laplace[1] first pointed out this generalization, in their *Mémoires sur la chaleur*, published between 1780–4. Consequently, under a given set of conditions, it seems as if each atom and each molecule is charged with an amount of energy which is as definite as the quantity of matter itself. The important conclusion of A. L. Lavoisier and P. S. de Laplace was later verified by the work of H. Hess (1836–40), T. Andrews (1844), P. A. Favre and J. T. Silbermann (1844–6), T. Woods (1851), and others,[2] and data were accumulated showing the thermal values of various chemical reactions. A large mass of thermochemical data for various chemical or physicochemical processes has been accumulated by J. Thomsen, M. Berthelot, and others, and most has been compiled in H. Landolt and R. Börnstein's *Physikalisch-chemische Tabellen* (Berlin, 1912).[3]

The symbols used in thermochemistry.—It will be remembered that in physics, the unit of heat is the **calorie,** and a calorie represents the amount of heat required to raise the temperature of one gram of water, at some convenient standard temperature, through 1° C. Consequently, 100 cals. will raise the temperature of 100 grams of water 1°, or of 1 gram of water 100°. Sometimes it is convenient to take a pound of water as the unit, and a **pound-calorie** is then the amount of heat required to raise the temperature of a pound of water 1° C.; if the degree Fahrenheit be the unit of temperature, the amount of heat required to raise the temperature of one pound of water 1° F.—say from 60° F. to 61° F.—is called a **British thermal unit**, B.T.U.; the latter unit is used by many engineers. To convert a big calorie into a B.T.U. multiply by 3·9681 and for the converse operation multiply by 0·2522; to convert a pound-calorie into a B.T.U. multiply by 1·8; and for the converse operation, multiply by 0·555.

In chemistry it is convenient to represent the thermal value or heat of a reaction by reference to the formula weight or the gram-molecule of the substance concerned in the reaction. Thus, the heat of formation of phosphorus pentoxide, taken at P_2O_5, is 370,000 cals. This means that 370,000 cals. are generated when 142 grams of phosphorus pentoxide are formed by burning 62 grams of phosphorus in oxygen; or 62 grams of phosphorus burning in oxygen will give sufficient heat to raise the temperature of 370,000 grams, or 370 kilograms of water, 1°. To avoid dealing with large numbers it will be more convenient to consider a **Calorie** as the amount of heat required to raise the temperature of 1000 grams of water 1° C. This is the so-called **kilogram-calorie,** or the **big calorie,** and calorie is then written with a capital C. Thus *cal.* refers to the gram-calorie, *Cal.* refers to the kilogram-calorie. Hence the energy degraded in the form of heat when phosphorus burns in oxygen is equivalent to 370 Cals. This is represented in symbols, $2P+5O=P_2O_5+370$ Cals. Some represent gases by means of italics, solid by clarendon type, and liquids by ordinary type; and some put a bar over the symbol for gases, and under the symbol for solids; some also abbreviate the first equation $(2P, 5O)=370$ Cals.

Within certain limitations to be discussed later, the heat produced in a chemical reaction has been attributed solely to the degradation of chemical energy, but in many cases there are disturbing factors from differences in the physical properties of the initial and end products of the reaction, etc. For example—

(1) *Differences in the states of aggregation or volume of the initial and final products of the reaction.* Thus, a compound formed in a gaseous reaction may become liquid or solid. If the states of aggregation of the reacting constituents are not self-evident, they must be represented in the equation, otherwise, latent heats of fusion or vaporization may lead to ambiguity. Thus, with vapour at 0°, $2H+O=H_2O_{gas}+57·82$ Cals. means that the union of 2 grms. of hydrogen with 16 grms. of oxygen is attended by the evolution of 57·82 big calories when the water produced is in the form of steam; if the steam be condensed to a liquid at 0°, $2H+O=H_2O_{liq}+68·63$ Cals. The extra 10·81 Cals. represent the heat given out when 18 grms. of steam are condensed to a liquid; for solid ice, another 1·4 Cals. would have to be added to allow for the heat of solidification of 18 grms. of liquid water into ice.

It is necessary to distinguish clearly between the observed heat changes and the real heat changes due to the degradation of chemical energy as heat. The observed thermal value of a chemical reaction may be greater or less than that which corresponds with the chemical energy actually degraded during a given chemical reaction. For example, in the reaction between metallic sodium and chlorine gas, $2Na_{solid}+Cl_{2gas}=2NaCl_{solid}+194·6$ Cals., there is a large *contraction,* and work is done *on* the system by the pressure of the atmosphere; on the other hand, when hydrochloric acid acts on zinc, there is a comparatively large *expansion,* and work is done *by* the system against atmospheric pressure. With hydrogen and chlorine, when one volume of each elementary gas produces two volumes of hydrogen chloride, $H_2+Cl_2=2HCl+22·0$ Cals., there is no disturbing factor of this kind. Suppose that we start with a mixture of two volumes of hydrogen and one volume of oxygen, and finish with liquid water, there is a tremendous contraction in volume. This contraction occurs under atmospheric pressure (76 cm.). Hence, the atmosphere does work *on* the system, and that work appears as heat which raises the temperature of the system, and makes the observed heat of combination appear greater than it really is. The work can easily be calculated, and it is equivalent to 0·9 Cal.

One gram-molecule of steam occupies 22·3 litres. The gases from which the steam was formed occupied 1½ times this volume, *i.e.* 33·45 litres. A column of mercury 1 sq. cm. sectional area and 76 cm. long weighs $76\times13·59=1033$ grms.—since the specific gravity of mercury is 13·59. This pressure exerted along a path of 33·45 cm. will be $33·45\times1033$

gram-centimetres, or 33·45 × 1·033 kilogram-centimetres. Since 42·65 kilogram-centimetres are equivalent to one calorie, 33·45 × 1033 ÷ 42·65 = 80 cals., or 0·8 Cal. This discussion can be generalized. Every kilogram-molecule of any gas at 0°, occupying 22·4 cubic metres, when evolved during a chemical reaction, will absorb 0·542 Cal., and $0{\cdot}542(1+0{\cdot}00366\theta)$ cal. when the gas is evolved at the temperature θ. The heat absorbed in this way is evolved again when the gas is absorbed by a liquid or solid.

Correcting the observed heat of combination of hydrogen and oxygen 69·3 Cals. for the contraction due to the condensation of steam to liquid water, we get, per kilogram-molecule (18 kilograms) of water:

Apparent energy degraded in the reaction	69·53 Cals.
Energy due to the contraction	0·81 Cal.
Energy actually due to the reaction	68·72 Cals.

Consequently, when the gases are measured at constant pressure, not quite one per cent. of the heat of the reaction is due to work done on the gas by atmospheric pressure. Otherwise expressed, the thermal value of the reaction at constant volume will be 68·72, and at constant pressure 69·53. The difference is not great, and it is within the limits of experimental error when the results of different observers are compared.

Gas engineers [4] express the calorific power of a gas in terms of the number of pounds of water which can be raised 1° F. by the complete combustion of one cubic foot of the gas, at n.t.p., on the assumption that the water formed during the combustion is condensed to the liquid state at 212° F. This is the *gross calorific value.* If the steam formed by the burning gas remains as a gas, the latent heat of steam must be deducted from the gross calorific value, the result is termed the *net calorific value* of the gas.

The apparent failure of chemists to handle the great mass of thermochemical data satisfactorily is in part due to the fact that the real heats of chemical reactions are obscured by unknown latent heats, and heat spent in doing work of different kinds. W. Sutherland (1895) [5] claims that "the ideal condition in which thermochemical data should be presented, is that in which they relate to the heats of formation at constant volume of the gaseous products from gaseous elements." By direct calculation he makes an estimate of the heats required to vaporize a number of metals and non-metals, and also of their binary compounds. He corrects the heats of formation of a number of binary compounds so as to make them represent the heats of formation of gaseous compounds as the result of the combination of gaseous metals and non-metals. It is then found that the atoms in combining chemically evolve integral multiples of a quantity of heat 3·8; and that each atom in passing from the elementary to the combined state evolves a definite amount of heat irrespective of the other atoms with which it combines. This generalization has not yet been established directly from observed data; if it be true, allowance would have to be made for a third factor since the available evidence rather shows that the amount of heat evolved during a chemical combination also depends upon the mutual relations of the atoms in the molecules.

(2) *Reactions in solution.*—Again, if the reacting substances are in solution, a certain amount of heat may, or may not, be dissipated in the act of solution. For example, 13·7 Cals. are evolved when a dilute solution of sodium hydroxide is mixed with a dilute solution of hydrochloric acid. The dilute solution is represented by the suffix *aq*. Thus, $\mathrm{NaOH_{aq.}+HCl_{aq.}=NaCl_{aq.}+H_2O+13{\cdot}7}$ Cals. If the sodium chloride were prepared by passing hydrogen chloride gas into a dilute solution of sodium hydroxide, more heat is evolved, because 17·4 Cals. are evolved when 36·4 grms. of hydrogen chloride are dissolved in water: $\mathrm{NaOH_{aq.}+HCl_{gas}=NaCl_{aq.}+H_2O+31{\cdot}1}$ Cals.

(3) *Effects of allotropism and isomerism.*—Again, the physical and chemical condition of the reacting substances must be taken into consideration. At the beginning of his thermochemical studies, M. Berthelot [6] was careful to emphazise

the fact that *la quantité de chaleur dégagée dans une réaction quelconque mesure la somme des travaux chimiques et physiques accomplis dans cette réaction.* The heats of combination of hydrogen in oxygen and in ozone would not be the same because of the reaction $2O_3=3O_2+68{\cdot}2$ Cals. Allowance would have to be made for the extra energy associated with the ozone. The molecules of ozone are charged with energy at a higher potential than the molecules of oxygen, and when the ozone passes into ordinary oxygen, this energy is degraded in the form of heat. The fact that the molecules of ozone are charged with a large amount of energy is supposed to explain why ozone decomposes so readily into oxygen—sometimes with explosive violence. Precipitated silver (108 grms.), dried at 120°, liberates 0·76 Cal. when dissolved in mercury, while the same amount of silver beaten into a thin plate, and treated similarly, evolves 2·03 Cals. The extra energy stored in the hammered metal is liberated as heat during the dissolution in the mercury. If two similar springs, one wound, and the other unwound, be dissolved separately in acid, it is said that a greater amount of heat is developed during the dissolution of the wound spring, because the energy stored in the wound spring is degraded as heat during the dissolution in acid.

(4) *Preliminary dissociation of the reacting molecules.*—It will be observed that in the reaction between two gaseous elements A and B, with molecules respectively A_2 and B_2, the heat evolved or absorbed in breaking the molecules down into atoms is ignored. The assumption is virtually made that the heats of formation of the molecules of the elements from their atoms is zero. This cannot be justified even if we are ignorant of these constants. The observed heat Q of the formation of the compound AB from the molecules of its component elements is a resultant effect. Let q_a denote the heat of formation of the molecules A_2, and q_b the corresponding value for the molecules B_2. It then follows (from Hess' law, *vide infra*) that the heat of formation, q, of the compound AB from its elements is really $Q+\frac{1}{2}(q_a+q_b)=q$. An estimate of the thermal values of chemical reactions can be made when the equilibrium constant K is known. In this way, E. Briner (1914)[7] computed the heats of formation of a gram-molecule of the following elements :

	I_2	Br_2	Cl_2	S_2	H_2	N_2
Temperature . .	1390°	1050°	1670°	2177°	2427°	3500°
Equilibrium constant	0·66	0·06	0·01	0·50	0·10	—
Heat of formation .	32·4	57·0	113·0	120·0	130·0	150·0 Cals.

Hence, in the reaction $H_2+Cl_2=2HCl+44{\cdot}0$ Cals., the dissociation of the hydrogen molecules absorbs 130·0 Cals. and the chlorine molecules 113·0 Cals., or jointly, 243·0 Cals., so that the observed thermal value of the reaction 44·0 Cals. must be increased to 287·0 Cals., if the hydrogen chloride molecules are formed from atoms. Hence, the real thermal value of the reaction $H+Cl=HCl$ is not 22·0 but 143·5 Cals. Similarly,

	HCl	HBr	HI
Heats of formation from molecules, Q .	22·0	12·4	1·45 Cals.
Heats of formation from atoms, q . .	143·5	105·9	84·8 ,,

So far as the evidence goes, E. Briner (1914) concludes : **The heats of formation of all the compounds from the atoms of their elements are exothermal.** The observed heat of formation, Q, of a compound from its elements is therefore the difference between two magnitudes such that $Q=q-\frac{1}{2}(q_a+q_b)$, and a compound will appear to be exo- or endo-thermal according as the heat of its formation from atoms is greater or less than the mean of the heats of formation of the molecules of its component elements from their atoms. The heat of formation of the nitrogen molecule from its atoms is comparatively large, and accordingly, this element forms many endothermal (NO, N_2O, NCl_3, etc.) or feebly exothermal (NH_3, etc.) compounds. K. Fehrle (1918) has attempted to calculate the heat of a reaction on the assumption that the atoms of spherical molecules rotate about a common centre.[8]

(5) *Differences in the specific heats of the initial and final products of the reaction.*—Heat may also appear to be generated during a chemical reaction which is partly due to differences in the specific heats of the initial and final products of the reaction. If the latter be less than the former, some of the heat generated will be due to the fact that latent heat originally present can no longer be accommodated, so to speak, owing to the diminished capacity of the system for heat, and there is an output of heat during the reaction in excess of that corresponding with the degradation of energy. In illustration, J. Thomsen (1882) has shown that when ½N-sodium hydroxide is neutralized by an equivalent amount of hydrochloric acid, the thermal capacity of the system increases about 1·37 per cent. Hence, measurements of the thermal changes which occur during a chemical reaction should be supplemented by measurements of the heat capacities of the substances concerned in the reaction.

The temperature coefficient of a reaction.—Consider a reaction in which a substance A changes into B such that A→B. Let the reaction proceed at the temperature T_1 when Q_1 units of heat are absorbed; then heat the product B to the temperature T_2. If C_p and C_p' respectively denote the thermal capacities or molecular heats of the initial and final products of the reaction, the total energy absorbed in changing A at T_1 to B at T_2 is equal to $Q_1+C_p'(T_2-T_1)$. Again, the same final state can be obtained by heating A to T_2, and allowing the reaction to occur at that temperature. Let Q_2 denote the heat of the reaction at T_2, then it follows from the law of conservation of energy: $Q_2+C_p(T_2-T_1)=Q_1+C_p'(T_2-T_1)$; or $(Q_2-Q_1)/(T_2-T_1)=C_p'-C_p$. If the difference T_2-T_1 be taken indefinitely small, say dT, the difference Q_2-Q_1 will also be indefinitely small, say dQ, and at the limit, we thus obtain

$$\frac{dQ_p}{dT}=C_p'-C_p$$

where dQ/dT is the so-called *temperature coefficient of the reaction*. This equation is sometimes called—after G. Kirchhoff (1858)[9]—**Kirchhoff's equation.** The equation can be taken to mean that *at any assigned temperature, the change in the quantity of heat concerned in a reacting system, kept at constant volume, per degree rise of temperature is equal to the difference in the thermal capacities of the initial and final states of the system*, which for convenience can be written $-\Sigma C_p$. From Mayer's formula, $C_p-C_v=R-p$, it follows that $-\Sigma C_p=-\Sigma(C_v+R)$, and hence

$$\frac{dQ_p}{dT}=-\Sigma C_p;\text{ or, }\frac{dQ_p}{dT}=-\Sigma(C_v+R)$$

The influence of temperature on the heat of a reaction is *directly* determined by measuring the heat of the reaction at two different temperatures; the equation enables this magnitude to be calculated when the specific heats of the initial and final products of the reaction are known. If the molecular heats of the initial and final products of a reaction are the same, $C_v=C_v'$, and the temperature coefficient will be zero, otherwise expressed, the amount of heat evolved during the reaction will be the same at all temperatures. If C_p' be greater than C_p, the molecular heat of the product of the reaction will be greater than the original initial substance, the heat of the reaction will decrease with the rise of temperature; and if C_p be greater than C_p', the molecular heat of the product of the reaction will be less than that of the initial substance, the heat of the reaction will increase with rise of temperature.

EXAMPLES.—(1) According to L. Holborn and F. Henning (1907), the molecular heat of hydrogen, H_2, and of oxygen, O_2, is $4·68+0·00026T$, and of water, H_2O, $5·61+0·000717T$. Hence, the difference between C_v' and C_v for the reaction $2H_2+O_2=2H_2O$ at constant volume is $3(4·68+0·00026T)-2(5·61+0·000717T)=2·82-0·000654T$, and this is the temperature coefficient of the reaction.

(2) According to H. V. Regnault (1862), the molecular heat of hydrogen at constant

volume is $4{\cdot}82(\theta-18)$, of oxygen $4{\cdot}96(\theta-18)$, and of steam, H_2O, $18(\theta-18)$; and J. Thomsen observed that at 18°, the thermal value of the reaction $H_2+O=H_2O+67{,}484$ cals. What is the thermal value of the reaction $H_2+O=H_2O$ at 50° at constant volume? Here $H_2+O=H_2O$ is represented by $(4{\cdot}82+2{\cdot}48-18)\ (50-18)$ or $-10{\cdot}7\times32=342{\cdot}4$. Hence, the thermal value of the given reaction at 50° is 67,484 less $342{\cdot}4=67{,}142$ cals., nearly, when the volume of the system is the same at 50° as it was at 18°.

(3) According to L. Holborn and F. Henning (1907), the molecular heats of oxygen or carbon monoxide is $4{\cdot}68+0{\cdot}00026T$, and of carbon dioxide $5{\cdot}106+0{\cdot}00334T-7{\cdot}35\times10^{-7}T^2$. Hence show that dQ/dT for the reaction $2CO+O_2=2CO_2$ is $3{\cdot}828-0{\cdot}0059T+0{\cdot}000000735T^2$.

According to I. W. Cederberg,[10] the molecular heat of a vapour C_p and of solid or liquid C_p', at $T°$ is $C_p=2{\cdot}5R+1{\cdot}3125aT^{\frac{3}{4}}$; $C_p'=1{\cdot}3125a'T^{\frac{3}{4}}$, where a and a' are constants characteristic of particular substances. Consequently, from G. Kirchhoff's equation, for the heat of vaporization λ,

$$\frac{d\lambda}{dT}=2{\cdot}5R-1{\cdot}3125(a-a')T^{\frac{3}{4}}\text{; or, }\lambda=\lambda_0+2{\cdot}4RT-0{\cdot}75(a-a')T^{\frac{7}{4}}$$

where λ_0 denotes the latent heat of vaporization at absolute zero. Similarly, for the thermal value of a reaction Q_v,

$$\frac{dQ_p}{dT}=\Sigma2{\cdot}5R-\Sigma1{\cdot}3125(a-a')T^{\frac{3}{4}}\text{; }Q_p=Q_0+2{\cdot}5\Sigma RT+0{\cdot}75\Sigma(a-a')T^{\frac{7}{4}}$$

where Q_0 represents the heat of the reaction at 0°.

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§ 3. The Principle of Maximum Work

> In exothermic combination the sum of the specific energies of the component elements exceeds the specific energies of the compounds formed, while in endothermic combination, the specific energies of the compounds formed is greater than the aggregated specific energies of the components.—J. B. Stallo.

The heat developed during a reaction represents a certain amount of potential energy which was associated with the atoms in some way; and there is a temptation to generalize, as J. Thomsen [1] did in his paper *Die Grundzüge eines thermochemischen Systems*, in 1853, and assume that the total quantity of heat developed during a chemical reaction is a measure of the chemical affinity of the reacting substances—*die ganze durch eine chemische Wirkung erzeugte Wärmemenge ist also ein Masse für die durch dem Process entbundene chemische Kräfte*—and that every chemical change which can take place without the aid of external energy will be accompanied by an evolution of heat. *L'affinité était la cause*, said H. St. C. Deville (1860), *la chaleur dégagée est l'effet produit par cette force et lui est proportionelle.* The same idea was emphasized by M. Berthelot in his *Recherches de thermochimie* in 1869, when he boldly formulated his celebrated **principle of maximum work : Every chemical change which takes place without the aid of external energy, tends to the production of that system which is accompanied by the development of the maximum amount of heat**—*le principe du travail maximum : tout changement chimique, accompli sans l'intervention d'une énergie chimique étrangère, tend vers le production du corps ou du système de corps qui dégage le plus de chaleur.* To take an oft-cited mechanical analogy, the heat evolved by the impact of a falling body on the ground bears a definite relation to the height from which it fell, and heights might be measured by the heat developed by falling bodies if it were not that more convenient methods are available. With chemical reactions, the heat evolved is assumed by M. Berthelot to measure the mechanical work done, *i.e.* the loss of chemical energy; otherwise expressed, **elements with the stronger affinity for one another disengage most heat during chemical action.** The production of heat does not of course explain why the reaction takes place any more than the heat developed when a falling body strikes the earth explains gravitation.

It follows from Berthelot's principle that reactions which proceed spontaneously, when once they have started, liberate some form of energy, generally heat, during the progress of the reaction. In illustration, the heat of formation of calcium oxide is 131 Cals.; of lead oxide, 50 Cals.; and of mercuric oxide, 31 Cals. Calcium oxide is not decomposed by heating it to redness in a tube, either alone or in a current of hydrogen; lead oxide is not decomposed by heating it alone, but it is decomposed by heating it in a current of hydrogen; and mercuric oxide is reduced by either treatment. Again, the heats of solution of the following metals in dilute hydrochloric acid, per equivalent of metal, expressed in grams, are:

K	Na	Ca	Mg	Zn	Fe	Cu
61·8	57·2	54·3	54·1	17·4	10·7	−10 cals.

This agrees with the order of affinity for these metals deduced from other considerations. The negative heat of the reaction between copper and dilute hydrochloric acid corresponds with the fact that the action does not occur under ordinary circumstances, and the heat of the reaction has to be determined indirectly from the action of the acid on the oxide of the element in question.

There are some objections to the principle of maximum work as formulated by M. Berthelot. Lord Rayleigh, in a paper *On the dissipation of energy* (1875), showed that it is not the evolution of heat but the dissipation of energy which determines whether a chemical transformation is possible or not; no dissipation of energy, no transformation. Six years earlier, A. Horstmann[2] had also shown that the evolution of heat is not the real criterion for the possibility of chemical change. The main facts which indicate that something is wrong with Thomsen's and Berthelot's criteria, are as follows:

(1) The principle assumes that reactions proceed completely to an end, whereas in a balanced reaction, the reaction may be exothermal in one direction, and endothermal in the other. According to the principle of maximum work, the exothermal change ought to go completely to an end. Hence, the principle is not in agreement with facts.

(2) A reaction may not always proceed to the stage directly which develops the maximum amount of heat, as illustrated by successive reactions—*e.g.* the action of chlorine on sodium hydroxide gives a mixture of sodium hypochlorite and chloride which involves a smaller heat of reaction than if all the sodium was converted into

chloride. This objection might be met by insisting on the importance of the word *tends* in the enunciation of the principle, were it not for some evidence that the products are sometimes comparatively stable.

(3) In a series of compounds of the same type, those with the greatest heat of formation are not always the most stable. Thus, the heats of formation of the carbonates of silver and lead are respectively 25·96 Cals. and 72·88 Cals.; and of the nitrates of silver and lead, respectively 30·06 Cals. and 54·05 Cals. Hence, it might be concluded that the lead salts are the more stable when heated. This is not the case. Lead nitrate begins to decompose at 203° (20 mm. pressure), while the silver salt does not decompose at 350° (in vacuo) to any appreciable extent. It is probable that lead nitrate is the more stable salt when in solution.

(4) Several spontaneous chemical reactions are known to be accompanied by an absorption of heat. The heat of the endothermal reaction between iodine and hydrogen is nearly −6 Cals. The solution of many salts in water, the action of lead iodide on potassium sulphate, etc., are further illustrations of endothermal reactions which proceed contrary to the principle of Berthelot. When a solution of ammonium nitrate is mixed with a solution of potassium carbonate, −3·1 Cals. are absorbed in the formation of potassium nitrate and ammonium carbonate. No measurable amount of heat is absorbed or evolved when the two latter compounds are mixed, and hence, $K_2CO_3+2NH_4NO_3=(NH_4)_2CO_3+2KNO_3-3{\cdot}1$ Cals. This endothermal reaction has been explained by assuming that heat is evolved by the reaction between the potassium carbonate and ammonium nitrate, and that the dissolution of the products in water accounts for the absorption of heat. It may be true that the solution of salts in water involves (i) a physical process—the liquefaction of the salt attended by an absorption of heat; and (ii) a chemical process—the union of the salt with water. The cooling effect which attends the solution of many salts was once thought to be explained by saying that the heat absorbed in the first-named process exceeded that in the second.

(5) Many systems require a preliminary impulse to start the reaction, and hence, it would be necessary to introduce a clause to provide for this phenomenon.

The principle of maximum work must therefore be either amended or abandoned. For example, it has been amended to read: **Every change which takes place without the aid of external energy must do work, and a system which cannot do work is incapable of spontaneous change and is in stable equilibrium.** Hence, the criterion for spontaneous reactions is not the production of heat, for many spontaneous reactions absorb heat. The reaction between hydrogen and iodine can do positive work equivalent to +5·0 Cals. per gram-molecule of iodine, but the heat of the reaction is negative, −6·0 Cals. Further investigations have shown that it is not at all improbable that all chemical and physical reactions will be exothermal and complete at absolute zero, −273°; and consequently, the principle of maximum work will probably apply at that temperature. At ordinary temperatures, the principle is only approximately exact.

Explosive compounds.[3]—Chemical *union* is usually (not always) accompanied by the evolution of heat, and chemical separation by an absorption of heat. There are some exceptions—endothermal compounds—which are formed with an absorption of heat, and hence decompose exothermally. If the thermal value of a reaction is a measure of the available energy which is degraded as heat during the reaction, it follows that energy must somehow be stored up in endothermal compounds, and that such compounds are ready to give up energy to form another state of things with less potential energy. Just as a bent strip of flexible steel will fly back to its original position on being released, so does the potential energy of endothermal compounds tend to "fly back" so to speak, other compounds with less potential energy being formed. If a reaction takes place in a very short time it is frequently explosive. The non-explosibility of endothermal reactions corresponds with the fact that these reactions are self-cooled and brought to a standstill by the absorption of heat, whereas in exothermal processes, the reaction once begun, is rapidly accelerated by the self-heating which results from the evolution of heat. Other things being equal, the greater the evolution of heat, the greater the probability of an explosive reaction. Thus, with the oxalates of the metals—RC_2O_4—which decompose: $RC_2O_4=R+2CO_2$, where R is the symbol for one of the metals, Zn, Pb, Cu, Hg, Ag_2,

$$\text{Heat of decomposition}\ .\quad \underbrace{\overset{ZnC_2O_4}{-49}\quad \overset{PbC_2O_4}{-17}}_{\text{Non-explosive.}}\qquad \underset{\text{Doubtful.}}{\overset{CuC_2O_4}{+6}}\qquad \underbrace{\overset{HgC_2O_4}{+17}\qquad \overset{Ag_2C_2O_4}{+30\ \text{Cals.}}}_{\text{Explosive.}}$$

The heat of decomposition of a given compound will vary if the course of the reaction varies. Hence, a compound might decompose with explosive violence one way and non-explosively another—*e.g.* potassium chlorate. Nitroglycerol, too, when ignited by a flame burns quietly enough, but if it be subjected to a mechanical shock, or heated to a high enough temperature, it decomposes with spectacular violence.

It does not follow that because the heat of formation of a compound from its elements is positive, therefore the compound cannot decompose exothermally, since other products of decomposition may be formed, *e.g.* the heat of formation of liquid nitroglycerol—$C_3H_5N_3O_9$—from its elements is +415 Cals., and if it be decomposed back into its elements, the heat of decomposition must be −415 Cals. As a matter of fact, when the compound decomposes into carbon dioxide, water vapour, free nitrogen, and free oxygen, +1580 Cals. are evolved, not absorbed. The absorption of heat during the formation of an endothermal compound, from its elements, in general, shows that more energy is needed to tear asunder the atoms of the reacting molecules, say $A_2=A+A$, and $B_2=B+B$, than is given out by the union $2A+2B=2AB$. Take acetylene or cyanogen in illustration. Endothermal compounds are not therefore to be regarded as compounds which have been formed in opposition to the affinities of their constituent elements, because that would imply the existence of a *negative affinity* or a negative form of energy which is an idea quite outside the range of experience. If the atoms in the molecule of an endothermal compound repelled one another, it seems highly probable that the molecule would break up unless it were continually subjected to an external stress.

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§ 4. The Principle of Reversibility

While a transformation of energy is initiated only when equilibrium is unstable, yet it occurs always in the direction of a recovery of stability.—S. A. REEVE.

We do not know what is the exact relation between the thermal value Q of a reaction and temperature although we do know that the heat of a reaction alters with variations of temperature. It is assumed *pro tempore* that the relation between Q and the absolute temperature T can be represented by an expression of the form $Q=Q_0+\alpha T+\beta T^2$, when the numerical values of the constants α and β can be determined from measurements of Q at three or more different temperatures; Q_0 should represent the value of Q at absolute zero. For the reaction $CO_2+H_2=CO+H_2O$, it has been found that the constants assume these values: $Q=-10232$

$0{\cdot}1685T+0{\cdot}00101T^2$. When the heat of the reaction is zero, $Q=0$, and T ust be either 3100° or 2830°. Experiment shows that the second value is nearer e truth. Hence, the reaction must be exothermal below 2830°, endothermal ove, and thermally neutral near this temperature. The reaction $H_2+I_2=2HI$ endothermal below 320°, exothermal above, and thermally neutral near this mperature. This shows that **some endothermal compounds become exothermal** ; **higher temperatures**—*e.g.* the formation of hydrogen sulphide, and probably one, hydrogen peroxide, silver oxide, etc.; and conversely, **some exothermal ompounds become endothermal at higher temperatures**—*e.g.* the formation of licon hexachloride, the reaction between carbon dioxide and hydrogen, etc. hese changes correspond with a reversal of the thermal value of the reaction at he elevated temperature. The consequence is that a compound may be unstable t low temperatures, and stable at higher temperatures, and conversely, stable t low temperatures, and unstable at higher temperatures. Hydrogen peroxide nd ozone are examples of the former, water an example of the latter.

This reversal of the direction of a reaction with a change of temperature shows ow necessary it is to indicate the conditions of a reaction when stating the character f the change. Thus, carbon dioxide is usually a neutral gas, but it oxidizes zinc vapour at elevated temperature, and steam likewise is an oxidizing agent for iron and carbon at high temperatures.

The most stable compounds are usually but not always those with the greatest heats of formation. In a general way, the higher the temperature, the less the stability of exothermal compounds; and conversely, endothermal compounds generally become more stable as the temperature is raised, because an absorption of heat is necessary for their formation. Here is another illustration of the principle of reversibility previously discussed. **A compound formed with the evolution of heat is decomposed by the addition of heat**; water, for example, is an exothermal compound, and steam is decomposed when heated to a high temperature; the higher the temperature the greater the amount decomposed, or dissociated into its elements: $2H_2O \rightleftharpoons 2H_2+O_2$. For instance, W. Nernst and H. von Wartenberg (1906) found:

Temperature	1000°	1500°	2000°	2500°
Amount dissociated	0·00003	0·0221	0·5880	3·98 per cent.

This means that if 100 grms. of steam be heated to 2500°, at atmospheric pressure, the mixture will be in equilibrium when it contains approximately 96 grms. of steam, 3·55 grms. of free oxygen, and 0·45 grm. of free hydrogen. If the temperature be lowered some of the hydrogen and oxygen will recombine; if the temperature be raised more steam will be decomposed. When a substance decomposes with a change in the physical conditions—temperature, pressure, etc.—and the products of decomposition recombine when the original conditions are restored, the process of decomposition is said to be **dissociation.** Conversely, **a compound formed by the absorption of heat is decomposed by the withdrawal of heat**; for instance, ozone is an endothermal compound. The equilibrium conditions at different temperatures in the presence of oxygen are:

Temperature	0°	100°	500°	1000°	2000°	3000°
Per cent. of ozone	$9{\cdot}5\times10^{-16}$	$3{\cdot}5\times10^{-11}$	$9{\cdot}6\times10^{-5}$	$2{\cdot}2\times10^{-2}$	0·9	3·6

Quite an appreciable amount of ozone will be in equilibrium with oxygen at the higher temperatures, but at ordinary temperatures the amount is inappreciable. W. Ostwald (1891)[1] has said:

> It is generally believed that at a high temperature, such as that which exists in the electric arc, and in the sun's atmosphere, all compounds must be dissociated into their elements. This view is certainly not justified. On the contrary, what we actually know about the stability of compounds is that all compounds which are formed with an absorption of heat become more stable with rising temperatures, and *vice versâ*. Owing to the fact that the majority of compounds known to us are formed from their elements with the evolution of heat, and in consequence, become more unstable as the temperature rises,

it has been concluded that this is generally the case; but if we remember that acetylene and cyanogen—two compounds formed with the absorption of heat—are readily formed in quantity at the high temperature of the blast furnace, and in the arc light, we see the possibility that spectra occurring at high temperatures may belong to compounds which exist only at elevated temperatures.

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§ 5. Hess' Law

> Each element as well as each compound embodies a distinct and invariable amount of energy as well as a distinct and invariable amount of matter, and the energy is as constitutive and essential a part of the existence of such element or compound as its weight.—J. B. STALLO.
>
> The calorimeter is perhaps as necessary for determining the energy communicated to or from a system undergoing chemical change as the balance is for determining the masses affected.—C. J. REED (1901).

G. H. Hess (1840)[1] measured the heat developed during the formation of a compound made in several different ways and came to the conclusion that **the amount of heat evolved during the formation of a given compound is the same whether the compound is formed directly or in a series of intermediate stages**—*wenn eine Verbindung stattfindet, so Warmemenge constant, es mag die Verbindung direct oder indirect und zu widerholten Malen geschehen*—this is called **Hess' law.** This law tacitly assumes the law of conservation of energy; G. H. Hess seems to have regarded the law as axiomatic or self-evident without proof. It is a direct corollary from the law of conservation of energy, and is interesting since it came before J. R. Mayer or J. P. Joule. The principle may be illustrated by making calcium chloride by the action of quicklime on dilute hydrochloric acid. It is found that:

$$CaO+2HCl_{aq}=CaCl_{2aq}+H_2O+46 \text{ Cals.}$$

Instead of this, (i) first slake the quicklime, and $CaO+H_2O=Ca(OH)_2+15$ Cals.; then (ii) dissolve the calcium hydroxide in water, and $Ca(OH)_2+Aq=Ca(OH)_{2aq}+3$ Cals.; finally (iii) mix the lime with dilute hydrochloric acid, and $Ca(OH)_{2aq}+2HCl_{aq}=CaCl_{2aq}+H_2O+28$ Cals. These three steps in the formation of the solution of calcium chloride give a total $28+3+15=46$ Cals. as the heat of formation. The same result was obtained by the direct action of the dilute acid on quicklime.

Just as in mechanics the work done by a falling body is always the same whatever be the path described, and whatever be the time occupied in the descent, for the body may fall perpendicularly, down an inclined plane, down a parabolic or other path, yet the work in every case is measured by the perpendicular height it actually falls, so experiments have led to the inference that

(i) **The heat of formation of a compound is independent of its mode of formation.**—This result is but a particular application of the law of persistence of energy, and it may be expressed by saying that the change of energy of a system in passing from one state to another depends upon the initial and final states of the system, and not on the intermediate states. Starting with given raw materials, suppose that it were possible to make a compound by two different processes so that the total heat of formation of the compound formed by one of the processes were greater than that by the other process, then it would be possible to devise a process involving the creation or destruction of energy.

(ii) **The thermal value of a reaction is independent of the time occupied by the process.**—The thermal value of a reaction is the same whether it takes place slowly or quickly. In the former case, the heat may have time to be dissipated by conduction or radiation, and, in consequence, appear to be less than when the tion takes place quickly—it is here assumed, of course, that the system is not cted by external forms of energy. In practice, the risk of error, and consequently the experimental errors, are great with very slow reactions.

It also follows as a corollary to Hess' law that **the thermal value of a reaction e sum of the heats of formation of the final products of the reaction less the ts of formation of the initial products of the reaction.** Let Q denote the thermal e of a reaction, Q_1 the heat of formation of the initial products, and Q_2 of the l products of the reaction, then $Q=Q_2-Q_1$. This corollary to Hess' law is able because it enables the heat of formation of a compound from its elements be computed when a direct determination is either impracticable or very cult. This may occur when the heat evolved during the mutual action of two ls is difficult to measure accurately. For instance, if the heat of formation of on dioxide from carbon is $C+O_2=CO_2+96{\cdot}96$ Cals., and from carbon monoxide $+O=CO_2+68{\cdot}20$ Cals., we have $(C+O_2)-(CO+O)=96{\cdot}96-68{\cdot}20$, or 28·76 ., and consequently the heat of formation of carbon monoxide $C+O=CO$ 28·76 Cals. Again, it is required to compute the thermal value of reaction $SO_3+BaO=BaSO_4$, when measurements show that SO_3+H_2O $_2SO_4+18{\cdot}7$ Cals.; $BaO+H_2O=Ba(OH)_{2sol}+13{\cdot}9$ Cals.; and that $Ba(OH)_2$ $_2SO_4=BaSO_4+2H_2O+18{\cdot}4$ Cals. Hence, $BaO+SO_3=BaSO_4+51{\cdot}0$ Cals. in, to determine the heats of formation of hydrogen iodide and hydrogen bromide n it is known that $Cl+HBr=HCl+Br_{liq}+12{\cdot}5$ Cals., and that $Cl+HI=HCl$ $_{olid}+28{\cdot}2$ Cals.; and that the heat of formation of hydrogen chloride is 22·0 . In the first case, $22{\cdot}0-12{\cdot}5=9{\cdot}5$; and in the second, $22{\cdot}0-28{\cdot}2=-6{\cdot}2$. ce, $H+Br=HBr+9{\cdot}5$ Cals. and $H+I=HI-6{\cdot}2$ Cals.

imilarly, the thermal value of a reaction can be calculated when the heats of ation of the different substances which take part in the reaction are known. s, by consulting some book of Laboratory Tables we can write the heats of ation of the substances concerned in the reduction of lead oxide by carbon oxide:

$$\begin{array}{l} CO+PbO=CO_2+Pb \\ 29{\cdot}2 \quad 50{\cdot}3 \quad 97{\cdot}3 \text{ Cals.} \end{array}$$

$29{\cdot}2+50{\cdot}3=97{\cdot}3+x$, where x denotes the thermal value of the reaction; equently, $x=97{\cdot}3-(29{\cdot}2+50{\cdot}3)$, or 17·8 Cals., and the reaction is accordingly bolized: $CO+PbO=CO_2+Pb+17{\cdot}8$ Cals. The heat of formation of silver ride, AgCl, is 29 Cals. and of silver bromide, AgBr, 27·1 Cals. Is the reaction $r+Cl=AgCl+Br$ likely to occur? The heat of the last reaction is 29—27·1 9 Cals., and hence the reaction is likely to take place. Further, if copper preates silver from a dilute solution of silver nitrate, $2AgNO_{3aq}+Cu=Cu(NO_3)_{2aq}$ $g+25{\cdot}3$ Cals., will zinc precipitate silver from dilute silver nitrate when it is wn that $Cu(NO_3)_{2aq}+Zn=Zn(NO_3)_{2aq}+Cu+61{\cdot}7$ Cals.? Probably yes, because heat of the reaction $61{\cdot}7-25{\cdot}3=36{\cdot}4$ Cals. Both conclusions are in agreement observations. *The energy of a chemical reaction is not primarily inherent in any f the reacting components, but belongs to the system as a whole*; this energy may epresented as the sum of two or more constants which are peculiar to the ective elements involved in the reaction.

XAMPLES.—(1) It is required to compute the heat of formation of $K+Cl=KCl$, when known that the heat of formation of $K+O+H+Aq=KOH_{aq}+117$ Cals.; $2H+O$ $O_{liq}+68{\cdot}4$ Cals.; $H+Cl_{aq}=HCl_{aq}+39{\cdot}3$ Cals.; heat of solution of KCl in r, $-4{\cdot}4$ Cals.; and that $KOH_{aq}+HCl_{aq}=KCl_{aq}+H_2O+13{\cdot}7$ Cals. This last ion can be written: $(H+Cl+Aq)+(K+O+H+Aq)-(K+Cl+Aq)-(2H+O)$ 13·7 Cals. Consequently, after substituting the given data, and transforming algeally, we get $K+Cl+Aq+101{\cdot}6$ Cals.; and hence, $K+Cl+Aq=KCl_{aq}+101{\cdot}6$

Subtract the heat of solution $-4{\cdot}4$ Cals., and we get $101{\cdot}6-(-4{\cdot}4)=106$ Cals. for thermal value of the reaction $K+Cl=KCl$. It will be noticed that the solution of ssium chloride in water is an endothermal process, and hence, the heat of formation of $_{aq}$ is less than that heat of formation of KCl.

2) Show that when silver chloride, AgCl, is mixed with hydriodic acid, HI, silver

iodide, AgI, and hydrochloric acid, HCl, will probably be formed when it is known that the heat evolved during the formation of silver iodide is $Ag+I=AgI+18{\cdot}6$ Cals. of silver chloride, $Ag+Cl=AgCl+34{\cdot}8$ Cals.; hydrochloric acid (aqueous solution), $H+Cl_{aq}=HCl_{aq}+39{\cdot}3$ Cals.; and hydriodic acid in aqueous solution, $H+I=HI_{aq}+13{\cdot}2$ Cals. Ansr. 10·0 Cals. will be evolved during the reaction $AgCl+HI=AgI+HCl$, and reactions generally occur which are attended by the evolution of an appreciable quantity of heat.

The heat of formation of many substances has been determined from the **heat of combustion,** *i.e.* the heat which is developed when the substance is completely oxidized. The method is particularly applicable for compounds whose heats of formation cannot be directly determined, either because the reaction is too slow or because the compound cannot be formed directly from its elements. It is, however, necessary to know the heats of formation of the products of combustion as well as the heat of combustion.

EXAMPLE.—The heat of combustion of methane, CH_4, is 213·5 Cals., and the heats of formation of the carbon dioxide 96·96 Cals.; and of water, 68·6 Cals. Hence, since $CH_4+4O=CO_2+2H_2O+213{\cdot}5$, $Q_2-Q_1=$ the required heat of formation of methane is $(96{\cdot}96+2\times68{\cdot}6)-213{\cdot}5=20{\cdot}26$ Cals.

The heats of combustion of a few compounds are indicated in Table II. Heats of combustion are dependent on constitution, so that isomeric compounds may have different values; similar remarks apply to the heats of combustion of polymeric substances. Each radicle in a compound has a definite heat of combustion, called its **thermochemical constant**—given the thermochemical constants of the constituents of a molecule, the heats of combustion follow additively. Conversely, given the heats of combustion of a compound, the presence of particular radicles can be inferred.[2] The principles just outlined can thus be applied: (1) To the determination of the thermal values of reactions which cannot be conveniently determined by calorimetric measurements; and (2) To the prediction of various chemical transformations.

TABLE II.—HEATS OF COMBUSTION.

	Heat of combustion.	Heat of formation.		Heat of combustion.	Heat of formation.
Methane, CH_4	213·5	18·5	*o*-Xylene, C_8H_{10}	1084·0	20·3
Ethane, C_2H_6	372·3	23·3	Naphthalene, $C_{10}H_8$	1241·8	−27·4
Propane, C_3H_8	528·4	30·5	Anthracene, $C_{14}H_{10}$	1694·3	−33·3
Butane, C_4H_{10}	687·2	35·0	Methyl alcohol, CH_3OH	170·6	61·4
Ethylene, C_2H_4	341·1	−14·6	Ethyl alcohol, C_2H_5OH	325·7	69·9
Acetylene, C_2H_2	313·8	−51·4	Methyl ether, $(CH_3)_2O$	344·2	51·5
Benzene, C_6H_6	784·1	−4·0	Ethyl ether, $(C_2H_5)_2O$	651·7	70·5
Toluene, C_7H_8	933·1	2·3			

It must be borne in mind that all deductions from these principles are "subject to revision" owing to our ignorance of all the factors concerned in the reactions. It might also be well to emphasize the fact that there is a relatively large error of experiment in the determination of the heats of chemical reactions. The numbers obtained by different experimenters vary, sometimes considerably. For instance, the heats of combustion of acetylene and ethylene are variously given:

	W. G. Mixter (1901).	M. Berthelot (1893).	J. Thomsen (1884).
Acetylene	313·8	315·7	310·0 Cals.
Ethylene	345·8	341·1	333·4 Cals.

These discrepancies are sometimes of considerable magnitude. For example,[3]

J. Thomsen found the heat of the reaction between lead acetate and zinc to be 34·95 Cals., P. Favre gave 31·2 Cals., and T. Andrews, 37·71 Cals.—a total variation between the extremes of 6·51 Cals. The heat of formation of cupric oxide, CuO, and therefore of all salts derived from it, is 37·16 Cals. according to J. Thomsen; 43·77 Cals. according to P. A. Favre and J. T. Silbermann; and 38·30 Cals. according to T. Andrews. The heat of formation of ferric chloride, $FeCl_{3}aq$, is variously given by J. Thomsen at 99·95 Cals., by P. A. Favre and J. T. Silbermann at 106·76 Cals., and by T. Andrews at 102·06 Cals.

These errors are magnified very much when the thermal value of a reaction is estimated indirectly by the application of Hess' rule.

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§ 6. The Degradation or Dissipation of Energy

There can be little question that the principle of the dissipation of energy implicitly contains the whole theory of chemical combination.—P. G. TAIT.

Water may be transported from the top of a mountain to the valley below in a variety of ways; it may come down in underground channels, rivers, or rain; or in the form of snow, glaciers, or an avalanche. So may energy pass from a state of high to a state of low potential in many and various ways, giving rise to mechanical, thermal, actinic, chemical, electrical, or magnetic phenomena. In reality, the so-called different forms of energy correspond with the tendencies which any given system may have to change in particular directions. If there is a tendency for the different parts of a system to come into closer contact, we have gravitation and cohesion; if there is a tendency to an equalization of temperature, thermal energy; and when there is a tendency to undergo transformation into another substance, chemical energy. Hence, the definition: **a chemical reaction is one mode by which energy can be transferred from one state to another.** Energy cannot be developed from nothing, but it is derived from certain natural reservoirs—living beings, falling water, moving air, fuels, etc.—in which energy is accumulated; and certain machines—the steam engine, galvanic battery, turbine, etc., draw from the reservoir and transform one form of energy into another form without changing the total amount of energy. Thus, heat, light, and electricity may be liberated during chemical changes. To avoid the assumption that this energy comes from nothing, it is postulated that the original system contained a definite amount of free or available energy—chemical energy. As H. Hertz (1894) expressed it: In order to explain what is palpably before our eyes we are compelled to imagine behind the things we see, other invisible things, and to search behind the barriers of sense for a secret hidden accomplice. The hidden factor is here conveniently assumed to be potential or chemical energy.

Not dead is matter though inert it seems,
A hidden life ensouls the eternal mass.—C. A. LANE.

If a substance can unite with another, it is said to possess chemical energy, because it can do chemical work; and conversely, substances which cannot combine chemically with other substances have no available chemical energy, for they can do no chemical work. During a chemical reaction, the chemical energy is transformed into an equivalent amount of some other form of energy which is usually, though not always, heat. Hence, the relation between chemical energy and heat (thermal energy) is an important subject, which, for convenience, is called **thermochemistry**; and the general study of heat as a form of energy is called **thermodynamics.** Chemical energy may also be transformed into electrical energy during a chemical reaction, and that branch of chemistry which deals with the relation between chemical energy and electricity (electrical energy) is called **electrochemistry.** Just as chemical changes which are always accompanied by an evolution of heat are called *exothermal reactions*, so reactions which are accompanied by an evolution of electrical energy have been called *exo-electrical reactions;* and conversely, for *endothermal reactions* and *endo-electrical reactions*. So far as we can tell, in all phenomena, the same energy is at work, and the same fundamental principles apply to all the specialized forms of energy. There is not a set of mutually exclusive laws for chemistry, another set for electricity, another for heat or for mechanics. Convenience alone dictates specialized versions of the same fundamental laws for electricity, chemistry, etc. Strictly speaking, no form of energy can be singled out and called potential energy, since each form of energy is potential with respect to the other forms into which it can be converted.

The factors of energy.—Water will flow from one vessel to another only when there is a *difference in the level* of the liquid in the two vessels. The actual volume of the water in either vessel does not matter. Again, heat will pass from one body to another only when the temperature of the one is higher than the temperature of the other. The flow of heat is not determined by the quantity of heat in either the hot or the cold body, but rather by the *difference in the temperature* of the two bodies. The heat in the fire-box of a locomotive can do work, not because it is hot, but because it is hotter than its surroundings. In his well-known *Réflexions*, N. L. S. Carnot (1824)[1] compared the production of work by *une chute d'eau* with the fall of heat from a higher to a lower temperature, and referred to the latter as *une chute du calorique*. Again, if two reservoirs of gas be connected by a cylinder fitted with a sliding piston, the motion of the piston will not be determined by the volume of the reservoir, nor by the quantity of energy contained in the gas, but it will be determined by the *difference in the pressure* of the gas in the two cylinders. Air confined in a closed vessel at atmospheric pressure might appear to possess no energy because it can do no work; but reduce the pressure of the surrounding air, and the air confined in the vessel is then capable of performing work.

It is therefore possible to show that each form of energy has a dual nature, and that every form of energy appears as if it were of two dimensions, for it can be compounded of two factors [2]—mass and difference of level; thermal capacity (or maybe entropy) and temperature; volume and pressure of gas. The one factor is called the **quantity, mass, or capacity factor,** and the other, the **strength, or intensity factor.** The two factors are combined not as a sum but as a product, for if one factor diminishes towards zero, the other increases towards infinity:

$$\text{Available energy} = \text{Capacity (quantity) factor} \times \text{Intensity (strength) factor}$$

To pass from generals to particulars, it is convenient to say that with **volume energy,** the factors are pressure and volume; with **surface energy,** the factors are surface area and surface tension; with **distance energy,** distance and force; with **kinetic energy,** mass ($\frac{1}{2}m$) and velocity (V^2); with **electrical energy,** quantity and difference of potential; etc. When the capacity factor is high and the intensity factor low, more or less work may be got from that form of energy than if the capacity factor is low and the intensity factor is high—all depends on the relative magnitudes of the two different factors; and two different sources of energy with very different intensity and capacity factors may be able to perform the same amount of work. If $C_1, C_2, \ldots$ denote the capacity factors, and $I_1, I_2, \ldots$ the corresponding intensity factors of the different forms of energy associated with a system, then, when the respective intensity factors change by small amounts $dI_1, dI_2, \ldots$, the work dW done by the system will be equivalent to

$$dW = C_1dI_1 + C_2dI_2 + \ldots; \text{ or } dW = \Sigma C.dI$$

The degradation of energy.—The law of conservation of energy does not describe the direction in which a change will occur. It simply states that the amount of energy lost by one body must be precisely equal to that gained by another; it does not say whether heat will flow from a hotter to a colder body or conversely. Experience answers the question. Heat will be conducted from a hot to a colder dy ; salt will diffuse from a solution of high to one of lower concentration ; and nerally, the trend of natural processes is all in one direction. This general tendency n be formulated mathematically in terms of the transformations of energy which me into play, and the relations which determine the final state of equilibrium. is enables a prediction to be made as to the direction in which any given chemical physical process will progress.

In 1856, R. Clausius[3] laid down the hypothesis: *Die Wärme kam nicht von lbst aus einem kälteren in einen wärmeren Körper übergehen*—**heat cannot sponta-eously pass from a body at a low to a body at a higher temperature,** but it can e forced to do so either (i) by the application of energy from an external supply, *g.* freezing machines and refrigerators raise heat from a cold to a hotter body by erforming work on the system ; or (ii) by a double transformation first into another orm of energy, say mechanical motion, and back again into heat. The pre-eding is one of the protean forms under which the **second law of thermodynamics** r **the second law of energetics** can be stated ; it is also known as **Carnot's principle,** ecause N. L. S. Carnot first developed the idea in his celebrated memoir entitled, *Réflexions sur la puissance motrice du feu,* published in Paris in 1824. W. Ostwald (1892) expressed the same idea in his *Studien zur Energetik* previously cited : **The unlimited conversion of energy without intensity differences is impossible.** Several attempts have been made to deduce the second law from the first by W. J. M. Rankine, S. H. Burbury, C. Szily, R. C. Nichols, L. Boltzmann,[4] etc. R. Clausius says that the second law is not contained in the first.

Just as water will always run down from a high to the lowest level that circumstances will permit, so generally, **in all processes with which we are acquainted, every known form of energy at a high potential always tends to run down to energy at the lowest potential circumstances will permit—the law of minimum free energy**—and one of the most interesting facts in connection with all natural changes is this constant running down or degradation of energy. The law of minimum free energy is analogous with the counter-statement in mechanics that a body will always fall as far as it can, and that if it be free to fall, it will fall. The energy so degraded has no longer a capacity for doing work, and the definition of energy as a capacity for work is therefore faulty, for the principle of the conservation of energy cannot be taken to mean that as the result of a given transformation the capacity of the system to do work has remained constant.

Energy may be degraded slowly in a long series of transformations, or suddenly in one bound ; in either case, the free energy under the new conditions becomes less available for doing work. **Every change which takes place in nature does so at the cost of a certain amount of available energy.** When we inquire whether or not a certain transformation can take place, the question to be answered is : Will the occurrence involve the degradation of energy ? If not, the transformation will not take place under the given conditions. A moment's reflection will show that in every transformation, the intensity factor will be diminished, and energy then becomes less available for doing work. **The intensity factor of energy controls the direction of a given transformation,** while the capacity factor largely controls the quantity of change, that is, the amount of work performed during the change. Water placed in a series of vessels in communication with one another will come to rest when the surface of the water is at the same level in both vessels. Difference of level here means that the gravitational energy has a different intensity in each vessel. An electrical current will flow whenever there is an inequality of the intensity factor—*i.e.* a difference of potential—at different parts of the circuit. **If the intensity factors of any particular form of energy in a system are not equal, the system will be in a state of unstable equilibrium ; such a condition will not be permanent, and energy will flow, so to speak, from one part to another until the different intensity factors become equal.**

This principle is true for any closed system, and if the universe is a closed system, it must also dominate the universe. It has been pointed out that the earth is only part of the universe, and it is continually gaining energy from the sun by radiation, and losing energy, also by radiation from itself. Accordingly, owing to the universal and unceasing tendency towards a degradation of energy, the universe is steadily passing from a state in which energy at a high potential will be uniformly distributed at one uniform low potential. The universe will then have a dead inert motionless existence at a uniform temperature. Then follows the so-called *thermodynamic paradox*—energy is continuously being degraded ; the past duration of the universe extends through infinite time, therefore, unless energy at a low potential is being restored to a higher potential, the degradation of energy should have been completed long ago. Hence, it has been postulated that by some hitherto unrecognized phenomenon, unavailable energy at a low potential is being raised to available energy at a high potential, and that the second law of thermodynamics is being somewhere and somehow reversed. It is, however, mere speculation to assume that because the second law of thermodynamics is based on experience, and that there *may be* localities in the universe where it does not apply, or that it *may not* have held good in past times, therefore there *must be* a source for the restoration of degraded energy. H. Elliot (1895) argued that it is just as likely that the universe is infinite as that past time is infinite, and that even the lapse of infinite time would not involve the extinction of all differences of potential.

An ancient philosopher—Heracleitus of Ephesus—has said that πavτà ῥεῖ—all things are in motion, and it might be added that that motion always involves the degradation of energy. The transformation of energy in a given system only ceases when the available energy has run down to the level of its surroundings. The system is then said to be in a **state of stable equilibrium.** The stability of a system thus indicates how the system is related to its surroundings. For stability, a system must be in equilibrium with its environment. A physical or chemical change will progress until the different forms of energy which come into play are exactly balanced, and this determines the final state of equilibrium of the system.

The condition of equilibrium.—In an isolated system, the condition necessary for the equilibrium of any form of energy is that its intensity shall have the same uniform value throughout. For instance, if the opposite sides of a bar of metal have a different temperature, heat will be conducted from the hot to the cold end until the temperature is everywhere the same ; a mass of gas will be in equilibrium when it has one uniform pressure (of course neglecting the effect of gravitation, which may be regarded as extraneous energy) ; etc. **When one form of energy is exactly balanced by another form, the system is in equilibrium, and a virtual change of one form of energy will be balanced by a corresponding change in the other form or forms of energy.** *Virtual change* is a convenient term often used to represent an infinitesimally small change " existing in effect, but not in actuality." It is not clear at first sight what this phrase means. A virtual change is not a real change, but rather an abstraction, and in place of " virtual," possible or potential might be substituted.[6] For instance, if a ball be suspended by an elastic string, gravitation pulls the ball downwards, and elastic energy pulls it upwards ; a virtual displacement of energy will occur if the ball were pulled an infinitesimally small distance downwards, and the gravitational energy so expended were exactly counterbalanced by the gain in the opposing elastic energy. The algebraic sum of the energies involved in a virtual displacement of equilibrium must be zero when the system is in equilibrium. This is the so-called **principle of virtual work,** which is symbolized :

$$\Sigma dE=0\ ;\ \text{or,}\ \Sigma dW=0$$

where E and W respectively denote the energy and work performed ; and the summation symbol Σ is intended to show that the algebraic sum of all the correlated forms of energy is to be taken. For example, in a reversible chemical reaction in equilibrium, the reacting substances and the products of the reaction are to be taken ; the energy of the one increases and of the other decreases by a virtual displacement of equilibrium. In a system where the mechanical forms of energy capable of doing work are balanced, the principle of virtual work states that the sum of the virtual work performed by the forces will be zero, that is, $\Sigma dW=0$. The principle of virtual work was described by J. Bernoulli in 1717, and developed by J. L. C. Lagrange in 1788. Its application to chemistry was emphasized by W. Ostwald in 1892.

The law of mass action has been deduced from this principle. When a system of reacting substances is in equilibrium, the volume energy of the component substances is $\Sigma vdp = 0$. Let p and v respectively denote the partial pressures and volumes of the initial substances, and P and V corresponding values for the products of the reaction. From Boyle's law, $pv = nRT$, and $p = nRT/v$; by differentiation, $dp = -nRTdv/v^2$; by substitution of dp in the condition of equilibrium, $-RT(n\Sigma d\log v - N\Sigma d\log V) = 0$. Consequently, at a constant temperature, replacing the molecular volumes v by their reciprocals, the molecular concentrations c and C, we obtain $n\Sigma d \log c - N\Sigma d \log C = 0$; and on integration, $\Sigma \log c^n + \log k = \Sigma \log C^N + \log k'$, where k and k' are integration constants; and n and N respectively denote the relative number of gram-molecules of the initial and final products of the reaction. The last expression can be represented $k\Sigma c^n = k'\Sigma C^N$, or

$$\frac{c_1^{n_1}c_2^{n_2}\ldots}{C_1^{N_1}C_2^{N_2}\ldots,} = \frac{k'}{k} = K$$

Expressed in words, in an opposing reaction, at equilibrium, the product of the concentrations of the original substances is equal to the product of the concentrations of the end-products of the reaction and the equilibrium constant, or, the effect of each reacting substance is proportional to its concentration. This is the famous law of mass action of Guldberg and Waage. J. Larmor and T. B. Robertson[7] have shown that the mass law of Guldberg and Waage can be derived from the gas law $pv = RT$, or $p(v-b) = RT$, where b is constant.

Metastable equilibrium.—We are very familiar with systems in which the energy has not run down to the level of its surroundings and yet everything appears to be in a state of stable equilibrium. The stability is only apparent. As a matter of fact, available energy does not always *of itself* run down to the level of its surroundings. For some unknown reason, an influence—conventionally called *chemical inertia, hysteresis, or passive resistance*—prevents the initiation of the process of degradation of energy, a preliminary impulse is needed to start the process of degradation in motion. Passive resistance is here used as a grouping or classification term. It explains nothing. Just as the throttle-valve of a steam-engine must be moved before the engine can start on its journey, or some watches, after winding, require a slight shake before they start, so may a preliminary impulse be required to set the process of the degradation of energy in motion. The flapping of an eagle's wing may suffice to start an avalanche rolling down the mountain side; with gunpowder, the preliminary impulse may take the form of heat; with a mixture of hydrogen and oxygen, an electric spark, or the mere presence of spongy platinum; with a mixture of hydrogen and chlorine, a flash of light, or the addition of a piece of charcoal; with fulminate of mercury, a sudden shock; while the addition of a minute crystal will start the process of crystallization in a supercooled solution of sodium thiosulphate. We may thus have **a state of metastable, apparent or false equilibrium,** as well as a state of true or stable equilibrium. We naturally inquire: Is there any test to distinguish between states of real and states of apparent equilibrium? We know that if a gas is in equilibrium with regard to volume and pressure, it will satisfy the conditions of Boyle's law; volume and temperature, Charles' law; etc., but we have not always such useful tests at our disposal.

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§ 7. Bound and Free Available Energy

> Matter, whatever it is, must be held to be so adorned, furnished, and formed that all virtue, essence, action, and motion may be the natural consequence and emanation thereof.—FRANCIS BACON.
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> Energy is the result of a particular state or condition of matter in virtue of which any definite portion may effect changes in any other portion.—C. F. BARKER (1892).

Mechanical and other forms of energy can often be transformed completely into heat, but the reverse operation is subject to certain limitations since a certain proportion always escapes conversion and is lost. Similarly, when a system undergoes a chemical or physical change, a certain portion of the energy is simultaneously transformed into heat. The loss or leakage of energy does not mean that energy is annihilated; there is nothing to suppose that the law of the perdurability or conservation of energy is invalid. The so-called loss of energy means that part of the energy is degraded—by friction, viscosity, etc.—from a high to a low potential, and the capacity of the transformed energy for work is diminished. It is impossible to transform a quantity of heat into work without an accompanying change in the condition of a portion of the energy of such a nature that its capacity for work is correspondingly diminished. It therefore follows that the principle of conservation of energy is incapable of experimental demonstration, for it is only possible to measure the ratio in which the transformation of energy from one form to another is accomplished. Again, the definition of energy as capacity for work is not altogether satisfactory because a fractional part of the heat does not conserve its capacity to perform work when a transformation of heat into work is attempted.

H. von Helmholtz, in his *Ueber die Thermodynamik der chemischen Prozessen* (1882),[1] pointed out a useful concept by showing that the total available energy of a system appears as if it were on two different planes—one portion, called the **free energy** of the system, is capable of doing chemical, electrical, or mechanical work; and a second portion, called the **bound energy,** is rendered unproductive during the change, for it is frittered away as heat. The latter can be regarded as energy which must of necessity be wasted during the operation, or as the **energy-cost of the reaction.** The free energy of a system is a measure of the work which can be performed by the chemical process; the bound energy represents the energy lost by leakage during the reaction, because nature has determined that the rate of exchange, so to speak, is against the conversion. This must not be taken to mean that the energy of a body or system of bodies is not homogeneous, and can be separated into two parts with different properties; for the proportion of free to bound energy in any given process changes with the temperature. The actual proportion appears to be determined by the changes in the kinetic energy of the molecular or atomic motions; by the separation of the molecules against intermolecular attractions; by changes in the rotational or vibratory energy of the atoms; by alterations in the electrical state or thermal capacity of the molecular systems concerned in the reaction; etc. Again, the free energy, or the energy which can perform work during an isothermal change, is not always derived from the internal energy, thus, the internal energy of an approximately ideal gas does not change during an isothermal expansion when the gas performs no external work.

Free energy.—The maximum amount of work a reaction can do when it is carried out reversibly at a constant temperature, is called the free energy of the reacting system. If the free energy of a spontaneously occurring natural process were negative, it would progress without absorbing energy from its surroundings, and on being reversed (by the addition of heat), it would transform this heat into work, and a perpetual fount of energy would be available. This is in conflict with the law of excluded perpetual motion; and it is accordingly inferred that every spontaneous process must do work, and that a system incapable of doing work is incapable of spontaneous change; such a system must also be in a state of stable equilibrium, and accordingly, **for stable equilibrium, the free energy of a system must have a minimum value.** If a system can do no work, it cannot change except by the application of external energy. **The decrease in the free energy of a reacting system is a measure of the work which can be performed by the chemical process.** Free energy is thus synonymous with the ability to perform work. That system which can perform the greatest amount of work, when it is carried out isothermally and reversibly, will be most likely to occur; *i.e.* **of all possible chemical changes, that which involves the greatest decrease in the free energy will be most likely to occur.** Given a table of the free energy changes which occur during the formation of various compounds from their elements, by different processes, it would be possible to calculate the change in the free energy attending other reactions, just as in ordinary thermochemical calculations, the thermal value of a given reaction can be calculated from the heat of formation of the various reacting components. Tables of the free energy may thus take the place of tables of the heats of formation of different compounds, and be employed to predict (i) The maximum work which may be expected from a given reaction; (ii) The minimum amount of work which would be necessary to produce a certain reaction; (iii) The circumstances under which a given reaction will progress; and (iv) How nearly a given reaction will run to an end.

The available, total, or internal energy.—The absolute amount of energy of a substance cannot be measured because all measurements are concerned with differences of energy existing between different bodies or systems of bodies, or between a substance in two different states. This is not particularly a disadvantage, since it is all that is required in the present state of science. For convenience, the total available energy involved in any reaction is considered to be the algebraic sum of the free and bound energy. The total intrinsic or internal energy U—sometimes called the potential energy—transformed in a reaction is measured in a calorimeter as the heat of the reaction Q when due allowance is made for external work done on or by the reacting system against atmospheric pressure. In the latter case, the *potential energy* of the system is the difference between the heat energy Q and the external work. The total energy must not be confused with the free energy. The whole of the free energy in any given system may disappear without diminishing the total energy of the system. If U represents the total energy of an isolated system, W the free, and q the bound energy, then, by the law of the conservation of energy, U is constant; and if W becomes zero, $q=U$. In that case, the Q units of energy of the system can do no work. On the other hand, if $q=0$, then $U=W$, and all the energy of the system is free and capable of doing work. If $q=\frac{1}{2}U$, half the total energy can do work, and half will not be utilizable for doing work. M. Berthelot's principle of maximum work assumes that the total energy of a chemical reaction is equal to the free energy, that is, to the energy available as work, when the work is carried out reversibly. There is nothing to show that $U-W=0$, and accordingly, heat may be absorbed or evolved when a reaction is carried out under these conditions. It is not the maximum production of heat energy which determines if a reaction will necessarily occur, since some spontaneous reactions absorb heat.

Reversible and irreversible processes.—When a body has fallen a certain distance in vacuo, it would rise again the same distance as it fell if its velocity could be reversed; and by relieving the pressure on liquid water confined in an air-tight cylinder, fitted with a frictionless piston, and maintained at a constant temperature, the water could all be vaporized, and by reversing the pressure, the vapour could be condensed back to its original liquid state. In reality, a frictionless piston is impossible, and only when the pressure required to compress the vapour is exactly equivalent to that required for the expansion is the process considered to be strictly reversible. Again, by raising the temperature of a closed vessel containing calcium carbonate, the compound will dissociate, and by lowering the temperature, the products will recombine to form the original compound; similarly, if a cylinder contains a saturated solution of, say, potassium nitrate in the presence of some of the undissolved salt, the solution will alter its strength by diffusion, if the temperature be slowly raised; and if slowly cooled to its former temperature, the original condition will be restored. If there were any leakage of energy due to the viscosity of the solution, so that more heat energy were required for the heating than for the cooling, the process would not be considered strictly reversible. A process is considered to be strictly reversible only when it can be made to pass back from its final to its initial stage successively, and in the reverse order through all the stages traversed in the direct process by the application of external agents which are equal in magnitude but in opposite directions. In illustration of an irreversible process, if a cylinder containing a saturated solution of magnesium sulphate, $MgSO_4$, in presence of an excess of the same salt, be treated as in the case of the cylinder of potassium nitrate, the heptahydrate, $MgSO_4.7H_2O$, separates during the cooling. Again, if potassium chlorate be heated in a closed vessel, the oxygen and potassium chloride which are formed will not recombine to reform potassium chlorate when the system cools, and hence the process is irreversible. G. H. Bryan[2] has stated:

> While students of reversible phenomena have had fairly straightforward problems to solve, the problem of irreversibility still remains to a great extent a mystery and nobody seems to have got to the bottom of it. The irreversible phenomena of the universe all have a certain definite trend, and lead to the transformation of energy into certain definite forms. We say that certain forms of energy are less available than others, but why the less available forms are those associated with what are commonly called heat phenomena is a riddle . . . still unsolved.

No known natural process is strictly reversible, because, if a process goes in one direction, experience shows that it cannot be made to go in exactly the opposite direction by reversing the same outside agency. Among the various causes which make real processes more or less irreversible are viscosity in liquids, imperfect elasticity in solids, friction, diffusion, radiation, radioactivity, conduction, and types of electrical, magnetic, and chemical action. It is, however, possible to imagine two transformations—direct and inverse—to be conducted by a continuous series of infinitesimally small changes so that the system is all the time infinitely near being in a state of equilibrium; and it has been agreed to call such a process reversible. Hence, **in a reversible transformation or process, two imaginary operations are performed on a system whereby the system traverses the same intermediate states in a continuous series of indefinitely small stages, but in the reverse order,** so that the transformation is attended by the production of as much external work W as would have been expended in restoring the system to its original condition W', and the total work performed in a reversible cycle is zero, for $W=W'$. *More* work cannot be produced by a direct transformation than is required for its reverse, or perpetual motion would be possible; and if *less* work is required, the system is irreversible. Hence, **if a change is reversible, it works under the most favourable conditions, for it furnishes the maximum amount of work which it is capable of producing,** or else the minimum amount of work is expended in bringing about the change—otherwise expressed, in a reversible transformation, the free energy is a maximum, the bound energy a minimum.

References.

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[2] G. H. Bryan, *Proc. Roy. Soc.*, 80. 13, 1908.

§ 8. The Amount of Heat which can be Utilized for doing Work

Every change in the distribution of matter in a given system, under given conditions is accompanied by a definite energy change. Therefore the laws which govern changes of energy, are the laws which govern transformations of matter.—A. J. Lotka (1913).

To what extent can heat be converted into work ? The maximum quantity of heat q which can be reversibly converted into work W under ideally perfect conditions, working between the temperatures T and $T+dT$, at constant volume without doing external work, was shown by N. L. S. Carnot (1824) [1] to be equal to the product of the change of temperature into the quantity of heat q absorbed, divided by the absolute temperature. In symbols,

$$dq=dW=q\frac{dT}{T}; \quad \text{or,} \quad dW=\frac{q}{T}dT \quad . \quad . \quad . \quad (1)$$

Hence, said R. Clausius (1850),[2] when the temperature of a quantity of heat q is changed by a small amount dT, the fraction dT/T of q is transformed into work provided no heat is lost. N. L. S. Carnot illustrated the principle by referring to an arrangement for utilizing a fall of water. Suppose water to be in a reservoir T_1 feet above sea-level feeding a mill T_2 feet below ; let w denote the amount of water which falls in unit time. If the disposition of the system be ideally perfect, the energy of the falling water available per minute at the mill will be the weight of water multiplied by the fall, or wT_2, or, referred to sea-level, the free energy of the water at the reservoir, per minute, is wT_1. The free energy of the water starting on its downward journey from the mill is wT_1-wT_2, or $w(T_1-T_2)$, so that the amount of free energy utilized at the mill is $w(T_1-T_2)/wT_1$ or $(T_1-T_2)/T_1$ per minute. If q represents the total quantity of free energy of the water in the reservoir, the amount actually utilized will be $q(T_1-T_2)/T_1$. Making the necessary changes in the meaning of the terms, this same result is obtained by integrating equation (1), if W is put equal to W_1-W_2 or to q_1-q_2,

$$W=q\frac{T_1-T_2}{T_1}$$

meaning that the theoretical maximum quantity of work W which can be obtained from a quantity of heat q working between the absolute temperatures T_1 and T_2, is equal to the product of the quantity of heat into the change of temperature divided by the higher temperature, and is independent of the nature of the working substance. If the combustion of carbon under a steam boiler furnishes a quantity of heat q, then, under the very best (ideal) conditions, the amount of work W which can be derived from the steam engine will be $q(T_1-T_2)/T_1$, where T_1 denotes the temperature of the boiler, and T_2 that of the condenser. This shows that the ideal limit to the efficiency of a thermal process, or the fraction of the total energy q capable of doing work W/q, is equal to the ratio of the difference of the absolute temperatures between which the operation is performed and the maximum absolute temperature.

In processes available industrially, the lower temperature limit is fixed by the temperature of the cooled water, and the upper temperature limit is fixed by the temperature generated by the combustion of the fuel in air—about 1500°. The efficiency of a process dependent on steam and cold water is increased by using higher pressures in the boiler, but the pressure of steam in a boiler rises very rapidly with rise of temperature, and this limits the efficient use of high pressure steam boilers.

Carnot's theory has been reasoned out another way : The amount of energy given out by a cooling gas is proportional to the change of temperature, so that the maximum amount of energy can be obtained only by cooling the gas to absolute zero, and consequently, if the gas be cooled one-tenth of its way to zero, it will yield but one-tenth of the available energy.

Examples.—(1) The explosions in the cylinder of a gas engine raise the temperature to 927°, and the temperature of the exhaust is 127°, what is the theoretical efficiency of the process? Since the efficiency of a process indicates the fractional part of the total energy utilized in doing work, the required efficiency will be $dq/q=dT/T$, or $(1200-400)/1200$, or two-thirds of the heat would be converted into useful work under ideal conditions, and the remaining third would be wasted.

(2) The temperature of the boiler of a steam engine is 127°, and the condenser 17°, what percentage of the heat is theoretically wasted? Here the theoretical efficiency is $(400-290)/400=0{\cdot}275$, or 27·5 per cent. Hence, 72·5 per cent. of the heat energy is wasted.

Equation (1) may be called **Carnot's equation.** It can be extended to chemical reactions by assuming that the reaction takes place in one direction at the temperature T, and in another direction at a temperature $T+dT$; and if W and Q respectively denote the free and total energy at the temperature T, q in the expression dq/q, or $dW/q=dT/T$, can be replaced by $W-Q$, where W represents the free energy or maximum work, and Q the thermal value of the reaction, *i.e.* the heat absorbed (+) or evolved (−) in the reaction as measured in the calorimeter. Hence, $W-Q=q$, and $W-Q$ represents the bound energy absorbed or evolved during the reaction. Consequently,

$$W-Q=T\frac{dW}{dT} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This form of the expression is called **Helmholtz's equation,** after H. von Helmholtz (1882), although A. Horstmann[3] had previously deduced a similar equation in 1870. Equation (2) means that the difference between the free and total energy in a chemical reaction under the given conditions is equal to the product of the absolute temperature T and the temperature coefficient of the free energy, dW/dT, which represents the change in the amount of work performed per unit change of temperature.

It will be evident that Berthelot's rule—that the total energy of the thermal value of a reaction is numerically equal to the free energy or maximum work which the reaction can perform—will be strictly valid only at absolute zero, when $T=0$, for dW/dT always has a finite value, and the term $T.dW/dT$ can be suppressed. At absolute zero, therefore, $W-Q=0$, or $W=Q$, and the thermal value of the process measures the driving force of the reaction. At ordinary temperatures, which, after all, are not very far removed from absolute zero, the difference between $W-Q$ and $T.dW/dT$ is not usually great, and Berthelot's rule becomes a useful approximation, particularly in chemical technology, where a measure of chemical energy in terms of the thermal energy of a process is desired. There are so many cases where the rule is approximately correct, that one is apt to forget that it is after all but a "half truth" and not the "whole truth."

H. von Helmholtz's equation is used in the interpretation of a great many phenomena. W. Nernst (1907)[4] was so impressed with its importance that he said: "It contains in a general manner all that the laws of thermodynamics can teach concerning chemical processes." In illustration, it can be applied (1) to show the influence of temperature on the thermal value of a reaction—J. H. van't Hoff's equation; (2) to show the relation between pressure and processes of volatilization, melting, and allotropic transformations—Clapeyron's and Clausius' equations; (3) to show the effect of temperature on the electromotive force of a cell—H. von Helmholtz's equation; (4) to show the influence of temperature on the surface energy of a liquid—Lord Kelvin's equation; etc.

EXAMPLE.—How does the pressure of an ideal gas kept at a constant volume change with temperature? For an ideal gas, $Q=0$. Let the gas at a temperature T change to a temperature $T+dT$, when the pressure changes from p to $p+dp$. Then, $W=pdv$, and $dW=dp.dv$. Substituting these results in Helmholtz's equation, $pdv=T(dp.dv/dT)$, or $p/T=dp/dT$, which is virtually Charles' law.

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[3] A. Horstmann, *Liebig's Ann. Suppl.*, **8**. 112, 1872; *Liebig's Ann.*, **170**. 192, 1873; *Ostwald's Klassiker*, 137, 1903; H. von Helmholtz, *Sitzber. Akad. Berlin*, **22**, 825, 1882; *Wissenschaft Abhandlungen*, Berlin, **2**. 958, 1884; *Ostwald's Klassiker*, 124, 1901; *Physical Memoirs*, London, **1**, 43, 1891; F. Massieu, *Journ. Phys.*, **6**. 216, 1877; J. W. Gibbs, *Trans. Conn. Acad.*, **3**. 343, 1878; *Scientific Papers*, London, **1**. 56, 1906.

[4] W. Nernst, *Experimental and Theoretical Applications of Thermodynamics to Chemistry*, London, 1907.

§ 9. Non-productive Energy. Entropy

Nature never undertakes any change unless her interests are served by an increase of entropy, while man endeavours so to make use of those changes allowed by nature that his own interests—namely the acquisition of available energy—are served as completely as possible.—M. Planck (1903).

No change occurs in nature without incurring waste.—J. Swinburne (1904).

The driving force of all natural events is the difference between the existing entropy and its maximum value.—L. Boltzmann.

While work may be wholly converted into heat, only a definite fraction of heat can be converted into work; otherwise expressed, if a quantity of heat Q_1 is received by a system at a temperature T_1, only the portion $Q_1-Q_2=Q_1(T_1-T_2)/T_1$ can be converted into work by a reversible process; the remaining quantity of heat Q_2 is simply transferred to the lower temperature T_2. The reversibility of the process implies that the portion of heat which was not transformed into work can be restored to its former temperature level T_1, with the same expenditure of work $Q_1-Q_2=Q_1(T_1-T_2)/T_1$. If the process is not reversible, and no known natural process is reversible in this sense, more heat flows to the lower level T_2 than in the reversible process, and accordingly less heat is transformed into work; the surplus cannot be brought up to its former level T_1 except by the expenditure of more work than is represented by $Q_1(T_1-T_2)/T_1$. Hence, in all real thermal processes, a fraction of the heat is lost for mechanical work; and there is a constant wastage of mechanical energy. The expression $Q_1-Q_2=Q_1(T_1-T_2)/T_1$, indicated above, reduces to

$$\frac{Q_1}{T_1}=\frac{Q_2}{T_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

meaning that when a body changes from one state to another by the addition of a quantity of heat Q_1 at T_1, the change can be reversed by taking away a quantity of heat Q_2 at T_2, provided these four quantities are related so that $Q_1/T_1=Q_2/T_2$. A gas, therefore, which receives Q_1 units of heat at T_1 will retain its energy until it has given up the equivalent of Q_2 units of heat at T_2. If the process is not reversible, $Q_1/T_1-Q_2/T_2$ is not zero, but some greater magnitude.

In 1854, W. J. M. Rankine [1] called the magnitude Q/T the *thermodynamic function*, but R. Clausius' term **entropy**—from ἐντροπή, a change—has alone been adopted. R. Clausius said:

> I hold it better to borrow terms for important magnitudes from the ancient languages so that they may be adopted unchanged in all modern languages . . . I have intentionally formed the word *entropy* so as to be as similar as possible to the word *energy*; for the two magnitudes, to be denoted by these words, are so nearly allied in their physical meanings, that a certain similarity in designation appears to be desirable.

Entropy is here symbolized by ϕ. When a body at the absolute temperature T receives a small amount of heat dQ, the entropy is said to have increased by an amount $d\phi=dQ/T$. If a gas of entropy ϕ, pressure p, temperature T, and volume v receives heat and performs work so that it undergoes various changes and returns to its former values of T, p, and v, its entropy will be the same as it originally possessed—*viz.* ϕ. Neither the heat added to and taken from the gas nor the work done by and upon the gas are necessarily the same; but the entropy given to and taken from the gas is exactly the same.

It can be shown (i) that what is true of a gas is also true of a liquid and of a solid—homogeneous or heterogeneous; (ii) that the entropy ϕ of a complex system is the sum of the entropies of its component parts $\phi_1+\phi_2+\phi_3+\ldots=\phi$; and (iii) that if the entropy of unit mass of a material in a given state be ϕ, the entropy of a mass m of the same material in the same state is $m\phi$; accordingly also (iv) that $m_1\phi_1+m_2\phi+\ldots=m\phi$, where m_1, m_2 . . . denote the masses of the component parts of the system of mass m; ϕ_1, ϕ_2 . . . their entropies.

The measurement of entropy.—When a body receives 100 units of heat at a temperature 50° K., its entropy will be increased 100/50 or 2 entropy units. This unit was called a *claus* by J. Parker (1891), and a *rank* by J. Perry [2]—respectively after R. Clausius and W. J. M. Rankine. Hence entropy can be measured as

$$\text{Entropy}=\frac{\text{Units of heat}}{\text{Absolute temperature}}\text{ units}$$

The measurement of the entropy of a system is made under such conditions that, excluding changes of volume, the system gives up no energy other than heat. The external pressure of a changing body may not be equal to the internal pressure; for instance, in most chemical reactions, the volume of the system alters quite independently of the heat changes. The total change of energy is then equivalent to the heat energy Q evolved or absorbed from outside minus the amount of energy W consumed in the work of expansion against an atmospheric pressure p, plus the change $p.dv$ in the volume energy. The total change of energy divided by the absolute temperature T represents the change expressed in entropy units, or

$$\text{Entropy}=\frac{Q-W+pdv}{T}\text{ units}$$

Here, $Q-W$ represents the change in the internal energy. If the conditions are such that the external pressure is equal to the internal pressure required to produce the change in volume, W will be equal to pdv, and the entropy will then be $\phi=Q/T$. This condition is not usual; in general, the entropy depends on the total change of internal energy, plus the change in volume energy. For example, when a gas expands into a vacuum, its temperature does not change, and its internal energy is not changed, for Q and W are both virtually zero, but the volume energy is increased by pdv. The entropy of the change is therefore pdv/T. To bring the gas back to its former condition requires an expenditure of energy equivalent to pdv. The entropy of the two operations can change only by the gas receiving or giving up heat to its surroundings. Hence, the entropy of the gas at the end of the operation is the same in magnitude as it possessed just after expanding into the vacuum, and this value is greater than it possessed at the beginning by the magnitude of the volume change pdv. The change of ice into water at 0° in vacuo is measured by the heat rendered latent, λ/T, since both W and pdv are zero.

EXAMPLE.—If a gram of water at the absolute temperature T receives dQ units of heat as its temperature is raised to $T+dT$, then, since dQ for water is very nearly equal to dT, the gain of entropy $d\phi$ will be $d\phi=dQ/T$, or $d\phi=dT/T$; and if the entropy of liquid water at 0° or 273° K. be conventionally regarded as zero, the entropy ϕ, at T° K., will be, in natural logarithms,

$$\int_0^T d\phi=\int_{273}^T\frac{dT}{T};\ \text{or}\ \phi=\log\frac{T}{273}$$

If the water at T° be also converted into steam at T°, it will be necessary to add on the term λ/T, where λ denotes the latent heat of vaporization, at T°.

If a body absorbs an amount of heat dQ so that its energy increases by an amount

$C_v dT$, where C_v denotes the thermal capacity at a constant volume, and the work pdv is done against atmospheric pressure, $dQ=C_\iota dT+pdv$, and the entropy of the body will be

$$d\phi=\frac{dQ}{T}\text{ ; or }d\phi=\frac{C_\iota dT+pdv}{T}\quad . \quad . \quad . \quad . \quad (2)$$

From the gas equation $pv=RT$, it follows that $p/T=R/v$, and supposing that C_v is independent of the change of temperature, the entropy ϕ of a perfect gas, per gram-molecule, is

$$=C_v\int\frac{dT}{T}+R\int\frac{dv}{v}+I\text{ ; or }\phi=C_v\log T+R\log v+I\quad . \quad . \quad (3)$$

Several different but equivalent forms of this relation for ideal gases can be obtained by means of the relation $pv=RT$; and $C_p-C_v=R$. The integration constant, I, can be evaluated only by the introduction of another assumption. To overcome this difficulty, W. Nernst[3] postulates what he calls the *third law of thermodynamics : In an isothermal process involving liquid or solids, the change of entropy approaches zero as the temperature approaches absolute zero; and at the limit, the absolute zero of temperature, the entropy of every substance is zero* Consequently, if the entropy at absolute zero be taken as zero, the entropy at any assigned temperature will have a definite positive value determined solely by the thermodynamic state of the system. This means that when a body is heated from the absolute temperature T, the entropy will be given by

$$\phi=\int_0^T\frac{dQ}{T}\text{; or, }\phi=\int_0^T C_v\frac{dT}{T}\quad . \quad . \quad . \quad . \quad (4)$$

when the changes of volume are negligibly small, provided also that the body suffers no change of state—*e.g.* from solid to liquid ; or from one crystalline form to another. It will be observed that the integration constant has been eliminated in virtue of Nernst's assumption. It cannot be assumed that the specific heat at constant volume is independent of temperature ; and before the integration is performed, the relation between the specific heat at constant volume, C_r, and temperature must be known.

For very low temperatures P. Debye's limiting equation[4] $C_v=a(T/\theta)^3$ can be used for evaluating ϕ ; here a is a universal constant, and θ is a characteristic constant for each substance. For ordinary temperatures, P. Debye's formula is too complicated for practical use. S. Pagliani (1915), and G. N. Lewis and G. E. Gibson (1917) have evaluated the integral for a number of elements ; the latter, using a method of approximation, obtained the values for the atomic entropies of the 48 elements indicated in Table III.

In order to determine the free energy of formation of any compound from its elements, it will be sufficient to know the entropy of the compound and of its elements at the same temperature, as well as the heat of formation of the compound from the equation $dE-dQ=-Td\phi$, where dE denotes the increase of free energy ; dQ the thermal value of the reaction ; and $d\phi$ the increase in entropy at the constant temperature T. G. N. Lewis and G. E. Gibson add : The atomic entropies of the elements appear to show the same sort of periodicity with respect to atomic weights that occurs with other important atomic properties ; and according to S. Pagliani the entropies at the melting point calculated from (4), for C_p in place of C_v, diminish as the atomic weights increase—particularly for the groups in Mendeléeff's system when the metals are separated from the non-metals. As a result of his examination of G. Tammann's statement[5] that the entropy per gram atom of the metals before fusion is the same for all the metals, S. Pagliani found that the products of the entropies and the atomic weights of the elements are not constant.

Physical analogies of the mathematical concept of entropy.—It is extremely difficult to get a physical apart from a mathematical conception of entropy. The work W performed by an ideal gas expanding a volume v against a constant pressure p, is $W=pv$; so is the entropy related to the quantity of heat and temperature by the formally analogous expression $Q=T\phi$. We are here in the same position with regard to the entropy ϕ as if in the former case we had no conception of volume v. We might then speculate as to the physical significance of volume just as to-day we wonder what is the physical significance of entropy. Volume would then be defined as something whose change is measured by the ratio W/p, just as entropy is a magnitude whose change is measured by the ratio Q/T. Again, just as volume is regarded as the capacity factor and pressure the intensity factor of the volume energy of a gas, so it has been suggested that entropy is the *capacity factor* and temperature the intensity factor of heat energy. G. Zeuner[6] called entropy, *heat weight—Wärmegewicht*—probably as a result of an analogy between the part entropy plays in the energy developed by the fall of heat from a state $T_1\phi_1$ to the state $T_2\phi_2$, and the part played by weight in the energy developed by the fall of a mass from a state h_1w_1 to a state h_2w_2—when h represents the height, and w the weight of the bodies indicated by the subscripts.

TABLE III.—THE ATOMIC ENTROPIES OF THE ELEMENTS AT 25°.

Element.	Entropy.	Element.	Entropy.	Element.	Entropy.
Aluminium	6·9±⅓	Iodine	15·7±1	Potassium	19·7±⅓
Argon (gas)	36·4±2	Iridium	8·7	Rhodium	7·6
Beryllium	7·3	Iron	6·6	Ruthenium	6·9
Bromine (liquid)	18·5±2	Lanthanum	13·7	Silicon (metal)	4·7±⅓
Cadmium	11·6	Lead	15·4±⅓	Silver	10·2±⅓
Calcium	11·0±⅓	Lithium	7·6	Sodium	12·2±⅓
Carbon-diamond	0·6±⅓	Magnesium	8·3±⅓	Sulphur (rhom.)	7·6±1
Carbon-graphite	1·3±⅓	Manganese	7·3	Sulphur (monoc.)	7·8±1
Cerium	13·8	Mercury (liquid)	17·8±1	Thallium	14·6±⅓
Chlorine (gas)	25·7±2	Molybdenum	7·5	Thorium	13·6
Chromium	5·8	Nickel	7·2	Tin	11·5
Cobalt	7·2	Nitrogen (gas)	22·8±1	Titanium	6·6
Copper	8·0±⅓	Oxygen (gas)	24·1±1	Tungsten	8·4
Gold	11·0	Osmium	7·8	Uranium	11·1
Helium (gas)	29·2±1	Palladium	8·9	Zinc	9·8±⅓
Hydrogen (gas)	15·9±1	Platinum	10·0	Zirconium	9·5

Following a suggestion by O. E. Meyer, in 1872, L. Boltzmann[7] showed an intimate relation between the entropy of a system and *the probability of a particular state* in which the system can exist. It is assumed that the state of the system can be defined by the volume, temperature, etc. When an isolated system can pass from one state A to another state B, the probability of, say, the state A represents the relative chance that the system will exist in that state and not in the other. If the probability of the state A were ½, there is an even chance that the system will exist in either state just as there is an even chance of heads or tails appearing after the toss of a penny. In all spontaneous natural processes, the probability of the state of the system increases and tends towards a maximum probability (unit probability is certainty). The entropy of a system, said L. Boltzmann, is determined by the probability of the state of its molecular motion; and M. Planck has shown that if P denotes the probability of the state of a system, and ϕ its entropy, $\phi=k\log P$, where k is a universal constant which is independent of the chemical nature, and other variations in the condition of the system. In illustration, it is just as probable that heat will pass from a cold to a hotter body—say that a kettle of water over a fire will become colder—as that the entropy of a system will decrease by a spontaneous natural change. With R. Clausius, the transformation value of a particular state is equal to the difference between the entropies of the initial and final states ; with L. Boltzmann, the entropy of a physical system is a definite condition which depends solely on the probability of that state.

The law of maximum entropy.—If a system of two bodies A and B, respectively at the absolute temperatures T_1 and T_2, be in thermal communication, and so isolated that no heat is lost or gained from external sources, the total energy remains unaltered although heat passes from the hotter body A, at the temperature T_1, to the colder body B, at the temperature T_2. When the infinitesimally small quantity of heat dQ has passed from A to B, the entropy of A is diminished by dQ/T_1, and the entropy of B is increased by dQ/T_2. Consequently, the entropy of the whole system will be increased so that

$$\text{Gain of entropy}=\left(\frac{1}{T_2}-\frac{1}{T_1}\right)dQ$$

This expression must be positive, since T_1 is greater than T_2. The effect of the transfer of an infinitesimally small quantity of heat dQ from a hot to a colder body is to increase the entropy of the system. The transfer of heat, and consequently also the gain of entropy, will continue by a series of infinitesimally small stages until the bodies A and B have one common temperature, when the entropy of the system will have attained its maximum value. While the first law of thermodynamics says that in an isolated system, all possible changes of state leave its energy unaltered, the second law may be understood to mean that in an isolated system all possible spontaneous changes of state produce an increase in its entropy. The law of maximum entropy holds good however many bodies be included in the system, and unless something has been overlooked, it will apply to the whole universe considered as one system. In all changes, nature seeks to realize the condition of maximum entropy ; every spontaneous change is accompanied by an increase of entropy, and the tendency to change ceases only when the increase of entropy is the greatest possible. If the entropy of a system were to decrease, heat would pass from a cold to a hotter body ; the equalization of temperature which attends the passage of heat from a hot to a colder body increases the entropy of a system.[8] The very process which increases the entropy of the system is attended by a loss of available energy, so that, in this sense, an increase of entropy and a decrease of available or free energy are correlated phenomena. The degradation of energy will be complete when the entropy acquires a maximum value, and the free energy is zero.

Entropy and work of diffusion.—From equation (3), if a series of gases of molecular weight M_1, M_2 . . . which have no chemical action on one another, be contained in separate compartments, respectively of volume v_1, v_2 . . ., the entropy of the gas of molecular weight M_1 contained in the first compartment will be $\phi_1=M_1(C_{v_1}\log T+R\log v_1)$, and the total entropy of the gases in all the compartments will be

$$\phi=\Sigma MC_v\log T+\Sigma MR\log v \quad . \quad . \quad . \quad . \quad (5)$$

Similarly, the entropy of an intimate mixture of a volume V, of the same gases when $V=v_1+v_2+$ . . ., is

$$\phi_m=\Sigma MC_v\log T+\Sigma MR\log V \quad . \quad . \quad . \quad (6)$$

The difference between these two magnitudes represents the change of entropy which occurs on diffusion. The difference $\phi_m-\phi$ with a mixture of two gases, where $V=v_1+v_2$, reduces to

$$\text{Increase of entropy, } \phi_m-\phi=\mathrm{R}\log\frac{\mathrm{V}^M}{v_1^{m_1}v_2^{m_2}} \quad . \quad . \quad (7)$$

where $M=m_1+m_2$ and $V=v_1+v_2$. The numerator of this expression is always greater than the denominator, and therefore the entropy of a uniform mixture of gases is greater than the entropy of the same gases before they were mixed by diffusion. Hence, the diffusion of gases is an irreversible process, for work will have to be expended in separating the mixture into its constituents ; and work should be obtained if the gases are allowed to mix in suitable vessels.[9] In 1875, Lord Rayleigh showed that the work performed during the physical mixing of volumes v_1 and v_2 of two different gases at the same temperature and pressure is the same as that which would be gained during the expansion of the first gas from the volume v_1 to the volume $V=v_1+v_2$—namely, $pv_1 \log V/v_1$, where p denotes the partial pressures of the two gases of volumes v_1 and v_2 when $V=v_1+v_2$, *vide supra*, together with the work gained during the expansion of the second gas from a volume v_2 to a volume $V=v_1+v_2$—namely, $pv_2 \log V/v_2$—when the expansions are made in a vacuum. Consequently, the work gained by mixing two gases of volume v_1 and v_2 respectively at the constant pressures p, when $v_1+v_2=V$, is

$$\text{Work of diffusion} = p \log \frac{V}{v_1^{v_1}+v_2^{v_2}} \quad . \quad . \quad . \quad (8)$$

Thus the rule is brought under Dalton's principle that each gas behaves towards the other as a vacuum. In all cases the gases are supposed to follow Dalton's partial pressure law, where the total pressure is the sum of those pressures which would be exerted by each gas in the absence of the other. The result does not depend upon the physical nature of the gases, and there appears no reason why the argument should not be valid for two portions of the same gas. Hence arises the so-called *Gibbs' paradox*, because it follows that if the gases are chemically identical, there will be no change of state, and no change of entropy, accordingly $\phi_m-\phi$ will be zero and $\phi_m=\phi$. Consequently, M. Planck regarded the increase of entropy on diffusion as a sign that the gases are chemically different, and he suggested that the *chemical difference* between two substances cannot be represented by a magnitude which varies in a continuous manner, because the magnitude varies discontinuously; on the other hand, the *physical differences* between two bodies can be represented by a continuous function. This is taken to establish a fundamental difference between the chemical and physical properties of a substance.[10]

The relation between the laws of maximum entropy and the degradation of energy.—Imagine a system of three bodies, A at a temperature T_1 which is higher than T_2, the temperature of the second body B; and let C be the third body at a temperature T, the lowest temperature of all. If a small quantity of heat dQ performs work in passing A to C by a Carnot's cycle, the maximum available work is $(T_1-T)dQ/T_1$. Similarly, when a portion of heat dQ is transferred from B to C, the maximum available work is $(T_2-T)dQ/T_2$. By subtraction, it will be seen that there is a decrease dE in the availability of the energy of the system which is equivalent to

$$dE=T\left(\frac{1}{T_2}-\frac{1}{T_1}\right)dQ$$

but the increase in the entropy of the system is represented by the product of the bracketed and succeeding term. Consequently,

$$dE=Td\phi$$

A finite quantity of heat can be so transferred by the summation of a succession of infinitesimal instalments. This means that when heat passes from one part of an isolated system to another part, in consequence of a difference of temperature, there is a degradation of energy which is equal in amount to the product of the increase of the entropy of the system, and the absolute temperature of the coldest part. An increase of entropy thus corresponds with a decrease of the available and an increase of the unavailable energy. For stable equilibrium, the entropy of a system must have a maximum value.

The relation between entropy and free energy.—Under what conditions is it possible to predict the direction in which a particular process or reaction will proceed? In answer, the change will take place in that direction which involves a decrease in the free energy or an increase in the entropy of the system. The so-called intrinsic or internal energy U represents the work the system can do in virtue of its actual condition without any supply of energy from without. For example, when heat energy is communicated to a gas, it may separate the molecules or the atoms further apart against molecular or atomic attractions; it may change the kinetic energy of molecular or atomic motion; it may change the rotational or vibratory energy of the atoms; and it may change the electrical state of the molecules. If a system with the total intrinsic energy U_1 and entropy ϕ_1 changes or reacts so as to produce another system with the total intrinsic energy U_2 and entropy ϕ_2, at any given temperature, T, a reaction can take place only with the expenditure of free energy, and U_1-U_2 must be greater than $T(\phi_1-\phi_2)$. In reversible isothermal changes, a system with a positive value of $(U_1-U_2)-T(\phi_1-\phi_2)$ will tend to react; and whether or not a reaction will take place in a particular mixture depends on whether what H. von Helmoltz [11] called the

$$\text{Free energy of a system}=(U_1-U_2)-T(\phi_1-\phi_2) \quad . \quad . \quad (9)$$

$$\text{Free energy of a system}=(U_1-T\phi_1)-(U_2-T\phi_2) \quad . \quad . \quad (10)$$

has a positive, negative, or zero value. This function $U-T\phi$, is sometimes symbolized ψ; so that $\psi=\psi_1-\psi_2$; if ψ be negative, the system will be stable; if ψ has a positive value, the system will be unstable; and if ψ be zero, the system will undergo no change. Hence, this expression may be regarded as a **stability function**—it is usually called a *potential*, or *thermodynamic potential*, and ψ may be taken to represent the driving force of a reaction. The entropy itself is a test of the stability of a system, for equilibrium is stable when the entropy has a maximum value. As a rule, the application of the entropy test to a system is more difficult than the free energy or the thermodynamic potential test. It was not possible to give an exact definition of chemical affinity until thermodynamics had been developed. The thermodynamic potential or free energy can be employed as a measure of chemical affinity.

In ordinary thermochemical calculations, the quantities of energy absorbed and evolved during the reaction are made to balance. The balancing is quite illusory. The fallacy underlying the assumption that the driving force of a reaction $\psi_1-\psi_2$ represents the thermal value or heat of a reaction as measured in a calorimeter, rests on the fact that the energy $T(\phi_1-\phi_2)$ which is not available for doing work is ignored. In formulating the principle of maximum work it was tacitly assumed that the driving force of a reaction which occurs without change of state is equivalent to U_1-U_2 units of heat, and that if U_1-U_2 be a positive quantity, the reaction is necessarily exothermal. It will be obvious that the term $T(\phi_1-\phi_2)$ can be suppressed only at absolute zero, for only when $T=0$ will $T(\phi_1-\phi_2)$ be also zero. Consequently, the thermal value of a reaction can be a measure of the driving energy of a reaction, only at absolute zero. At ordinary temperatures, which are, after all, not far removed from absolute zero, the difference between (U_1-U_2) and $(U_1-U_2)-T(\phi_1-\phi_2)$ is not very great, and M. Berthelot's rule is a useful approximation—particularly in chemical technology—where a measure of chemical energy in terms of heat energy is required.

If a reaction can take place, with the absorption of heat, the internal energy of the system U_2, after the change, will be greater than the original internal energy U_1; and U_1-U_2 will have a negative value; but in order that free energy may be available for doing work during the change, ϕ_2 must be so much greater than ϕ_1 that when $T(\phi_1-\phi_2)$ is subtracted from U_1-U_2 the driving force of the reaction will still have a positive value. If the external work be involved in the change, as will be the case when work pv is performed on or by a uniform and constant pressure p, the term $p(v_2-v_1)$ must be included in the expression for the free energy of the system, and consequently,

$$\text{Free energy of a system}=(U_1-T\phi_1+pv_1)-(U_2-T\phi_2+pv_2) \quad . \quad . \quad (11)$$

The fundamental equation for the free energy of a system thus assumes the form

$$dE=dU-Td\phi \quad . \quad . \quad . \quad . \quad . \quad (12)$$

meaning that in any isothermal process, or chemical reaction, the increase dE in the free energy of the system is equal to the difference between the increase dU in the internal energy of the system and the product of the absolute temperature, T, and the increase, $d\phi$, of the entropy.

J. W. Gibbs (1878)[12] in his important paper, *On the equilibrium of heterogeneous substances* (1875), used these functions with the object of facilitating mathematical operations. He called $\psi=U-T\phi$, the *force function* for constant temperature; $\zeta=U-T\phi+pv$, the force function for constant temperature; and $\chi=U+pv$, the heat function for constant pressure. They are often styled the *psi, zeta,* and *chi functions of Gibbs*. P. Duhem (1895) called Gibbs' ψ-function the internal thermodynamic potential; and the ζ-function, the thermodynamic potential for constant pressure, or the thermodynamic potential or the potential of the system.

It will be observed that while the difference $(U_1-U_2)-T(\phi_1-\phi_2)$ represents the change in the free energy of the system during the isothermal change, (U_1-U_2) represents the change in the total intrinsic energy of the system; the remainder, $T(\phi_1-\phi_2)$ represents the unavailable energy which H. von Helmholtz called the *bound energy* of the system. J. Swinburne[13] has further emphasized H. von Helmholtz's conception by showing that the degradation of energy is a liability which is incurred when any form of energy is converted into heat, for only part may be available for work, the remaining part which is eventually and unavoidably produced or left as heat at the lowest possible temperature is of no use; it is waste. Entropy furnishes a measure of this waste, for

> An increase of entropy is a quantity which, when multiplied by the lowest available temperature gives the increased waste. In other words, the increase of entropy multiplied by the lowest available temperature gives the energy that either has been already irrevocably degraded into heat during the change in question, or must, at least, be degraded into heat in bringing the working back to the standard state.

The product of the absolute temperature of a process conducted at a constant uniform temperature T, into the difference between the entropy at the beginning and end of the operation, *viz.* $T(\phi_1-\phi_2)$, represents the energy cost of the reaction, or the amount of energy rendered unproductive during the change; it is in some respects analogous with the so-called latent heat of a change of state, and hence has also been called the *latent energy* of a reaction. The term *latent* suggested for say the heat of liquefaction by J. Black implied that the heat was still present, but latent, dormant, or held in abeyance. The term latent energy for that portion of energy which is degraded into a lower plane of availability during a process or reaction is quite inappropriate and should be avoided. The loss of work-value suffered by energy during a physical or chemical process may be due to a change in the constitution or the state of aggregation of the body, or to a change in the thermal capacity of the initial and final substances concerned in the reaction.

A reversible change is an idealized phenomenon which is supposed to take place in every respect, in an opposite direction, so that when completed, the system is in the same condition as it was at the beginning. *Actually*, no change takes place in nature without incurring some waste. Consequently, a reversible change is an imaginary cyclic phenomenon in which there is no waste of energy. If energy were wasted during a reversible change, there would be, on reversal, a decrease of the incurred waste, and a perpetual motion would be possible, for, in spite of friction, etc., the available energy would not diminish. The entropy of a reversible system remains constant, so that if there is an increase of entropy in one part, this must be compensated by an equal decrease in another part.

Consider an indefinitely large quantity of each of two reacting gases A and B in a state of equilibrium, to be confined in a suitable compartment, and further, suppose a compartment containing an indefinitely large quantity of pure A, and another compartment with pure B, each at the same concentration as it has in the equilibrium compartment. Let the component B be transferred by a semi-permeable membrane or other reversible method from the equilibrium compartment to its own special B-compartment, and replenish the equilibrium compartment with one equivalent of A taken from the A-compartment. Let the two operations be carried on simultaneously, so that the concentrations remain unchanged throughout the process. The temperature remains uniformly constant at T. If ϕ_1 denotes the entropy of an equivalent mass of A and ϕ_2 that of B,

$$\phi_1-\phi_2=-\frac{Q}{T} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where Q denotes the heat absorbed per equivalent at constant pressure, and the negative sign shows that the change of entropy is equal to the heat absorbed divided by the temperature. This is regarded as the symbolic expression of the second law of thermodynamics applied to chemical reactions. From equation (3), $\phi_1=C_{v1}\log T+R\log C_1+I_1$; $\phi_2=C_{v2}\log T+R\log C_2+I_2$. Accordingly, by substitution in (9), and rearranging terms,

$$\log\frac{C_1}{C_2}=-\frac{Q_p}{RT}-\frac{\Sigma C_v}{R}\log T-\frac{\Sigma I}{R} \quad . \quad . \quad . \quad (14)$$

The equilibrium constant K can be used in place of the ratio of the concentrations C_1/C_2. The sign Σ is used for the summation sign for the specific heats and the integration constants. The argument can be extended to include any number of reacting components on the assumption that the specific heats of all the gases taking part in the reaction are independent of temperature, and that the gases follow the ideal law $pv = RT$, so that their total energies are independent of the pressure. Equation (14) is the general form of the law of mass action.

Again, if equation (14) be differentiated, and G. Kirchhoff's equation $dQ_p/dT=-\Sigma(C_p+RT)$ be substituted, and remembering that $Q_p+\Sigma RT=Q_v$, J. H. van't Hoff's important equation

$$\frac{d\log K}{dT}=-\frac{Q_v}{RT^2}$$

showing the relation between the equilibrium constant and the thermal value of the reaction at constant volume, is obtained—*vide infra.*

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§ 10. The Work done by Affinity during a Chemical Reaction

The doctrine of chemical affinity is unquestionably the great and distinguishing principle of the science of chemistry as the laws of motion are of mechanical philosophy.—J. BLACK (1803).

Every chemical change performs work which is equivalent to a certain amount of mechanical energy.—W. STILLIE (1865).

Chemical action usually produces changes in the state of aggregation or density of the reacting substances, and so performs work as well as produces heat. As indicated above, H. von Helmholtz (1882) emphasized the necessity for distinguishing between that part, dE, of chemical energy, which can do work (free energy) from that part, $Td\phi$, which is degraded solely as heat (bound or latent energy), since, as previously indicated, the total chemical energy $dU=dE+Td\phi$. Every spontaneous reaction involves a decrease in its free energy, and an increase in the bound energy. It is the decrease in the free energy, and not the development of heat, which determines the direction of a chemical reaction. Hence, **the decrease in the free energy of a system is a measure of the work which can be done by chemical affinity during a chemical reaction; and is equivalent to the maximum work gained when the process is conducted reversibly at a constant temperature.**

J. H. van't Hoff, in his *Études de dynamique chimique* (Amsterdam, 1884), considers that the magnitude of chemical affinity is equivalent to that of the work the reaction can do when it is carried out in such a manner that the driving forces are always balanced by equal and opposite external forces; otherwise expressed, **the affinity of a chemical reaction can be measured in terms of the amount of work the reaction can do when it is carried out at a constant temperature in a reversible manner.** The work *in maximo* which can be obtained in a chemical change is closely related to the free energy of the reaction; this work cannot always be determined by direct measurement, although in the case of gases, and also in the case of dilute solutions when the gas laws are applicable, it can often be calculated from (i) The change in the vapour pressure, or, in the case of dilute solutions, the osmotic pressure; (ii) The chemical equilibrium constants; or (iii) The electromotive force of the reaction; for example, the chemical affinity of the reaction $H_2+Cl_2=2HCl$ can be determined by measuring the electromotive force of a cell whose electrodes are chlorine and hydrogen gases, with hydrochloric acid as electrolyte.

When a gas at a pressure p_1 changes its volume isothermally at $T°$, so as to correspond with a pressure p_2, the work, W_v, done by the gas is $W_v=RT\log(p_1/p_2)$, as previously indicated, provided that Boyle's and Charles' laws are applicable. Since the volume of a gas varies inversely as its concentration C, usually expressed in gram-molecules per litre, it follows that $p=CRT$, and hence, the free energy W_v involved in changing a gas from a pressure p_1 to a pressure p_2, at constant volume, is

$$W_v=RT\log\frac{p_1}{p_2};\ \text{or,}\ W_v=RT\log\frac{C_1}{C_2};\ \text{or,}\ W_v=RT\log K \quad . \quad (1)$$

for gaseous reactions of the type $A\rightleftharpoons B$, when $k_1C_1=k_2C_2$, where k_1 and k_2 are constants such that $C_1/C_2=K=k_1/k_2$. The equations, therefore, can be used to calculate the maximum work or the free energy of physical or chemical processes which pass isothermally from A with an initial concentration C_1 or vapour pressure p_1 to a state of equilibrium with B which has a concentration C_2 or vapour pressure p_2, without doing any external work, that is, the volume is supposed to be constant. These relations are generally applicable to reactions in gaseous systems or in dilute solutions at constant volume and temperature. One of the simplest illustrations occurs during the transformation of rhombic sulphur—vapour pressure p_1—to monoclinic sulphur—vapour pressure p_2.

EXAMPLE.—The affinity of a gram-molecule of water for a gram-molecule of an aqueous solution of sulphuric acid, $H_2SO_4.H_2O$, which has a vapour pressure 0·0184 cm. of mercury, at 25°, is given by the first of equations (1), when the vapour pressure of the acid with the addition of another gram-molecule of water, $H_2SO_4.2H_2O$, is 0·1125 cm. at the same temperature. Hence, $W_v=RT \log (p_2/p_1)$, or $W_v=2\times 298\times 2{\cdot}3\times \log$ (0·1125/0·0184), or $1371\times \log 6{\cdot}135$, or 1080·cals. The factor 2·3 transforms natural into common logarithms. The observed heat of the reaction, according to J. Thomsen (1870), is 1874 cals.

It was shown by J. H. van't Hoff, in his *Études de dynamique chimique* (Amsterdam, 1884), that if hydrogen and oxygen, of the concentrations C_{H_2} and C_{O_2}, pass isothermally and reversibly into water vapour when the initial concentration of the water vapour is c_{H_2O}, and the equilibrium concentrations of these three gases are respectively c_{H_2}, c_{O_2}, and c_{H_2O} at the absolute temperature T, the maximum work W is a measure of the affinity of the reaction $2H_2+O_2\rightarrow 2H_2O$ per gram-molecule of oxygen or per two gram-molecules of hydrogen, where

$$W=RT\left(\log \frac{C^2_{H_2}C_{O_2}}{C^2_{H_2O}}+\log \frac{c^2_{H_2O}}{c^2_{H_2}c_{O_2}}\right) \quad . \quad . \quad . \quad (2)$$

By Guldberg and Waage's law, for equilibrium, $c^2_{H_2O}=Kc_{H_2}c_{O_2}$, and the last equation can be reduced to

$$W=RT\left(\log K-\log \frac{C^2_{H_2O}}{C_{H_2}C_{O_2}}\right) \quad . \quad . \quad . \quad . \quad (3)$$

or generally

$$W=RT \log K-RT\Sigma n \log C \quad . \quad . \quad . \quad . \quad (4)$$

where C refers to the concentration of the saturated vapour of each constituent; and the term $\Sigma n \log C$ refers to $N_1 \log C_{B_1}+N_2 \log C_{B_2}+\ldots-n_1 \log C_{A_1}-n_2 \log C_{A_2}$—in the chemical equation $n_1A_1-n_2A_2+\ldots=N_1B_1+N_2B_2+\ldots$ If the concentrations of the initial and the final products of the reaction are arbitrarily made unity, the affinity of the reaction is simply expressed by the relation

$$W=RT \log K \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The affinity of the process $2H_2+O_2\rightarrow 2H_2O$ per gram-molecule of hydrogen is therefore $\frac{1}{2}W$.

EXAMPLES.—(1) The equilibrium constant in the reaction $H_2+I_2=2HI$ at 300° is nearly 80. What is the affinity of the reaction $H_2+I_2\rightarrow 2HI$ at this temperature when the initial concentration of the three components of the reaction is in each case unity ? From (4), $2\times 573\times 2{\cdot}3 \log_{10} 80=4631$ cals. nearly. The thermal value of the reaction is negative—6000 cals.—so that there is a marked difference between the free energy and the thermal value of the process.

(2) In the reaction $2H_2+O_2=2H_2O$ at 727°, the equilibrium constant is $1{\cdot}25\times 10^{-20}$. Hence, the free energy of the reaction $2H_2+O_2\rightarrow 2H_2O$ at this temperature, when the initial concentration of the hydrogen, oxygen, and water vapour are unity, is $-2\times 1000\times 2{\cdot}3 \log 1{\cdot}25\times 10^{-20}$, or 90,600 cals. nearly.

(3) In the reaction $CaO+H_2O\rightarrow Ca(OH)_2$, if p_0 be the initial and p the equilibrium pressure of the steam at a temperature T, the affinity of the reaction is $W=RT \log (p_0/p)$; and if the initial pressure of the steam be one atmosphere, $W=-RT \log p$. Except at a very high temperature, p is less than unity, so that W will be positive, meaning that steam

will unite with the lime, and if W be negative, the hydroxide will dissociate. At 25°, the dissociation pressure of calcium hydroxide is 9×10^{-13} atm., and therefore, the affinity of the water vapour for lime is $W = 2 \times 2{\cdot}3 \times 298 \times \log (9 \times 10^{-13})$, or $-2 \times 2{\cdot}3 \times 298 \times -13{\cdot}95 = 19{,}120$ cals. Similar remarks apply to the reaction $CaO + CO_2 \rightarrow CaCO_3$.

(4) What is the affinity of iron for oxygen under the partial pressure of oxygen in the atmosphere when the dissociation pressure of ferrous oxide at 1000° abs. is $3{\cdot}1 \times 10^{-18}$ mm. ? The equilibrium constant K for the reaction $2Fe + O_2 = 2FeO$ is $K = 1/p$, where p is the dissociation pressure of the gas from the ferrous oxide. The oxygen of the atmosphere is under the partial pressure of one-fifth of an atmosphere, and a pressure of $3{\cdot}1 \times 10^{-18}$ mm. is $3{\cdot}1 \times 10^{-18}/760 = 4{\cdot}1 \times 10^{-21}$ atm. Hence, $W = RT(\log\frac{1}{5} - \log p)$, or $2{\cdot}3 \times 2 \times 1000$ $(\log_{10} 0{\cdot}2 - \log 4{\cdot}1 \times 10^{-21})$, or 4600 (1·3010–21·6128), or $4600 \times 19{\cdot}6882$, or 90,000 cals. nearly. H. le Chatelier's number for the heat of the reaction of two gram-molecules of iron with a gram-molecule of oxygen is 129,900 cals.

It is sometimes possible to calculate the free energy of a reaction indirectly as in the case of heats of reactions. Thus, the equilibrium constant in the reaction $2CO = 2C + O_2$ is very small even at high temperatures; the free energy of the reaction at 1000° abs. can be computed from the free energy of the reaction $CO + \frac{1}{2}O_2 \rightarrow CO_2$, which is 47,200 cals.—and the free energy of the reaction $2CO \rightarrow C + CO_2$, which is -610 cals. Subtracting the latter algebraically from the former, and $CO + \frac{1}{2}O_2 - 2CO \rightarrow CO_2 - C - CO_2 + (47{,}200 + 610)$ cals., or $C + \frac{1}{2}O_2 \rightarrow CO - 47{,}810$ cals.; or the free energy of the reaction $2CO \rightarrow 2C + O_2$ is -95620 cals.

Examples.—(1) If the free energy of the reaction $2CO = 2C + O_2$ at 1000° is $-95{,}620$ cals., and of the reaction $2FeO = 2Fe + O_2$, $-95{,}400$ cals., show that the free energy of the reaction $FeO + C \rightarrow Fe + CO$ is 110 cals.

(2) According to G. Bodländer,[1] assuming that the thermal values of the reactions are independent of the temperature, the free energy of formation of zinc oxide is $Zn + \frac{1}{2}O_2 = ZnO + (85{,}800 - 30{\cdot}8T + 2{\cdot}29T \log p_0)$ cals., where p_0 denotes the partial pressure of the oxygen expressed in atmospheres. Similarly, the free energy of formation of water is $H_2 + \frac{1}{2}O_2 = H_2O + \{57600 - 22{\cdot}4T + 2{\cdot}29T \log (p_1{}^2 p_0/p_2{}^2)\}$ cals., where p_0 denotes the partial pressure of the oxygen, p_1 that of the hydrogen, and p_2 that of the water expressed in atmospheres. By subtraction of the first from the second equation, the free energy of the reaction, $ZnO + H_2 = Zn + H_2O$, at 1000° C., or 1273° K., will be $57{,}500 - 85{,}800 - (30{\cdot}8 - 22{\cdot}4)1273 + 2{\cdot}29 \times 1273 \times \log p_1^2 p_2^{-2}$ cals. This shows that zinc oxide is reduced at 1000° by hydrogen at atmospheric pressures only when the partial pressure of the water vapour does not exceed $p_2 = 0{\cdot}001$ atm. or 0·76 mm., because only under these conditions is free energy available for the reaction. Analogous results are obtained with the reduction of ferrous oxide by hydrogen, for the free energy of the formation of ferrous oxide is $Fe + \frac{1}{2}O_2 = FeO + (64600 - 25{\cdot}9T + 2{\cdot}29T \log p_0)$ cals.

References

[1] G. Bodländer, *Zeit. Elektrochem.*, 8. 833, 1902.

§ 11. The Effect of Temperature on Chemical Equilibria

Le problème de l'affinité est le problème central de la chimie.—S. Arrhenius.

There are four important stages in the evolution of the modern idea of chemical affinity: (i) The growth of the concept connotated by the term *affinity*; (ii) The discovery of the *law of mass action* as a result of the work of C. F. Wenzel (1777), C. L. Berthollet (1803), L. Wilhelmy (1850), A. V. Harcourt and W. Esson (1866), C. M. Guldberg and P. Waage (1867), etc.; (iii) The recognition of the significant part played by *free energy* in determining the character and state of chemical phenomena as a result of the work of J. W. Gibbs (1876), H. von Helmholtz (1882), J. H. van't Hoff (1884–7), W. Ostwald (1892), etc.; and (iv) The effect of *temperature* on chemical equilibria as a result of the work of J. H. van't Hoff (1884–7), H. le Chatelier (1884), F. Haber (1905), W. Nernst (1906), etc.

The two great principles of thermodynamics—embodied in the statements that all the changes which take place in an isolated system produce a decrease in the free energy (second law), and leave the amount of energy unchanged (first law)—have furnished Helmholtz's equation, $W-Q_p=T.dW/dT$, which shows a relation between the affinity, W, the thermal value, Q_p, and the absolute temperature, T, of a chemical process. With the aid of the calculus, this equation can be written:

$$\frac{d}{dT}\left(\frac{W}{T}\right)=-\frac{Q_p}{T^2};\ \text{or,}\ \frac{W}{T}=-\int_0^{\mathrm{T}}\frac{Q_p}{T^2}dT+I\quad . \quad . \quad . \quad (1)$$

where I is the so-called integration constant. The last equation embodies one solution of the main problem of chemical affinity, namely, to predict what will occur if a number of substances are mixed together under given conditions of temperature, pressure, electromotive force, etc. The affinity of a chemical reaction can be calculated for any temperature T when (i) the relation between the thermal value of the reaction and the temperature is known, and when (ii) the integration constant I has been evaluated. Since $W=RT\log K$, it follows, substituting for W,

$$\frac{d}{dT}(\log K)=-\frac{Q_p}{RT^2};\ \text{or,}\ \log K=-\int_0^{\mathrm{T}}\frac{Q_p}{RT^2}dT+I\quad . \quad . \quad (2)$$

The first of equations (2) can be written in the alternative form

$$\frac{1}{dT}\left(\frac{dK}{K}\right)=-\frac{Q_p}{RT^2}$$

which shows that the fractional change, dK/K, in the value of the equilibrium constant, per degree, dT, (i) is proportional to the heat Q_p of the reaction; and (ii) inversely proportional to the square of the absolute temperature. The equation also shows that a rise of temperature, dT, will displace the equilibrium conditions in the same direction as the reaction which absorbs heat. For endothermal reactions where Q_p is negative, the equilibrium constant increases with rise of temperature; and conversely, for exothermal reactions, where Q_p is positive, the equilibrium constant decreases with rise of temperature. This is *the principle of reversibility* previously discussed. The above result was obtained by J. H. van't Hoff in 1887, and has been called the equation of the *reaction isochore* (ἴσος, equal, χῶρος, place) by W. Nernst (1889), because the volume is kept constant during the change. J. H. van't Hoff's equation, (2), also represents the influence of temperature on the system kept at a constant volume; Q_p represents the heat emitted during the formation of a substance whose concentration appears in the numerator of $K=C_1/C_2$. There is a formal relation between Clapeyron-Clausius' and van't Hoff's equations:

$$\frac{d}{dT}(\log p)=\frac{\lambda_p}{RT^2};\ \frac{d}{dT}(\log K)=-\frac{Q_p}{RT^2}\quad . \quad . \quad . \quad (3)$$

The difference lies in the interpretation of the symbols; in the one case, p represents a pressure, while the corresponding K in the other case is a product of concentrations, but in dilute solutions and gases, concentration can be expressed in terms of osmotic or gaseous pressure. The term $\lambda=-Q_p$ refers to the diminution in the internal energy, or the heat evolved by the reaction under a constant pressure p.

If the numerical value of the integration constant I could be deduced from the known laws of heat, the problem concerning the effect of temperature could be solved, but the two laws of thermodynamics *per se* leave the problem undetermined. Although the two laws of thermodynamics can be applied generally to a great variety of phenomena, they fail to yield precise conclusions, applicable to particular cases, without the use of certain experimental data to evaluate the integration constants[1] which arise because of our ignorance of the absolute values of the energy of the system at any temperature. Nernst's theorem is an attempt to solve this problem by assuming that at absolute zero, the entropy is zero, and this is taken as a standard of reference. There are two cases to consider before the integration of equations (2) can be performed:

I. The thermal value Q_p of the reaction does not alter appreciably with changes of temperature.[2] If the equation be integrated on the assumption that Q_p is constant over a small range of temperature, and that K_1 and K_2 respectively denote the equilibrium constants at the two temperatures T_1 and T_2, then, since R is approximately 2,

$$\log_{10}\frac{K_2}{K_1}=1{\cdot}15Q_p\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \quad . \quad . \quad . \quad . \quad (4)$$

By means of this equation it is possible to compute the thermal value of a reaction which changes but little between the temperatures T_1 and T_2 when the equilibrium constants for these temperatures are known, Q_p may represent the heat of sublimation, the heat of vaporization, the heat of solution, the heat of dissociation, as well as the thermal value of strictly chemical reactions. The thermal values calculated by means of this equation are in close agreement with the observed values when the necessary conditions obtain ; this is illustrated by Table IV.

TABLE IV.—THE THERMAL VALUES OF PHYSICAL AND CHEMICAL CHANGES.

Heat of	Q in Cals.	
	Calculated.	Observed.
Vaporization of water	10·10	10·30
Solution of boric acid in water	5·2	5·6
Sublimation of ammonium sulphide	21·55	21·64
Combination of $BaCl_2+2H_2O$	3·82	3·83
Dissociation of nitrogen peroxide	12·90	12·50
Precipitation of silver chloride	15·99	15·85

When the heats of formation of a substance at any temperature are known, the percentage dissociation at any assigned temperature can be calculated on the assumption that this equation is valid, since if any four of these five magnitudes are known, the fifth can be computed.

EXAMPLES.—(1) Calculate the heat of solution of mercuric chloride from the change of solubility with temperature when the solubility at the absolute temperature 283° is 6·57, and 11·84 when the temperature is 323°. Substituting these numbers in the above equation, Q is 2700 (nearly) cals. The observed value is nearly 3000.

(2) At 670°, the dissociation pressure of barium dioxide is 80 mm., and at 720°, 210 mm. Show that the heat of the reaction, $2BaO_2=2BaO+O_2$, approximates $-36{\cdot}1$ Cals., and that the maximum work furnished by the formation of two gram-molecules of barium dioxide from the monoxide and oxygen at 670°, and at the same partial pressure as it occurs in the atmosphere, is equivalent to 1203 cals.

When but one value of K at the temperature T is available, the integration of (2) furnishes the expression :

$$\log_{10}K=-0{\cdot}22\frac{Q_p}{T}+I \quad . \quad . \quad . \quad . \quad (5)$$

where I is the integration constant, and Q_p the thermal value of the reaction at constant pressure, and does not vary with changes of temperature. F. E. C. Scheffer considers that the expression $\log K=aT^{-1}+b$ is sufficiently in agreement with measurements of the equilibrium for all reactions which have been studied. If the reaction takes place at a constant pressure, an allowance can be made for the work done, and the thermal value of the reaction at constant volume, Q_v, is related to that at constant pressure, Q_p, by the expression $Q_p=Q_v-\Sigma nRT$, where ΣnRT represents the work done by the system against this pressure, and Σn denotes the difference between the sum of the molecular coefficients of the products of the reaction taken negative, and of the initial products taken positive—for instance, in the reaction $2H_2+O_2=2H_2O$, $\Sigma n=2+1-2=1$.

II. The thermal value Q of the reaction changes with variations of temperature.—It has been assumed that Q is constant, but if Q varies with temperature, the relation between Q and T must be known before the integration of (2) can be performed. It is usual to represent the relation between Q and T by the empirical formula of the type $Q=Q_0+\alpha T+\beta T^2$ . . ., where Q_0, α, β . . . are constants whose numerical values are calculated from the observed values of Q and T, and Q_0 is the value of Q when the temperature is at the absolute zero. If this expression for Q be substituted in the second of equations (1), and the integration be performed,

$$W=Q_0+IT-\alpha T\log T-\beta T^2-\tfrac{1}{2}\gamma T^3-\ldots \qquad (6)$$

which represents the affinity W in terms of the heat of the reaction at the temperature T.

Liquid and solid systems.—In his memoir *Ueber die Berechnung chemischer Gleichgewichte aus thermischen Messungen* (1906), W. Nernst[3] introduced the hypothesis that in the case of *condensed systems*—that is, systems involving only liquid or solid substances—the temperature coefficients of the free and total energy—*viz.* dW/dT and dQ/dT—decrease to indefinitely small values as absolute zero is approached ; and, the limiting value of

$$\frac{dW}{dT}=\frac{dQ}{dT}=0, \text{ at absolute zero, when } T=0$$

Consequently, the curves showing the relation between the affinity W, or the total energy Q, and temperature T, will coincide at absolute zero, and the equality will be usually maintained only for a short region of temperature in the neighbourhood of absolute zero. The measurement of Q and of W cannot be performed in the vicinity of absolute zero, and consequently, Nernst's hypothesis—called **Nernst's heat theorem**—cannot be directly verified. The hypothesis, however, has been verified indirectly, and the results are in satisfactory accord with experiment. It will be observed that if dQ/dT be zero when $T=0$, the term involving α must vanish from the expression $Q=Q_0+\alpha T+\beta T^2+$ . . ., because otherwise, at absolute zero, when $T=0$, $dQ/dT=\alpha$. The differential coefficient, dQ/dT, represents the specific heat of a gas, and consequently W. Nernst's assumption also includes the assumption that the specific heat of a gas is zero at absolute zero.[4] If very high temperatures be not under consideration, the higher powers of T can be neglected because their numerical coefficients are very small, and

$$Q=Q_0+\beta T^2 \qquad (7)$$

For similar reasons, if dW/dT be zero, I and α in the expansion (6) must vanish, and

$$W=Q_0-\beta T^2 \qquad (8)$$

Consequently, *for systems involving only liquids and solids the integration constant is zero*, in agreement with results previously obtained by G. N. Lewis (1899),[5] and others. Again, *for condensed systems, the numerical value of the affinity of a reaction can be computed from heat measurements alone.* Experiments show that for many reactions, where the evolution of heat is great, the coefficients β, γ . . . are very small, and W and Q have nearly the same value Q_0 ; and in these cases, M. Berthelot's rule—the principle of maximum work—will apply.

According to G. Kirchhoff's equation, the variation of Q with temperature, *viz.* dQ/dT, is equal to the difference in the specific heats, or rather the thermal capacities at constant volume of the initial (C_1) and final (C_2) products of the reaction ; in symbols, $dQ/dT=C_2-C_1$; and if γ, δ . . . are negligibly small, $dQ/dT=2\beta T^2$ $=C_2-C_1$, which gives the value of β ; hence, if Q be determined for any temperature T, Q_0 can be calculated from (7), and hence the free energy or affinity W, or log K can be calculated when Q_0, β, and T are known.

EXAMPLE.—From H. V. Regnault's measurements (1844) of the specific heats of rhombic and monoclinic sulphur, the numerical value of C_2-C_1 is nearly $0{\cdot}1840-0{\cdot}1764=0{\cdot}0076$. Consequently, $329\beta=0{\cdot}0038$, or $\beta=1{\cdot}15\times10^{-5}$. The heat of transformation at 368° absolute, according to G. Tammann (1903), is nearly 3·13 cals. Hence, $3{\cdot}13=Q_0+1{\cdot}09\times10^{-5}\times368^2$; or $Q=1{\cdot}57+0{\cdot}0000115T^2$. According to J. N. Brönsted,[6] the results obtained by comparing the observed and calculated values of Q at different temperatures are satisfactory. Similarly, $W=RT\log K=1{\cdot}57-0{\cdot}0000115T^2$. The curves obtained by plotting corresponding values of Q and T and W and T are indicated in type II, Fig. 2. Here, W decreases, and Q increases with increasing values of T, and at absolute zero the two curves coincide.

Equations (7) and (8) show that the two curves change symmetrieally for solid and liquid systems as indicated in Fig. 2, for the coefficients β, γ . . . may be positive or negative, and there are two possibilities for the slopes of the curves representing the changes of W and Q with temperature T. Deviations from symmetry occur when the change in the specific heat of the reacting substance is not a linear function of temperature.[7] For the reaction $CuSO_4+H_2O_{ice}\rightarrow CuSO_4.H_2O$, H. Schottky [8] found $Q=4520+0{\cdot}00408T^2$, and $W=4520-0{\cdot}00408T^2$, and this reaction is therefore representative of type II, Fig. 2, where the free energy W decreases, while the thermal value Q of the reaction increases with rise of temperature, and at 291° K. the free energy is less than the thermal value of the reaction. Again, for Clark's cell, $Zn+Hg_2SO_4+7H_2O_{ice}\rightarrow ZnSO_4.7H_2O+2Hg$, W. Nernst [9] finds that $Q=38505-0{\cdot}0017T^2$, and $W=38505+0{\cdot}0017T^2$. Here, the free energy W increases with temperature, while the thermal value Q of the reaction decreases as illustrated by the curve type I, Fig. 2.

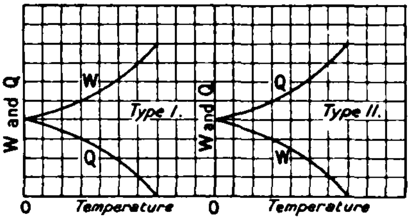

FIG. 2.—Variations of Q and W with Temperature.

At the transition point, say, in the passage of rhombic to monoclinic sulphur, the free energy must be zero, and $W=0$. Consequently, the transition temperature $T=(Q_0/B)^{\frac{1}{2}}$ from (7) and (8). The free energy of the change of rhombic to monoclinic sulphur is represented by the relation $W=1{\cdot}57-0{\cdot}0000115T^2$, consequently, the transition temperature is approximately 368° K., or (368°−273°)=95°. The observed value is 94·4°.

Gaseous systems.—The preceding discussion refers to solid or liquid systems, and it has been extended to gaseous systems when the molecular heat of the reaction at one temperature and the molecular heats of the gaseous substances at a few other temperatures are known. If Q denotes the heat of the reaction, it has been shown that $Q=Q_0+\alpha T+\beta T^2+\gamma T^3+\ .\ .\ .$, and this value of Q may be substituted in van't Hoff's equation (2). On integration,

$$RT\log K_v=Q_0+\alpha\log T+\beta T+\tfrac{1}{2}\gamma T^2+\ .\ .\ .\ +I \quad . \quad . \quad (9)$$

To evaluate the integration constant I, turn to Clapeyron-Clausius' equation, $\lambda=RT^2(d\log p)/dT$, a solution of which is possible when λ can be represented as a function of the temperature. If $\lambda=-\lambda_0+\alpha'T+\beta'T^2+\ .\ .\ .$, where λ_0 represents the internal molecular heat near absolute zero, and α', β' . . . are numerical constants. It follows, after the substitution and integration, that

$$\Sigma n\log C=-\frac{\Sigma n}{R}\left(\frac{\lambda_0}{T}-\alpha'\log T-\beta'T-\frac{\lambda'}{2}T^2-\ .\ .\ .\right)\Sigma nI' \quad . \quad (10)$$

Substituting $W=Q_0-\beta''T^2-\tfrac{1}{2}\gamma''T^3-\ .\ .\ .$, and the above value for $\Sigma n\log C$, in van't Hoff's equation $W=RT\log K-RTn\log C$, the result can be reduced to the form

$$RT\log K=(Q_0'-\Sigma n\lambda_0)+\Sigma n\alpha'T\log T-(\beta''-\Sigma n\beta')T^2-\ .\ .\ .\ +RT\Sigma nI'$$

This deduction from Clapeyron-Clausius' equation has a formal analogy with the deduction (9) from van't Hoff's equation, and both refer to the same quantity RT log K. Assuming that the equations are identities, the coefficients of like powers of T in both equations can be equated each to each: $Q_0=Q_0'-\Sigma n\lambda_0$; $-a=\Sigma na'$; $-\beta=-\beta''+\Sigma n\beta'$; and $I=\Sigma nI'$. Hence, the integration constant of the equations for the vapour pressures of the reacting components can be used to evaluate the constant I of a given reaction, for the revised equation (9) may be written

$$\log K_v=\frac{Q_0}{RT}-\frac{a}{R}\log T-\frac{\beta}{R}T-\frac{\gamma}{2R}T^2+\ .\ .\ .\ +\Sigma nI' \quad . \quad (11)$$

It will be remembered that K_r, the equilibrium constant of the chemical equation $n_1A_1+n_2A_2+\ .\ .\ .\ =N_1B_1+N_2B_2+\ .\ .\ .$, is equivalent to

$$K_v=\frac{c_1^{n}c_2^{n}\ .\ .\ .}{C_1^{N_1}C_2^{N_2}\ .\ .\ .}\text{; and } K_p=\frac{p_1^{n}p_1^{n_2}\ .\ .\ .}{P_1^{N_1}P_2^{N_2}\ .\ .\ .}$$

when the partial pressures are used. From Boyle's law $p=CRT$ it follows that $P_{B_1}^{N_1}=C_{B_1}^{N_1}(RT)^{N_1}$, etc., and consequently, $K_p=K_v(RT)\Sigma n$, or log $K_p=$log K_v $+\Sigma n$ log $R+\Sigma n$ log T. Substituting for log K_v in equation (10); using common instead of natural logarithms; and

$$\log_{10} K_p=\frac{Q_0}{4{\cdot}57T}-\frac{a-\Sigma nR}{R}\log T-\frac{\beta}{4{\cdot}57}T-\ .\ .\ .\ \frac{\Sigma n(I+\log R)}{2{\cdot}3} \quad (12)$$

The constant $\Sigma n(I+\log R)/2{\cdot}3$ is represented by $\Sigma n\mathbf{C}$, where **C** is called by W. Nernst the **chemical constant** of the substance. When the different terms of the vapour pressure equation (10) have been introduced, the constant I' for any given substance can be calculated, and thus **C** can be determined. To evaluate the chemical constants, it is therefore necessary to have a great number of accurate measurements extending over a wide range of temperature: (1) The thermal value of the reaction at a given temperature; (2) the equilibrium constant of the same reaction at the given temperature; and (3) the specific heats of all the substances which take part in the reaction, from the given temperature T down to absolute zero. The observation data available are not very accurate, and a number of empirical formulæ have been recommended. For example, W. Nernst recommended $\mathbf{C}=1{\cdot}33\log T_b-0{\cdot}00098T_b$, where T_b denotes the absolute boiling point of the substance. This equation is obtained from the empirical observation, that the chemical constant is nearly 0·14 times Trouton's constant λ/T, and W. Nernst's observation that $\lambda/T=9{\cdot}5\log T_b-0{\cdot}007T_b$.

It follows from what precedes, that the chemical constant

$$\mathbf{C}=\frac{I+\log R}{2{\cdot}3}=\frac{\lambda_0}{4{\cdot}57T}-1{\cdot}75\log_{10}T+\frac{\beta}{4{\cdot}57}T+\log_{10}p \quad . \quad (13)$$

where λ_0 is the molecular latent heat at absolute zero; and β is a constant depending on the change of specific heat with temperature, The number 1·75 was obtained on the assumption that at the lowest temperatures, the molecular heats of all gases are 1·5 greater at constant volume, and 3·5 greater at constant pressure than the molecular heats of the corresponding condensation products. W. Nernst's later work showed that these assumptions cannot be justified, and the formula there becomes an empiricism.[10] A. C. Egerton deduced an expression from $\lambda=RT^2(d\log p)/dT$; $\lambda=\lambda_0+S_0C_pdT-S_0c_pdT$; $c_p=c_v+aT^{\frac{1}{2}}$, or $c_p=c_v+9a^2vT/\beta$, whence $9a^2vT/\beta=aT^{\frac{1}{2}}$; and W. Nernst and F. A. Lindemann's molecular heat formula. His expression enables the chemical constant to be evaluated from β_v, a.

and two values of p, or one value of p and the value of λ_0. A. C. Egerton thus obtains for the chemical constant of

Hg	Cd	Zn	W	Mo	Pt	A	H
1·633	1·42	1·49	3·5	4·4	1·5	1·65	1·68

The chemical constants for a few substances (pressure in atmospheres) indicated in Table V have been calculated mainly by W. Nernst.

TABLE V.—NUMERICAL VALUES OF CHEMICAL CONSTANTS **C**.

	C		**C**		**C**
He . . .	−1·15	I_2 . . .	3·9	H_2O . .	3·6
Ne . . .	−0·10	HCl . .	3·0	CCl_4 . .	3·1
A . . .	−0·35	HBr . .	3·2	$CHCl_3$ . .	3·2
Kr . . .	0·82	HI . .	3·4	CH_4 . .	2·8
X . . .	1·10	NO . .	3·5	C_2H_6 . .	2·6
H_2 . . .	1·6	N_2O . .	3·3	C_2H_4 . .	2·8
N_2 . . .	2·6	H_2S . .	3·0	C_2H_2 . .	3·2
O_2 . . .	2·8	SO_2 . .	3·3	C_6H_6 . .	3·0
CO . . .	3·5	CO_2 . .	3·2	C_2N_2 . .	3·4
Cl_2 . . .	3·1	CS_2 . .	3·1	C_2H_5OH .	4·1
Br_2 . . .	3·2	NH_3 . .	3·3	Hg . .	1·4

The quotient obtained by dividing W. Nernst's chemical constant by the logarithm of the critical pressure in atm. varies from 1·5 to 1·8. Thus, the critical pressure of chlorine is 92·5 atm. and log 92·5=1·971 ; hence 3·1÷1·97=1·6. This means that the chemical constant **C** of a liquid is proportional to the logarithm of the pressure p, so that $\mathbf{C}=1\cdot65 \log_{10} p$. For monatomic gases, $\mathbf{C}=-1\cdot62+1\cdot5 \log M$, where M represents the molecular weight of the gas.

The methods of evaluating the chemical constants are: (1) Direct comparison with the vapour pressure curve; (2) The method of chemical equilibrium ; (3) Some empirical formulæ—*e.g.* S. Young's modification of Clapeyron-Clausius' equation, above. It must be added that the evaluation of the chemical constant is the weakest part of the discussion, and the results obtained by the different methods are not always concordant, probably owing to the inaccuracy of the available data. For example, two equally satisfactory empirical formulæ for the specific heat of a gas may lead to widely different values for the chemical constant. Thus A. Langen gives the chemical constants of nitric oxide, +0·92 ; oxygen. 1·021—0·539 ; carbon monoxide, —0·04 ; nitrogen, 0·05 ; carbon dioxide, —0·406 ; water, —1·930 ; and ammonia, —2·454. However, as B. Weinstein has emphasized, although the results which have been obtained *die Zulässigkeit des Gleichungssystems zweifellos feststellen*, yet the uncertainty in the numerical values of the constants can be removed only by observations extending over wide ranges of temperature.

Remembering that $a=-\Sigma na'$, where a' is a constant in the vapour pressure curve, and therefore $a-\Sigma nR=-\Sigma n(a'+R)$, W. Nernst puts $a'+R=3\cdot5$ cals. as a first approximation, so that $a-\Sigma nR=-\Sigma n3\cdot5$; or $(a-\Sigma nR)/R=\Sigma n1\cdot75$. Substituting these results in equation (12), and

$$\log_{10} K_p=\frac{Q_0}{4\cdot57}+\Sigma n1\cdot75 \log T-\frac{\beta}{4\cdot57}T- \dots +\Sigma n\mathbf{C} \quad . \quad (14)$$

the values of $a, \beta, \gamma, \dots$ can be determined from the relation $dQ/dT=a+2\beta T+3\gamma T^2+\dots$ from G. Kirchhoff's equation, where dQ/dT is equal to the difference between the molecular thermal capacity of the initial and end products of the reaction ; Q_0 is evaluated from the relation $Q=Q_0+aT+\beta T^2+\dots$ For gaseous reactions in which the initial and final products occupy the same volume, Σn is zero, and $\Sigma n1\cdot75 \log T$ is then a zero term, but neither $\Sigma n\mathbf{C}$ nor βT is necessarily zero.

These relations, obtained by the application of W. Nernst's theorem to J. H. van't Hoff's equation, enable the equilibrium constant of a gaseous reaction, and consequently also the free energy or affinity of a reaction, to be calculated from three sets of data : (i) The thermal value of the reaction at the temperature T ; (ii) The molecular heats of the reacting substance over the range of temperature in question ; and (iii) The chemical constants of the reacting substances. As H. le Chatelier[11] stated in 1888, the chemical constants are definite functions of certain physical properties of the reacting substances. Consequently, *the indeterminate integration constant in J. H. van't Hoff's equation can also be expressed as a sum of constants which are characteristic of each reacting substance.* This can also be done quite independently of W. Nernst's heat theorem (1906), as was demonstrated by M. Planck (1897) and by F. Haber (1905).[12] Another important feature of this investigation is that it enables the integration constant I to be calculated from the characteristic function $\Sigma nI'$, that is, the chemical constants of the substances concerned in the gaseous reactions can be computed without making any observations on the reaction itself. As H. le Chatelier predicted in 1888, the evaluation of the nature of this function will lead to a complete knowledge of the laws of chemical equilibrium, and it will enable chemists to determine the conditions of equilibrium of a given chemical reaction, *à priori*, and independently of new experimental data.

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CHAPTER XIII

THE KINETIC THEORY OF ATOMS AND MOLECULES

§ 1. The Molecular Theory of Matter

If we would become imbued with the spirit of the new philosophy of chemistry, we must begin by believing in molecules.—J. P. COOKE.

FOR purely chemical reasons, which culminated in Avogadro's hypothesis, chemists have invested matter with an imaginary structure which explains, very well, the various transformations which matter undergoes. Matter—which in bulk appears to the eye continuous and perfectly uniform in all its properties and parts—is supposed to be made up of extremely small discrete particles called molecules. **Molecules are the imaginary units which make up matter en masse.** Molecules are made up of one or more atoms. **Atoms are the imaginary units which make up individual molecules.**

Molecular structure of matter.—Matter must be either a discrete or a continuous medium. The phenomena which attend diffusion in solids, liquids, and gases lead us to reject the hypothesis that matter is continuous, for how can two continuous media occupy the same period of time ? A study of the compressibility of gases—Boyle's law—leads to the same view. There appears to be no limit to the expansion or dilatability of a gas ; and therefore, says A. W. Rücker (1901), it is inconceivable that any real substance or thing which can at the same time be present in every part of a given space would also be present in every part of a space a million times as great. How can a continuous medium on rarefaction (that is, diminution of pressure) expand indefinitely ? How can compression diminish the volume of matter itself ? If matter be discrete, we can readily answer these queries. Compression involves a closer packing or a crowding together of the molecules by diminishing the space between them. This very explanation was given by Hero of Alexandria[1] *circa* 177 B.C.

> The particles of air do not fit closely in every part, but void spaces are left between them as in the sand on the seashore ; the grains of sand must be imagined to correspond to the particles of air, and the air between the grains of sand to the void spaces between the particles of air. Hence, when any force is applied to air, the air is compressed, and, contrary to its nature, falls into the vacant spaces from the pressure exerted on its particles ; but when the force is withdrawn, the air returns again to its former position from the elasticity of its particles, as is the case with horn shavings and sponge, which, when compressed and set free again, return to the same position, and exhibit the same bulk.

Conversely, rarefaction involves an increase of the space between the molecules, so that the molecules become less closely packed and less crowded together. If matter be discrete we can also understand how one substance can diffuse into another—hydrogen into air ; and aniline dye into water. There are also numerous examples of the diffusion of one solid metal into another, the penetration of solid metals by gases, etc., which show that solid metals are porous to certain elements. Mercury will pass through a piece of tin, a centimetre thick, in half a minute. The porosity of metals was recognized by G. Homberg[2] in 1713, and, in his *Observations sur des matières qui pénètrent et qui traversent les métaux sans les fondre*, he gave examples of substances which will pass through the pores of the metals. Again, the volume of a mixture of two liquids is not necessarily the same as the joint volume of the separate components, even though no chemical reaction, recognized as such, occurs.

A mixture of 500 c.c. of alcohol and 500 c.c. of water occupies 940 c.c., which is much less than 1000 c.c., and the difference is still greater in the case of sulphuric acid and water provided the temperature at which the volume of the solutions is measured is the same. Conversely, a solution may occupy a greater volume than the joint volume of its separate constituents. Thus 111·1 c.c. of *p*-nitrotoluene and 100 c.c. of carbon disulphide give not 211·1 c.c. but 224·7 c.c. of the mixture—an expansion of 13·6 c.c. Similarly, the volumes of solutions of the ammonium halides in water are greater than the joint volumes of salt and water.

Many other examples might be quoted which indicate that (1) one substance may be actually penetrated by another; or that (2) the molecules of one substance may be so disposed that the molecules of another substance can be accommodated between them much as a scuttle of coal might at the same time accommodate a bucket of sand; (3) matter is compressible or expansible so that it occupies a different volume in contact with another substance than it does alone. The molecules seem to lead a more or less independent existence, and the space between the molecules furnishes accommodation for the introduction of other particles.

There are many other lines of argument pointing in the same direction: If transparent substances like glass or water were infinitely homogeneous, the velocity of propagation of light through them would be independent of the period of vibration or the wave-length of the ray of light. A. L. Cauchy (1836),[3] therefore, inferred that transparent substances are not infinitely homogeneous because the velocity of propagation of light does depend on the period of vibration; and the coarse-grainedness of liquids and transparent solids is comparable with the wave-length of light.

W. Ostwald in his *Grundriss der allgemeinen Chemie* (Leipzig, 1904) did not accept the interpretation of the evidence for the granular structure of matter, for he confessed that he did not then know any facts which could not be described without this assumption; but in a later edition (London, 1912), he said that after a fruitless search extending over a century, a final proof of the grained, atomistic, or molecular nature of matter has been obtained by studying the properties of colloidal systems, and the effects of electrical discharges in gases. A study of the physical and the chemical properties of matter has thus led to the conclusion: **Matter is discrete not continuous; and it is made up of minute particles called molecules.** This hypothesis is called the molecular theory of matter.

Are the molecules stationary or in motion? Here again the phenomenon of diffusion has led to the further assumption that the molecules of matter are in rapid motion. How could gases diffuse one into the other in such a remarkable way if the molecules were at rest? Again, in Rumford's celebrated experiment (1798) it was proved that mere friction produces heat in *unlimited* quantities, and hence it was argued that it is "extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being excited and communicated in the manner *heat* is excited and communicated in this experiment, except it be motion." Heat must be a mode of motion. Again, if heat be a mode of motion the motion is not apparent; it is not a motion of the body as a whole, but rather a motion of the fundamental particles of matter. This internal motion, too, must be more rapid the higher the temperature, a conclusion which is in harmony with the phenomenon of diffusion. Diffusion is produced by the internal movement of the particles of matter, and this is the more rapid, the higher the temperature. The fact that gases rapidly fill a confined space, however large, has been explained by assuming that the molecules repel one another, but, as H. Davy emphasized in his *Essay on heat, light, and the combinations of light*,[4] in 1799, the so-called repulsive force can be identified with the thermal oscillations of a body:

Heat may be defined as a peculiar motion, probably a vibration of the corpuscles of bodies, tending to separate them. . . . To distinguish this motion from others . . . the name *repulsive motion* has been adopted.

The phenomena which attend the expansion and diffusion of matter lead to the assumptions: (i) that matter has a granular structure, for it consists of discrete parts of molecules; and (ii) that the molecules are in a state of incessant independent motion, and that they are travelling to and fro in all directions. The physical evidence here outlined is altogether independent of assumptions as to the nature and properties of the molecules; it can be supplemented by an enormous mass of other facts from diverse sources; and it is strongly supported by chemical phenomena as interpreted by Dalton's and Avogadro's hypotheses.

According to the kinetic theory as expounded by P. Gassend in 1658, and others, the difference between solids, liquids, and gases is due to a difference in the average distances between the molecules, and in the mobilities of the molecules. The physicists' definition of a molecule is: a minute portion of a substance which moves about as a whole, so that its parts, if it has any, do not part company during the motions.

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§ 2. The Kinetic Theory of Gases—Boyle's Law

What *is* must be studied before what *was* can be inferred. Precedent states remain visionary unless they can be linked to actual and observable conditions.—A. M. CLERKE.

The molecules of a gas seem to lead to a more or less independent existence; and their average distance apart is much greater than with liquids or solids. The molecules of a gas appear to be continually moving with a great velocity in approximately straight lines in all directions. The molecules spend most of their time travelling about like missiles, without the kinetic energy of the motions predominating in any one direction. There is an interchange of energy during the collisions of the molecules, and the immense number of collisions leads to a rapid distribution of any excess of energy which the motions of any one molecule might possess, and thus the pressure, etc., is rapidly equalized. The molecules in their travels are not only colliding with one another but they are also bombarding the walls of the containing vessel; in consequence, the molecules are continually changing their speeds and directions. It is clear that an outside pressure must be exerted on the walls of the vessel every time a molecule strikes the boundary walls, but every bombardment known to human experience involves several losses—*e.g.* energy, velocity, and momentum are lost. **The molecules are supposed to be perfectly elastic** so that after each collision they rebound with the same velocities as before, otherwise, it is said, their momentum would decrease with each collision and the pressure of the gas would decrease with time, which it does not. Gases have been confined many months under pressure without sign of loss; but attempts to so detect a diminution of pressure are foredoomed to failure since any slackening the average speed of the molecules would probably be immediately restored by collision with the boundary walls, if the prevailing temperature determined the average speed of the molecules.

Hence, the kinetic theory of molecules postulates: (i) The molecules are perfectly elastic; and (2) in spite of the law of excluded perpetual motion, we have what H. Poincaré called *un éternal paradox*, for it is inferred that **the molecules of a gas**

are in a state of perpetual motion. A hypothesis is weak when it is based upon more or less arbitrary fictions, and not on something about which we have experience. Still there are hypotheses which are strong and vigorous in spite of their explaining the known in terms of the obscure—*ad obscurum per obscurum*. For instance, we have no experience of an interstellar æther, and yet the undulatory theory of light has thriven on such a medium ; nor yet have we any experience of perfectly elastic solids, and yet the kinetic theory of molecules has grown about this fiction. The preceding assumptions suffice for some important deductions which enable the condition of the molecules of a gas to be inferred with some degree of probability.

Boyle's law.—Assume that a closed vessel contains an indefinitely large number, n molecules, and that the ceaseless cannonade of these molecules on the walls of the vessel produces an average pressure p. Imagine n similar molecules to be squeezed into the same vessel. This will double the number of impacts on the sides of the containing vessel so that the pressure will rise from p to $2p$. The concentration of the gas will also be doubled. This is nothing but another way of stating Boyle's law. The argument is due to Robert Hooke[1] in 1678. R. Hooke's own words are :

> If therefore a quantity of this body be enclosed by a solid body, and that be so contrived as to compress it into less room, the motion thereof (supposing the heat the same) will continue the same, and consequently the Vibrations and Occursions will be increased in reciprocal proportion, that is if it be condensed into half the space the Vibrations and Occursions will be double in number. If into a quarter the Vibrations and Occursions will be quadruple. . . . Again, if the containing vesesl be so contrived as to leave it more space, the length of the Vibrations will be proportionally enlarged and the number of Vibrations and Occursions will be reciprocally diminished, that is, if it be suffered to extend to twice its former dimensions, its Variation will be twice as long, and the number of its Vibrations and Occursions will be fewer by one half, and consequently its endeavours outward will be also weaker by half.

The further mathematical study of a system of elastic spheres, ceaselessly moving at different speeds in all directions is based upon the principle of averages. It does not consider the motion of an individual molecule, but rather the average motions of the entire system of spherical particles.

Boyle's law can then be obtained in another manner : Suppose a gas containing n molecules, each of mass m, be confined in a cube with edges each l cm. long, and that the molecules are moving with a mean velocity V. Although the molecules travel about in every conceivable direction, it is fair, for purposes of calculation, to consider the molecules are divided into three equal sets with velocities parallel to three adjacent sides of the cube. At any instant, therefore, we assume that $\frac{1}{3}n$ molecules are travelling with a mean velocity V parallel to any particular edge, and therefore perpendicular to the two corresponding faces of the cube. One molecule moving with a velocity V will take l/V seconds to pass from side to side, and it will therefore strike a side $\frac{1}{2}V/l$ times per second. At each collision with the face of the cube, the velocity of the molecule is reversed in direction that its momentum changes from mV to $-mV$; that is, its momentum changes $2mV$. The total change of momentum by $\frac{1}{3}n$ molecules striking a side $\frac{1}{2}V/l$ times per second will therefore be the product $\frac{1}{2}V/l \times 2mV \times \frac{1}{3}n$, or $\frac{1}{3}nmV^2/l$. This measures the total force or pressure exerted on one face of the cube. But the total surface of one face of the cube is l^2. Hence, the total pressure per unit area is $p=\frac{1}{3}nmV^2/l \div l^2=\frac{1}{3}nmV^2/l^3$. But l^3 represents the volume v of the cube. Hence

$$pv=\frac{1}{3}nmV^2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The product of the pressure and volume of a gas is equal to one-third the sum of the masses of all the molecules into the square of the mean velocity of the translatory motions of all the molecules. For unit volume also, the average kinetic energy of the molecules of the gas is equal to the pressure p. If the number n, the mass m, and the mean velocity V of the molecules does not change, the expression $\frac{1}{3}nmV^2$

will be a constant; and hence also the product pv will be constant. This is in accord with Boyle's law. Since $pv=RT$ it follows that

$$RT=\tfrac{1}{3}nmV^2\text{; or } RT=\tfrac{1}{3}NV^2 \quad . \quad . \quad . \quad . \quad (2)$$

where N denotes the number of gram-molecules per c.c. **Dalton's law of partial pressures** follows as a corollary, because the total pressure exerted by a mixture of gases must be the sum of the partial pressures exerted by the individual molecules provided they exert no physical or chemical action upon one another. By definition, the mass M of any substance is equal to the product of the density D into the volume v, and accordingly, the density of a mass of n molecules each of mass m occupying a volume v will be $D=nm/v$. Substituting this relation in the preceding equation, and

$$p=\tfrac{1}{3}DV^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which is sometimes called **Bernoulli's equation,** and which shows that the pressure of a gas is equal to one-third the product of its density into the square of the mean velocity of the translatory motions of the molecules.

The **mean kinetic energy** of the molecules is $K=\tfrac{1}{2}nmV^2$, and accordingly, equation (1) can be written $\tfrac{3}{2}pv=\tfrac{1}{2}nmV^2$, showing that the product $\tfrac{3}{2}pv$ is equal to the mean kinetic energy of the molecules, or

$$\text{Kinetic energy}=\tfrac{3}{2}RT \quad . \quad . \quad . \quad . \quad . \quad (4)$$

since $pv=RT$. Hence, the pressure of unit volume of a gas is two-thirds the kinetic energy—expressed in proper units—whatever be the temperature. This enables the molecular energy of a gas to be expressed in terms of a magnitude which can be measured directly. Both magnitudes have their origin in molecular motion; and both change proportionally with the absolute temperature, so that

$$\frac{p}{T}=\frac{p_0}{T_0}, \text{ or } p=p_0(1+\alpha\theta)\text{; and } \frac{K}{T}=\frac{K_0}{T_0}, \text{ or } K=K_0(1+\alpha\theta) \quad . \quad (5)$$

where p_0 and K_0 represent the values of the pressure and kinetic energy per unit volume at 0°, or at $T_0=273$; and p and K the corresponding values at the absolute temperature T. It follows therefore that the kinetic energy of molecular motion is the mechanical measure of the temperature.

The mean kinetic energy is also equal to $\tfrac{1}{2}MV^2$, when $M=nm$. Consequently, $3RT/M=V^2$, and since the numerical value of R is $83{\cdot}15\times10^6$ ergs, the so-called mean velocity V of the molecules is

$$V=15800\sqrt{\frac{T}{M}} \text{ cm. per second} \quad . \quad . \quad . \quad (6)$$

From (3), when the pressure is constant, the velocity V will be inversely proportional to the square root of the density D, for $V^2=k/D$, where k represents a constant; or $V_1\sqrt{D_1}=V_2\sqrt{D_2}$. This is **Graham's diffusion law.** If V denotes the mean velocity of the molecules of a gas, the average kinetic energy is $\tfrac{1}{2}MV^2$, and by Graham's law, the velocity is equal to a constant, say $\sqrt{2k}$, divided by $\sqrt{D}$, or the mean kinetic energy is kM/D; but by Avogadro's rule, $M=k'D$, and hence the mean kinetic energy is equal to a constant k. The temperature and pressure are supposed to be invariable. Hence, **the mean kinetic energy of the molecules of all gases at the same temperature and pressure is the same.** Since the mean kinetic energy a gram-molecule of a gas, $\tfrac{1}{2}MV^2$, is equal to $\tfrac{3}{2}RT$, it follows that if there are $6{\cdot}062\times10^{23}$ molecules per gram-molecule of the gas, the kinetic energy per molecule at 0° and 760 mm. is $5{\cdot}62\times10^{14}$ erg.

How fast do the molecules move?—Bernoulli's equation makes possible an extraordinary calculation—no less than the mean velocity of the translatory motions of the molecules. The other two magnitudes which occur in the equation can be directly measured. J. P. Joule made this calculation in 1848; although J. J. Waterston presented an analogous calculation to the Royal Society nearly three years earlier.[2]

A gram-molecule of hydrogen—that is, 2·016 grms.—at 0°, and under a pressure of 760 mm., occupies very nearly 22400 c.c. The density of hydrogen is therefore very nearly 2·016/22400=0·0000896. Again, a pressure of 760 mm. of mercury is equivalent to a weight of 1033·3 grms. per sq. cm., and since a weight of one gram falling freely acquires an acceleration of 981 cm. per second, owing to gravitational attraction, it follows that 1033·3 grms. will acquire an acceleration of 981 × 1033·3 cm. per second. By substituting these results in Bernoulli's equation: $1033{\cdot}3 \times 981 = \frac{1}{2} \times 0{\cdot}0000896 \times V^2$, or $V = 184100$ cm. per second.

It is not to be assumed that all the molecules of hydrogen have this particular speed, nor that any single molecule retains this speed over any lengthened period. Some of the molecules no doubt have a greater velocity, others a smaller velocity. A molecule of hydrogen starting off with a velocity above the average will soon have both its speed and direction changed by encounters with other molecules. The velocity V under consideration represents the mean velocity, or the velocity of mean square of the whole of the molecules of the given gas at the temperature of melting ice. If the gas contains n molecules, and the velocities of the different molecules are $v_1, v_2, \ldots$ there must be a quantity V^2 such that $nV^2 = v_1^2 + v_2^2 + v_3^2 + \ldots + v_n^2$; this quantity V is called *the velocity of mean square* of the moving particles, and V is called here the *mean velocity*. At 0°, therefore, the mean velocity of the molecules of hydrogen is nearly 1·84 kilometres per second, that is, about 6100 ft., or just over a mile per second. The arithmetical mean U of the velocities of all the molecules is rather less than the mean velocity V, such that $U = 0{\cdot}921V$, or $V = 1{\cdot}08U$ or,

$$U = 14550\sqrt{\frac{T}{M}} \text{ cm. per second} \quad . \quad . \quad . \quad (7)$$

The speeds of the molecular motions of other gases can be calculated in a similar manner, or Graham's law can be used. The results for seven typical gases at 0° and 20° are indicated in Table I.

TABLE I.—THE MEAN VELOCITIES OF DIFFERENT GASES.

	Molecular weight, M.	Mean velocity V cm. per second.	
		At 0°.	At 20°.
Hydrogen, H_2	2·016	$1{\cdot}84 \times 10^5$	$1{\cdot}90 \times 10^5$
Oxygen, O_2	32·00	0·46	0·48
Nitrogen, N_2	28·02	0·49	0·51
Argon, A	39·88	0·41	0·43
Water, H_2O	18·016	0·61	0·64
Carbon dioxide, CO_2	44·00	0·39	0·41
Mercury, Hg	200·6	0·18	0·19

M. Cantor[3] has made an experimental demonstration of the speeds of molecular motion. When a copper plate is inserted in a vessel of chlorine, part of the molecules of the gas which bombard the plate rebound, and part unite with the metal to form the chloride. If p denotes the pressure of the gas on the surface of an inert substance, and p' the pressure on the surface of the copper, $p - p' = \frac{2}{3}wV$, where w denotes the mass of chlorine absorbed per sq. cm. per second. and V the velocity of the molecules which react with the copper, by suitably suspending plates of glass with the right half of one face and the left half of the opposite face coated with copper. M. Cantor was able to measure the difference of pressure $p - p'$ from the forward movement of the coppered faces; w could be determined by direct weighing. When $w=\frac{1}{3}\times10^{-6}$ grm., and $p-p'=10{\cdot}7\times10^{-4}$ dynes per sq. cm., the mean velocity of the molecules of chlorine absorbed by the copper is 48 metres per second. The mean velocity of *all* the molecules at 0° is 310 metres per second.

O. E. Meyer, in his *Die kinetische Theorie der Gase* (Breslau, 1877), has shown that in a gas at rest as a whole, the number of molecules which strike unit area of the containing vessel in unit time is $\frac{1}{4}nmU$, or since $nm=D$, the density of the gas, the number of grams of gas molecules which strike unit area in unit time is $\mu=\frac{1}{4}DU$, and since $D=M/v=Mp/RT$ from the gas equation, it follows that $\mu=MpU/4RT$, where p is expressed in bars. Substituting the value of U from (7), when $R=83{\cdot}15\times10^6$ ergs per degree.

$$\mu=43{\cdot}7\times10^{-6}p\sqrt{\frac{M}{T}} \text{ grms. per sq. cm. per sec.} \qquad (8)$$

A gram-molecule of gas contains $6{\cdot}062\times10^{23}$ molecules, and therefore, the number of molecules of gas which strikes a sq. cm. of surface per second is

$$N=2{\cdot}652\times10^{19}p\sqrt{\frac{M}{T}} \qquad (9)$$

For hydrogen, at a pressure $p=10^6$ bars, and 20°, $\mu=13{\cdot}8$ grms. per sq. cm. per second. That is, the total number of molecules striking a sq. cm. of surface is equivalent to the number of molecules contained in 154 litres of hydrogen gas—although, of course, the same molecules may strike the surface many times.

I. Langmuir[4] has applied this equation to compute the vapour pressure of tungsten, molybdenum, and platinum.

Consider a surface of metal in equilibrium with its saturated vapour. According to the kinetic theory, equilibrium is looked upon as a balance between the rates of vaporization and condensation. These two processes are conceived to be going on simultaneously at equal rates. At temperatures so low that the vapour pressure of a substance does not exceed a millimetre, the actual rate of evaporation of a substance may be considered to be independent of the presence of the vapour around it. That is, the rate of evaporation in a high vacuum is the same as the rate of condensation in presence of a saturated vapour. Similarly, the rate of condensation may be considered to be determined only by the pressure of the vapour.

I. Langmuir therefore argues that the vapour pressure of a metal like tungsten can be calculated, by means of equation (8), from the observed rate of evaporation or loss of weight at constant temperature when heated in vacuum tubes. At 2800° K., for example, the loss of weight of a tungsten filament was observed to be $0{\cdot}43\times10^{-4}$ grms. per sq. cm. per second. Consequently, from (8), the vapour pressure is $38{\cdot}1\times10^{-3}$ bar, or $28{\cdot}6\times10^{-6}$ mm. of mercury.

I. Langmuir has further compared the energy lost by convection from tungsten wire heated in hydrogen gas with the loss calculated from the kinetic theory, and found that the two results are in agreement at temperatures below 2100° K.; at higher temperatures, the observed losses are greatly in excess of the theoretical results. The increased loss of heat is supposed to be expended in the dissociation of the hydrogen molecules as they strike the tungsten wire. The augmented loss does not occur below 3500° K. in nitrogen or mercury vapour. The calculated dissociation of hydrogen $H_2\rightleftharpoons2H$ at 2500° K. is 3·7 per cent.; at 3330° K. 5·3 per cent.; and at 4500° K, the dissociation is almost complete. The number of hydrogen molecules which strike the hot wire at very low pressures can be calculated from (7), and the heat losses from the surface of the wire can be measured; consequently, the heat carried away by each molecule of the gas can be computed.[5] At high temperatures, the heat losses become approximately constant; and, assuming that every hydrogen molecule which strikes the filament is then dissociated, it is possible to calculate a lower limit for the heat of the reaction. In this way, it was found $2H\rightarrow H_2+130$ Cals. at constant volume and 3000° K.; and similarly, $2H\rightarrow H_2+136$ Cals. at constant pressure.

Again, I. Langmuir found that tungsten wires heated in oxygen gas are chemically attacked, and the tungstic oxide so formed volatilizes and condenses on the walls of the bulb, and leaves the surface of the filament clean. Equation (6) again enables the rate at which the oxygen molecules strike the wire to be calculated, and on comparing the result with the rate at which the filament is actually attacked, I. Langmuir found that only a fraction of the total number of molecules of oxygen which strike the filament are chemically fruitful. About 0·033 per cent. of the oxygen molecules which strike the filament react chemically with the tungsten at 800°, and 15 per cent. at 2500°. At this latter temperature, therefore, only one molecule in every seven of those which strike the tungsten actually form tungstic oxide, WO_3.

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§ 3. The Kinetic Theory of Gases—Charles' Law and Avogadro's Hypothesis

Nihil enim viveret sine calore.—L. A. SENECA (c. 50).

Heat is motion which in its strife acts upon the smallest particles of bodies.—FRANCIS BACON (1620).

That all kinds of fiery burning bodies have their parts in motion; that heat argues a motion of the internal parts, and that in all extremely hot shining bodies, there is a very quick motion that causes light, will be generally granted.—ROBERT HOOKE (1665).

Heat consists in a minute vibratory motion of the particles of bodies.—ISAAC NEWTON (1675).

Heat is considered by men of science to be a mode of motion of the molecules of matter; and the texts at the head of this section show that the idea is very old. The dynamical theory of heat was advanced as an hypothesis by F. Bacon, I. Newton, and R. Boyle, and established by the experimental work of Count Rumford, H. Davy, J. P. Joule, etc.

The kinetic theory and Charles' law.—The average speed of molecular motion is assumed to determine the temperature. Each change of temperature, however slight, is supposed to be attended by a corresponding change in the average speed of the moving molecules. From Boyle's and Charles' laws, $pv=RT$; when V is the mean velocity of the molecules of a gas, $pv=\frac{1}{3}nmV^2$, or $RT=\frac{1}{3}nmV^2$; and since R, n, and m are constant, it follows that $V^2=kT$, where k is a constant; otherwise expressed, for a given gas at a given pressure, the mean molecular velocity V^2 depends only upon the one variable—temperature. J. J. Waterston [1] first developed this hypothesis in 1845—**the mean kinetic energy of the molecules of a gas is proportional to the temperature—Waterston's hypothesis.** The same postulate was made independently by R. Clausius, and shown to be a necessary consequence of J. C. Maxwell's law of the equipartition of energy. It is sometimes called *Clausius' postulate.* The hypothesis that temperature is a quantity of the same kind as molecular kinetic energy is one of the most important fundamental postulates of the kinetic theory. From this it follows that at the same temperature, the mean kinetic energy of the molecules of all gases (which obey the ordinary gas laws) is the same. The total kinetic energy of a gas is proportional to the product pv. Hence, if the temperature be altered, pressure remaining constant, the kinetic energy (*i.e.* temperature) must alter to the same extent, and hence also the volume. Otherwise expressed, if the pressure remains constant, the same alteration of temperature will alter the volume to the same extent. This is Charles' law. Since the mean kinetic energy of the translatory motions of the molecules of any gas is constant, and when two or more substances at different temperatures are in intimate contact, their temperature will assume one constant value, it is accordingly assumed that equality of temperature means equality of the kinetic energies of the molecules, and Waterston's hypothesis takes the form: **Two gases are in thermal equilibrium when the mean kinetic energies of their molecules are the same.** Since real gases—which exert no chemical or physical action on one another and which are under the same conditions of temperature and pressure—can be mixed without change of pressure or temperature, it is assumed that the molecules of equal volumes of two gases at the same temperature and pressure possess the same total kinetic energies. The sense impression we call temperature is our mode of perceiving the kinetic energy of the translatory motions of the molecules.

The kinetic theory and Avogadro's hypothesis—From what has just been stated, it follows that equal volumes of two gases at the same temperature and pressure have the same value for the product pv. Hence, also, the total kinetic energy of the one gas will be equal to the total kinetic energy of the other; or the product $n_1m_1V_1^2$ for one gas will be equal to the product $n_2m_2V_2^2$ for the other. Again, the average kinetic energy, $\frac{1}{2}MV^2$, per molecule in the two systems will be equal if the temperature is the same; and hence, $\frac{1}{2}m_1V_1^2=\frac{1}{2}m_2V_2^2$; or, by substitution in the preceding relation, $n_1=n_2$. This is the symbolic way of saying that equal volumes of two gases under the same physical conditions contain the same number of molecules, or that the pressure of a gas at any temperature depends on the number of molecules and not on their kind; that is, Avogadro's hypothesis.[2] It is possible to argue backwards from Avogadro's hypothesis, and deduce the assumption indicated above. The one is dependent upon the other. Remember, therefore, that, contrary to what some enthusiastic writers have asserted, Avogadro's hypothesis has rendered it necessary to introduce *an unknown and unverifiable assumption* into the reasoning. According to J. C. Maxwell (1879):

> If the system is a gas, or a mixture of gases not acted on by external forces, the theorem that the average kinetic energy for a single molecule is the same for molecules of different gases is not sufficient to establish the condition of equilibrium of temperature between gases of different kinds, such as oxygen or nitrogen, because when the gases are mixed we have no means of ascertaining the temperature of the oxygen and nitrogen separately. We can ascertain the temperature of the mixture only by putting a thermometer in it.

The kinetic theory should not be quoted as a *proof* that Avogadro's hypothesis is true. Avogadro's rule is a corollary of J. J. Waterston's hypothesis.

The average distance traversed by a molecule between two collisions—the average free path.—The term average free path, L, of a molecule denotes the average distance traversed by a molecule between two successive collisions; that is, the sum of the free paths of all the molecules divided by the total number of molecular paths. The average free path is a pure length, and is determined by the concentration or number of molecules per unit volume, and it does not depend upon the average speed of the molecular movements. The magnitude in question for liquids at ordinary temperatures and pressures is of the same order as the millionth of a millimetre, for Lord Kelvin[3] has shown by several independent lines of argument—electrification of metals by contact, the tension of soap films, and the viscosity of air—that in ordinary solids and liquids the average distance between contiguous molecules is less than the hundred-millionth, and greater than the two-thousand-millionth of a centimetre. The length of the path L which a molecule, moving amid a swarm of molecules at rest, can traverse without collision is nearly

$$\text{Average free path, } L=\frac{\lambda^3}{\pi r^2}$$

where λ denotes the mean distance between any two neighbouring molecules, and r is the radius of the sphere of action of each molecule, so that πr^2 is the sectional area of one of these spheres. It is assumed that the sphere of action of a molecule cannot contain the centre of that of another molecule.

Let unit volume of a gas contain N molecules; let this volume be divided into N small cubes each of which on the average contains only one molecule; let λ denote the length of the edge of one of these imaginary cubes, and accordingly, only one molecule is contained in a cube of capacity λ^3. When a molecule A moves forward a distance x, it traces out a cylindrical space of volume $\pi r^2 x$, and if perchance [4] the centre of a molecule happens to be inside this cylinder, a collision will take place. Assume that the probability of a collision is in the ratio of these two volumes when x is small. Hence, the probability P of a collision when a molecule moves a distance x is $P=\pi r^2 x\lambda^3$. If there are n molecules moving like A, when n is very large, Pn molecules will collide in the distance x, and $Pn(1-P)$ molecules will pass on. Of the latter, $Pn(1-P)$ will collide in travelling another distance x, and $Pn(1-P)^2$ will pass on. Hence, Pn travel a distance between 0 and x; $Pn_2(1-P)$ travel a distance between x and $2x$; $Pn(1-P)^2$, a distance between $2x$ and $3x$; etc. The total paths traversed by all the n molecules before collision will therefore be $Pnx+Pn(1-P)2x+Pn\ (1-P)^2 3x+\ .\ .\ .$ When this series is summed by the rules of algebra, it becomes nearly equal to nx/P, meaning that a distance nx/P is traversed by n molecules before collision; or a distance x/P is traversed by one molecule before collision; but $P=\pi r^2 x/\lambda^3$, so that the average free path $L=\lambda^3/\pi r^2$ as indicated above.

It has been assumed that all but one of the molecules in the enclosure are at rest. It will be obvious that if all the particles are in motion, the probability that the particle A will collide with others will be increased, for the particles can also be struck by others from the sides and which would not be encountered as a result of its own motion. The increase in the probability of a collision shortens the free path to say l in accord with R. Clausius' demonstration [5] that the number of collisions will be increased in the proportion 4 : 3, and therefore the average free path of a particle in a swarm of molecules in uniform motion is

$$\text{Average free path, } L=\frac{3}{4}\cdot\frac{\lambda^3}{\pi r^2}$$

J. C. Maxwell, R. Clausius, and others have deduced relations between the viscosity η of a gas and the average free path of the constituent molecules. If a fluid—liquid or gas—streams through a tube of narrow bore, it experiences a resistance to flow so that the velocity of flow decreases uniformly from the centre outwards until it reaches the walls of the tube where the velocity is zero. Each layer of the fluid, parallel to the direction of flow, exerts a tangential force on the adjacent layer tending to decrease the velocity of the faster-moving layers, and to increase that of the slower-moving layers. The property in virtue of which a fluid exhibits this phenomenon is called the **viscosity of the fluid.** From the analogy between viscosity and friction some—particularly the Germans—employ the term *internal friction—innere Reibung*—of the fluid. Isaac Newton assumed that the viscosity is directly proportional to the rate of decrease of velocity V in the different layers of the fluid. If the tangential force be F, and the area of the plane be s, then $F=\eta sV$, where η is the constant of proportion, the so-called *coefficient of viscosity*, which can thus be defined as the tangential force per unit area required to maintain unity velocity gradient between two parallel plates in the fluid, at unit distance apart.

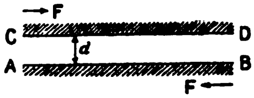

FIG. 1.

If a plane layer of fluid, CD, Fig. 1, moves with a velocity V_1 parallel to another plane layer of the same fluid, AB, at a distance d from it, and moving in the opposite direction with a smaller velocity V_2, the change of velocity per unit distance—the so-called *velocity gradient*—is $V=(V_1-V_2)/d$. Let the force acting on an area F required to produce this velocity gradient be F; this force must act in the direction CD on the upper plane and in the opposite direction on the lower plane. The simplest assumption regarding the force F was made by Isaac Newton, who assumed that the force F is proportional to the velocity gradient V, in the immediate neighbourhood of the plane; this force is also proportional to the area s of the plane. Hence, $F=\eta sV$.

The viscosity of gases is assumed to be an effect of the interchange of molecules between different layers of gas, and the tangential force per unit area is measured by the rate at which momentum is transferred per unit area between adjacent layers. The molecules which travel from a faster into a slower moving layer possess more momentum in the direction of flow than those moving in the opposite direction. The net rate of transfer of momentum across unit area of a plane is, according to Isaac Newton's second law, a measure of the force F,

$$F=\tfrac{1}{3}kL\eta MV$$

where k is a constant.

Let the velocity V of the layer CD, Fig. 1, be taken as $V_1=kd$, where k is a constant; and $F=\eta v/d$ per unit area. Assume that the motion of the molecules produces the same effect as would be obtained by resolving the particles into three groups—one-third move perpendicular to the plane CD, and the other two perpendicular to one another and parallel with the plane CD; and further on the average half the molecules moving vertical to the plane CD pass upward, and the other half downwards. Hence, one-sixth of the molecules moving with an average velocity V, that is $\tfrac{1}{6}nV$, traverse L, the mean free path, and their average velocity is the same as that of a layer at a distance L below CD, namely $k(d-L)$. These molecules carry a momentum $\tfrac{1}{6}k(d-L)nMV$, where M denotes the mass of each of the n molecules. A stream of the same number of molecules comes from AB, with the velocity of a layer $d+L$, and their momentum is $\tfrac{1}{6}k(d+L)nMV$. The difference, $\tfrac{1}{3}kLnMV$, represents the total momentum lost by the layers above the plane CD to those below.

The loss of momentum causes a drag on the adjacent layer such that $F=\eta v/d$ per unit area. Equate these two values of F together, and reduce the result to its simplest terms, remembering that $k=v/d$,

$$\eta=\tfrac{1}{3}LnMV\,;\ \text{or,}\ \eta=\tfrac{1}{3}LDV$$

where the density D of the gas is equal to nM. For instance, taking the density of air, $D=0{\cdot}001293$, and the experimentally determined viscosity $\eta=0{\cdot}00018$, and $V=48{,}000$ cm. per second; the mean free path is nearly $L=8\times10^{-6}$ cm. at 0°. In deducing this equation, it has been assumed that the molecules all possess the same velocity V, introducing the correction for Maxwell's distribution of velocities. L. Boltzmann represented the viscosity of a gas at 0° by the expression:

$$\eta=0{\cdot}3502DUL \quad . \quad . \quad . \quad . \quad . \quad (10)$$

where U denotes the average velocity of the molecules. Consequently, the average length L of the free path—that is, the average distance traversed by a molecule of the gas between two collisions—can be calculated, from the relation between viscosity and the free path. Some results at 0° and 760 mm., with L. Boltzmann's equation, are indicated in Table II. A molecule of nitrogen, for instance, travels about 450 metres per second, it collides with other molecules about five thousand million times per second, and the average distance between two consecutive collisions is about eight ten-thousandths mm. The density of the gases is known, and their

TABLE II.—AVERAGE FREE PATH AND COLLISION FREQUENCY OF GASES.

Gas.	Viscosity, η.	Average velocity U cm. per sec.	Density, D.	Average free path, L, cm.	Collision frequency, U/L.
Hydrogen, H_2 .	843×10^{-7}	$1{\cdot}696\times10^{5}$	$88{\cdot}73\times10^{-6}$	$16{\cdot}00\times10^{-6}$	$10{\cdot}6\times10^{9}$
Oxygen, O_2 . .	1905	0·425	1414	9·05	4·7
Nitrogen, N_2 .	1670	0·454	1234	8·50	5·3
Argon, A . .	2107	0·381	1758	8·98	4·2
Water, H_2O . .	904	0·566	798	8·91	6·3
Carbon dioxide, CO_2	1375	0·362	1951	5·56	6·5
Mercury, Hg .	1620	0·170	4200	12·88	1·3

viscosities have been experimentally determined from observations on the damping effects of the various gases on vibrating pendulums (O. E. Meyer), or oscillating discs (J. C. Maxwell),[6] and by other methods.

R. Clausius' theoretical value for the effect of temperature on the viscosity of a gas, is

$$\eta=20{\cdot}43L\sqrt{\frac{DT}{273}};\ \text{or},\ \eta=20{\cdot}43L\left(\frac{DT}{273}\right)^{0\cdot5}$$

where T denotes the absolute temperature of the gas; and D, the density at 0° C., and atmospheric pressure—air unity. Observations show that this expression gives better results if the exponent be empirically taken nearer 0·77 than 0·5. W. Sutherland's formula has an empirical constant dependent upon the nature of the gas.

From L. Boltzmann's equation, it follows that the average free path is inversely proportional to the pressure of the gas, so that while the average free path of the gas at 760 mm. is about 16×10^{-6} cm., the value increases to about 0·025 cm. when the pressure falls to 0·5 mm. Consequently, the average free path of a molecule of a gas is about 700 times its diameter, and over a million times the diameter when the pressure is reduced to about half a millimetre of mercury. The size of a molecule is therefore small in comparison with its average free path. With increasing pressures, the increase of density is proportional to the diminution of the average free path, so that the product Dl is constant. Consequently, the velocity depends only on the temperature of the gas. For any gas, therefore, the viscosity is independent of the pressure if the temperature is constant, and the viscosity increases with the temperature. The converse obtains with liquids, for here the viscosity usually increases with rise of temperature. These results were deduced from the kinetic theory for gases, and the prediction was subsequently confirmed experimentally. The relation did not obtain with very high and very low pressures—in the former case, attractive forces come into play, and in the latter case, the molecules might travel the whole distance between the walls of the confining vessel without encountering another molecule. In deducing the formula, the assumption is made that the free path is so small that terms involving higher powers of L can be neglected. When the gas is rarefied, the molecules have more free space for their movements, and they do not collide so frequently. When the gas is sufficiently rarefied to make the higher powers significant, the formula is no longer applicable.

Direct determinations [7] of the average free path have been made by J. Franck and G. Hertz, who measured the maximum distance at which two plates must be placed apart in a gas in order that the ions passing from one plate to another may produce fresh ions by collision one with another. The results with hydrogen agree but approximately with the computed values:

Pressure	45	81	152	1670 bars
Average free path (Obs.)	0·436	0·256	0·149	0·014 cm.
Average free path (Calc.)	0·388	0·215	0·115	0·011 cm.

The number of collisions between the molecules per second—the collision frequency.—If the average free path of the hydrogen molecule is 16×10^{-6} cm., and the average velocity of translatory motion is $16{\cdot}96\times10^{4}$ cm. per second, it follows that the number of collisions per second must be the quotient of the distance U traversed per second, into the length of the free path L, provided the paired time of the colliding molecules be negligibly small. Hence, a molecule undergoes nearly 10,000,000,000 collisions per second. The last column in Table II shows estimates made with a number of gases. Why does a gas not diffuse through another gas with a speed comparable with the velocity of translatory motion of its molecules? The hydrogen molecule, for instance, has a velocity of $1{\cdot}696\times10^{5}$ cm. per second, but the average free path is only $16\times10{-}^{6}$ cm., so that the molecule collides with other molecules nearly ten thousand million times per second. A molecule is therefore continually abutting against other molecules, and being deflected from a straight path, so that its rate of progress in any particular direction is comparatively slow.

The average diameter of the molecules.—It is difficult to define precisely what is meant by the size of molecules primarily because their shape is unknown. Whatever be the structure of the molecule, the diameter of the molecule is understood to be a number which represents the smallest distance apart to which the centres of two molecules can approach one another. It is highly improbable that the molecules are elastic spheres, and the assumption that the molecules are spherical will therefore introduce an error which affects the different magnitudes concerned in free path and collision formulæ approximately the same, and accordingly J. H. Jeans [8] defines the molecular diameter as the diameter of a sphere such that spheres of this diameter undergo the same number of collisions as occur in actual gases. With solids, however, where free paths and collisions do not come into consideration, he regards the molecular diameter as the diameter of a sphere which occupies the same space as the molecule, and the more the molecules differ from the spherical shape, the more will the value so obtained differ from the former value. Calculations of the molecular diameter based on the volume occupied by matter in the solid or liquid states of aggregation, with the additional assumption that the molecules are packed as close as is physically possible, must give results too large—they are, however, regarded as useful in fixing an upper limit to the size of the molecules.

Solid hydrogen at 13·2° K. has a density of 0·0763, or one c.c. weighs 0·0763 grm. Since the mass of a molecule of hydrogen is $3·27 \times 10^{-24}$ grms. the number of molecules per c.c. of the solid will be $2·33 \times 10^{22}$. If this number of spheres be packed as closely as possible, they will occupy a volume $2·33 \times 10^{22} \times d^3 \div N$ c.c., where d represents the diameter of each molecule. This volume must be less than 1 c.c. If it be 1 c.c., $d = 3·93 \times 10^{-8}$ c.c. This is therefore the upper limit to the molecular diameter. For some unknown reason, in some cases the upper limit so obtained is less than the values obtained by other methods of calculation presumably more exact—*e.g.* xenon, benzene, chlorine, carbon dioxide, ethylene, etc.

O. Loschmidt, in his memoir *Zur Grösse der Luftmolecule*, made the first estimate of the actual size of the molecules of a gas in 1865. R. Clausius, J. C. Maxwell, J. H. Jeans, S. Chapman, and W. Sutherland have deduced expressions for this constant. R. Clausius obtained $\pi n d^2 L = 0·75$; J. C. Maxwell made the constant 0·707; and J. H. Jeans made it 0·933, to allow for the persistence of the original velocity for a small period of time after a collision. J. H. Jeans, after making an allowance for the persistence of the velocity after a collision, found

$$\text{Mean free path, } L = \frac{1·2547}{\sqrt{2}\pi n d^2} \quad . \quad . \quad . \quad . \quad (11)$$

where d denotes the diameter of the molecule; n, the number of molecules per c.c.; and L, the average free path. From (10), $\eta = 0·350DUL$, when $D = 0·001293$; $U = 45100$ cm. per sec.; and on substituting the value of L from (11), it follows that $nd^2 = 3306$ sq. cm. The result now depends upon what value is assigned to the constant n, values for this constant are estimated in the next section. Estimates of the maximum and minimum diameter of a molecule have been made by several different methods—the viscosity of gases, the thermal conductivity of gases, the rate of diffusion, the deviations from Boyle's law, liquid films, contact electricity, refractive dispersion, and the dielectric constant or refractive index of a gas.[9] The results agree fairly well with those deduced from the kinetic theory. In illustration, J. H. Jeans, *The Dynamical Theory of Gases* (Cambridge, 1916), obtained the values indicated in Table III for the molecular diameters estimated by four different methods, and expressed in centimetres. M. Knudsen computes the molecular weight of a gas from the viscosity data.

TABLE III.—J. H. JEANS' ESTIMATES OF MOLECULAR DIAMETERS.

Gas.	Coefficient of viscosity I.	Conduction of heat II.	Coefficient of diffusion III.	Deviations from Boyle's law.	Average of I to III.
Hydrogen	$2{\cdot}68\times10^{-8}$	$2{\cdot}68\times10^{-8}$	$2{\cdot}68\times10^{-8}$	$2{\cdot}52\times10^{-8}$	$2{\cdot}68\times10^{-8}$
Helium	2·86	2·28	—	1·96	2·22
Steam	4·54	—	—	—	4·54
Carbon monoxide	3·78	3·80	3·72	—	3·76
Ethylene	5·52	5·52	5·48	—	5·50
Nitrogen	3·76	3·82	3·82	3·54	3·80
Air	3·82	3·82	3·82	3·30	3·72
Nitric oxide	3·82	2·84	—	—	3·72
Oxygen	3·62	3·60	3·62	—	2·62
Argon	3·64	3·60	—	—	3·62
Carbon dioxide	4·54	4·84	4·30	3·40	4·56
Nitrous oxide	4·6	4·62	4·54	—	4·58
Ethyl chloride	4·12	—	—	—	5·12
Chlorine	5·36	—	—	—	5·36
Benzene	7·44	—	—	—	7·44

The number of molecules in unit volume of a gas.—If all gases obeyed the laws of Boyle and Charles, and Avogadro's hypothesis were valid, all gases would have the same number of molecules per unit volume under the same conditions of temperature and pressure. Assuming that the molecules of a gas are spherical, then, the volume of each sphere will be $\frac{1}{6}\pi d^3$, where d denotes the diameter of the molecule. If the gas contains N molecules per gram-molecular weight of gas at 0° and 760 mm., their aggregate volume will be $\frac{1}{6}\pi Nd^3$. Again, let v denote the apparent or total volume of a gas, and let b denote the space occupied by the molecules; the volume not occupied by molecules will be $v-b$; and if $v=b$, the molecules will be in contact provided b does not vary with pressure. J. D. van der Waals' estimate[10] of the value of b from H. V. Regnault's observation is, for air, $b=0{\cdot}00198$; and J. Rose-Innes' estimate from H. Callendar's observations, $b=0{\cdot}00209$. The mean is 0·002035. The values of b expressed in c.c. per gram-molecule of the gas, and calculated from the deviations of the gases from Boyle's and Charles' laws, are

	H_2	O_2	N_2	A	H_2O	CO_2	Hg
b	16·28	31·56	39·50	32·22	30·52	42·83	35·67

According to J. D. van der Waals, the actual volume of the molecules is one-fourth the value of b; consequently, $\frac{1}{4}b=\frac{1}{6}\pi nVd^3$,

$$b=\frac{2}{3}\pi Nd^3$$

Consequently, $Nd^3=0{\cdot}00097$ c.c. Since $Nd^2=3306$ sq. cm., by eliminating d, it follows that $(Nd^2)^3/(Nd^3)^2=N=4{\cdot}92\times10^{19}$. This result, for air, is rather lower than the value obtained for other gases. The errors of observation are considerably magnified in the calculation—those of b are doubled, and those of η are trebled. Again, when evaluated by electrical methods N is approximately 4×10^{19} per c.c. The numerical value of the constant N has been determined by nearly a dozen independent methods, and the most reliable determinations approximate $N=6{\cdot}062\times10^{23}$ molecules per gram-molecule of the gas, and this number is called **Avogadro's constant.** The number n per c.c. of the gas is $N/22412$, or $2{\cdot}7048\times10^{19}$ molecules per c.c. of the gas at 0° and 760 mm. The approximate agreement of the numbers is so close that R. A. Millikan[11] could say:

> To-day we are counting the number of atoms in a given mass of matter with as much certainty and precision as we can attain in counting the inhabitants of a city. No census

is correct to more than one or two parts in a thousand. . . . There is little probability that the number of molecules in a cubic centimetre of gas under standard conditions (0° and 760 mm.) differs by more than this amount from $2·70 \times 10^{19}$.

The letter R used for the gas constant appears to have been taken by Isaac Newton in his *Philosophiæ naturalis principia mathematica* (London, 302, 1713) from the term resistance. In his study of the inner resistance of a gas, he showed that if two parallel plates, at a distance r apart, move with a difference of velocity v, the inner resistance for unit surface is proportional to the increase of velocity v/r so that $R=-\eta(v/r)$, where η is the coefficient of friction. E. Clapeyron (1834) employed R to represent the constant in the gas equation $pv=R(a+\theta)$, where a is constant, now represented by 273. E. Clapeyron used 267. According to the kinetic theory of gases, Newton's η is equal to $\frac{1}{3}nmvl$, so that $R=\frac{1}{3}nmv^2l/r$.[12]

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§ 4. Attempts to Obtain a More Exact Gas Equation

All nature widens upwards. Evermore
The simpler essence lower lies.
More complex is more perfect, owning more
Discourse, more widely wise.—TENNYSON.

The general equation of state $pv=RT$ does not exactly describe the behaviour of real gases with respect to changes in volume with variations of temperature and pressure. The same gas does not behave in the same way at high and at low pressures. The laws of Boyle and Charles are fairly exact for some gases—*e.g.* hydrogen, oxygen, etc.—at temperatures and pressures not far removed from normal atmospheric conditions; and it is often convenient to neglect small deviations with other gases—*e.g.* carbon dioxide, ethylene, etc. This means that gas calculations with $pv=RT$ are made upon imaginary gases sometimes styled *ideal or perfect gases.* When the pressure upon the gas is very great, the error becomes quite appreciable, and it is necessary to revise the simple gas law: $pv=RT$. This was emphasized by H. V. Regnault in his *Relation des expériences entreprises pour detérminer les principales lois physiques et les données numériques qui entrent dans le calcul des machines à vapeur* (Paris, 1847). He said:

> The law does not express the actual relations between the same quantities of gas and the pressure which they support, and it is desirable to find if it is possible to represent these relations by a new law. . . . Unfortunately this relation is evidently too complex to hope to find it by purely experimental methods. It is to be hoped that mathematicians will try to find the form of this function by developing certain hypotheses on the nature of molecular forces ; the necessary data for calculating the constants can be readily obtained from observed measurements, and the formulæ themselves subjected to *un criterium rigoureux*.

The effect of the size of molecules.—The reduction in the volume which occurs when a gas is highly concentrated is smaller than corresponds with Boyle's relation, and this is now explained in the following way : Under great pressures the volume of the molecule becomes comparable in magnitude with the space through which the molecule can move. The volume of the space in which the molecules move is alone reduced by pressure, and therefore only part of the total volume occupied by the gas can be reduced by pressure. Hence, at high pressures the apparent volume and the product pv appear to be greater than is described by Boyle's law. With hydrogen, for instance, when the pressure is doubled, the volume is not quite halved. The same remark applies to other gases, *e.g.* carbon dioxide, at great pressures. This is illustrated by the upward course of the curves, Fig. 3, Cap. IV.

Let b denote the space occupied by the molecule as it moves to and fro between the boundary walls AB, Fig. 2. If this distance be halved, AC, while the volume of the molecule remains constant, the molecule will have less than half its former distance to pass from one side to the other. For instance, suppose that AC represents one unit, and AB two units, and the diameter of the molecule is $\frac{1}{10}$th unit ; the molecule oscillating between AB then moves through 1·9 units of space in one journey ; and between AC through 0·90 unit, not 0·95 unit. Hence, the molecule will strike the walls more frequently than before per unit time, and the outward pressure due to molecular bombardment will increase more rapidly with decreasing volume, than is described by Boyle's law. Boyle's law refers to the whole volume of the gas, but rather should it refer to the space in which the molecules move. Consequently, $v-b$ should be substituted in place of the v of Boyle's law, and the result is: $p(v-b)=RT$, where b is called the **molecular co-volume.** An application of the theory of probability to the kinetic theory has led to the view that b is very nearly four times the volume actually occupied by the whole of the molecules contained in unit volume of the gas, so that a molecule is represented to be a complex vibratory system with a material nucleus $\frac{1}{4}b/n$ in size, which requires b/n volumes of space in which to perform its oscillatory movements—n represents the number of molecules in unit volume of the gas—hence b is also called the **vibratory volume** of the molecule. The fundamental assumptions have not been so firmly established that there is no room for doubt, and some consider that b represents the real volume of the molecules ; others believe that b is much greater than four times the size of the material nucleus of the molecules. In any case, virtually all are agreed that b is not quite constant, but varies with the temperature, and possibly also with pressure changes. J. D. van der Waals, in his celebrated *Over de Continuiteit van den Gasen Vloeistoftoestand*,[1] published at Leiden in 1873, worked on the assumption that b is constant.

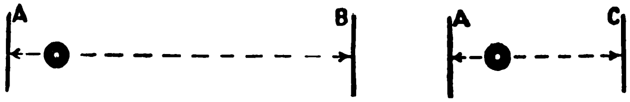

FIG. 2.—The Effect of the Size of the Molecules on the Volume of Gases.

The effect of molecular attraction.—If the molecules of a gas have appreciable cohesion or attraction for one another, they must be swerved from their rectilinear paths when they come within the sphere of one another's influence, and they must then move in curved, not in straight paths. Doubling the number of particles per unit volume will not then give exactly twice the number of impacts on the boundary walls. When the molecular attraction is marked, the product pv must be *less* than corresponds with Boyle's law. Molecular attraction deflects some of the molecules from the straight path so that they do not strike the walls of the vessel under conditions where they otherwise would, and the pressure is accordingly diminished. This appears to be the case with carbon dioxide, and most gases with a smaller apparent volume v, or a smaller value of pv, that is, a greater concentration, than corresponds with an increase of pressure as described by Boyle's law. This is illustrated by the downward slope of the pv curves, Fig. 3, for carbon dioxide below 150 atmospheres pressure. The closer the proximity of the molecules to one another, the greater will be the effect of the attractive forces between the molecules. This attractive force, which may be denoted by F, will tend to make the gas occupy a smaller volume. The effect is much the same as if the gas were subjected to the action of a greater external pressure $p+F$ than the observed or apparent pressure p of the gas. With these ideas before him, G. A. Hirn (1868) [2] proposed to use an equation of the form $(p+F)(v-b)=RT$ in place of the regular equation $pv=RT$. The assumption that the attractive force F between the molecules varies inversely as the fourth power of the distance between the molecules, leads to a/v^2 as the magnitude of the molecular attraction, F, where a is a constant which varies with the nature of the gas, and v denotes the observed volume of the gas. Granting the assumption, a/v^2 must be added to the observed pressure of the gas in order to indicate the total pressure tending to compress the gas. The magnitude of the internal or cohesive pressure a/v^2 for liquid water is nearly 11,000 atm.—a surprisingly large value which is in approximate agreement with results obtained by other independent methods of calculation.

On correcting the equation $pv=RT$ for the volume and cohesion of the molecules, J. D. van der Waals (1873) obtained the so-called **J. D. van der Waals' equation :**

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT \quad . \quad . \quad . \quad . \quad (12)$$

This amended equation agrees fairly well with a number of observations of gases under large pressures, and of gases near their points of liquefaction—*e.g.* ethylene, carbon dioxide, etc. It also describes many of the properties of liquids, and of the continuous passage of a gas to the liquid condition. The constants a and b can be evaluated from observations. The numerical values of J. D. van der Waals' constants a and b for some substances are indicated in Table IV.

TABLE IV.—NUMERICAL VALUES OF J. D. VAN DER WAALS' CONSTANTS.

Substance.	*a*	*b*	Substance.	*a*	*b*
Ammonia	0·00820	0·00162	Acetylene	0·00810	0·00210
Benzene	0·03827	0·00532	Methane	0·00379	0·00160
Water	0·01173	0·00151	Carbon dioxide	0·00727	0·00192
Ethyl alcohol	0·02512	0·00385	Sulphur dioxide	0·01345	0·00251
Acetic acid	0·03737	0·00492	Nitrous oxide	0·00723	0·00189
Carbon tetrachloride	0·04184	0·00586	Nitric oxide	0·00257	0·00115
Tin tetrachloride	0·05926	0·00771	Nitrogen	0·00266	0·00176
Hydrogen phosphide	0·00953	0·00235	Oxygen	0·00266	0·00139
Hydrogen sulphide	0·00887	0·00191	Carbon monoxide	0·00274	0·00168
Hydrogen chloride	0·00704	0·00174	Argon	0·00256	0·00134
Carbon disulphide	0·02412	0·00350	Krypton	0·00460	0·00177
Cyanogen	0·01480	0·00298	Xenon	0·00823	0·00231

J. D. van der Waals (1888) found that for carbon dioxide, $R=1{\cdot}00646$; $b=0{\cdot}0023$; and $a=0{\cdot}00874$, when the unit of pressure is one atmosphere, and the unit of volume is the volume of one gram at 0° and one atmosphere pressure. With these numbers, J. D. van der Waals' equation for carbon dioxide assumes the form

$$\left(p+\frac{0\cdot00874}{v^2}\right)(v-0\cdot0023)=1\cdot00646(1+a\theta)$$

This equation may be employed for comparing the observed values for a gas which is known to deviate rather considerably from R. Boyle's simple relation. Table V has been computed from the numbers obtained by E. H. Amagat (1893) [3] at 20°.

TABLE V.—COMPARISON OF BOYLE'S AND VAN DER WAALS' EQUATIONS FOR *pv* OBSERVATIONS WITH CARBON DIOXIDE.

p (atmospheres).	*pv*.		
	Observed.	Calculated. (J. H. van der Waals' law).	Calculated. (Boyle's law).
1	1·000	1·000	1·000
50	0·680	0·678	1·000
75	0·180	0·179	1·000
100	0·228	0·226	1·000
200	0·419	0·411	1·000
500	0·938	0·936	1·000

The agreement between theory (J. D. van der Waals) and fact (observed data) is quite good. It will be seen that if the gas behaved according to the Boyle's equation, the product *pv* would have had the same constant value for all pressures. As a matter of fact, the value of *pv* first decreases and then increases for all gases except hydrogen and helium. The two corrections act in opposite ways. At first the value of *pv* is decreased by the molecular attraction, but increased to a greater extent by the finite dimensions of the molecule; the two corrections balance one another at ordinary pressures; and at low pressures, the correction for molecular attraction preponderates over that required for the volume of the molecule. The correction for the volume of the molecule is relatively large when the volume of the gas is compressed very small by a large pressure. If the numerical value of the term a/v^2 could exceed that of $RT/(v-b)$, negative pressures would appear as indicated by the dotted line in Fig. 3. This is unreal and therefore unsatisfactory, and does not appear with a second approximation to the gas equation proposed by C. Dieterici [4] in 1899. The experiments of M. Berthelot (1850) and of A. M. Worthington (1892) are sometimes quoted to demonstrate the existence of negative pressures. Here, sealed tubes, quite full of liquid, were cooled slowly, and in some cases the thick-walled tube collapsed owing to enormous tension. It may mean that the molecules of the fluid exert an attractive influence on the walls of the vessel, whereas J. D. van der Waals' equation assumes that there is no such attraction. The alleged negative external pressure is probably a myth.

The numerical values of *a* and *b* of van der Waals' equation are, in reality, not constant at different temperatures; thus, F. B. MacDougall (1916) calculated from E. H. Amagat's results for carbon dioxide:

	20°	40°	60°	80°	100°	137°
a	0·00983	0·00919	0·00852	0·00797	0·00749	0·00708
b	0·00202	0·00221	0·00227	0·00228	0·00226	0·00227

showing that *a* decreases with increasing temperatures even above the critical temperature, while *b*, if it increases at all, increases very slowly; and above the critical temperature is virtually constant and independent of temperature. There are also indications that for low pressures, *b* is not affected, but diminishes when the pressures are very large. There is a wide divergence in the values of the constant a by different methods, thus, for carbon disulphide, numbers ranging from the 1683 (15°) of H. Davies to the 3363 (0°) of J. D. van der Waals, have been reported.[5]

There are various methods for evaluating the constant a of J. D. van der Waals' equation. These methods have been examined by A. P. Mathews. They are: (1) from the surface tension; (2) from R. Eötvös rule or T. Young's rule; (3) from J. D. van der Waals' equation at the critical temperature; (4) from the latent heat of vaporization; and (5) from A. P. Mathews' formula $a=1{\cdot}249\times10^{11}M\Sigma v$, where M denotes the molecular weight, and Σv, the number of valencies per molecule.

There has been a great deal of tinkering with J. D. van der Waals' equation. Over thirty attempts have been made to modify still further the gas equation to make it better describe the behaviour of gases under wide variations of pressure and temperature. C. Dieterici (1899) has made one of the best attempts. In most cases, other terms involving special constants which have to be evaluated from the experimental numbers, have been introduced. Such equations are therefore of limited application.

C. Dieterici's gas equation.—Instead of assuming that the observed pressure of a gas should be reduced by the subtraction of a term a/v^2, as was done by J. D. van der Waals, to give his equation the form

$$\left(p+\frac{a}{v^2}\right)(v-b)=RT\text{ ; or }p=\frac{RT}{v-b}-\frac{a}{v^2}\quad\ldots\quad(13)$$

C. Dieterici (1899) assumed that the term $RT/(v-b)$ should be reduced by multiplication with a function, $e^{-a/vRT}$, always less than unity. Consequently, his equation assumed the form

$$p(v-b)=RTe^{-\frac{a}{vRT}}\text{ ; or, }p=\frac{RT}{v-b}e^{-\frac{a}{vRT}}\quad\ldots\quad(14)$$

where e represents the base of the natural logarithms.

C. Dieterici argued that in the interior of the liquid the attractive forces between the molecules are balanced; at the surface, the molecules are subjected to an unbalanced force directed inwards. Consequently, the density of the layers near the surface will decrease from the interior outwards. Only those molecules with a velocity exceeding a certain value will be able to penetrate the surface layer and exert a pressure on the containing wall: molecules moving towards the interior are assisted by the force directed inwards. If the fraction of the total number of molecules which has a velocity greater than this limiting value can be estimated, it follows that the observed pressure p will be that fraction of the interior pressure $RT/(v-b)$. From the theory of probability, if a represents the most probable speed of the molecules; and S, the speed the molecules must possess to be able just to penetrate the surface, the required fraction will be e^{-S^2/a^2}; and if V denotes the mean velocity, more exactly, the square root of the mean of the squares of the speeds, $V^2=\frac{3}{2}a^2$, or $a^2=\frac{2}{3}V^2$. If M represents the mass of a molecule and n the number of molecules, e^{-S^2/a^2} becomes $e^{-\frac{\frac{1}{2}nmS^2}{\frac{1}{3}nmV^2}}$, and from (2), $\frac{1}{3}nMV^2=RT$; and $\frac{1}{2}MnS^2$ will represent the work W done by a molecule penetrating the surface layer of molecules against the molecular forces. The previous expression thus becomes $e^{-W/RT}$. C. Dieterici then assumed that the work W is proportional to the density of the gas or $W=a/v$, where a is a constant. Whence follows equation (14) above.

The curves obtained by plotting J. D. van der Waals' and C. Dieterici's equations have the same general form, Fig. 3. Both equations reproduce the critical state very well, but Dieterici's equation agrees better with the general results of observation particularly at high pressures, where J. D. van der Waals' equation usually breaks down. At low pressures, where v is large in comparison with b, both equations give equally good results. Since, under these conditions, C. Dieterici's equation reduces to that of J. D. van der Waals. This can be shown by expanding Dieterici's equation and omitting the higher powers of v, because when v is large, these terms are negligibly small. In that case,

$$p=\frac{RT}{v-b}\left(1-\frac{a}{vRT}\right)=\frac{RT}{v-b}-\frac{a}{v(v-b)}=\frac{RT}{v-b}-\frac{a}{v^2} \quad . \quad . \quad (15)$$

since, when b is small in comparison with v, $v(v-b)$ approximates to v^2. J. D. van der Waals' equation is thus a special case of C. Dieterici's equation applicable to low pressures, just as the equation $pv=RT$ is a special case of the same equation applicable to gases, for which a and b are negligibly small in comparison with p and v.

If the simple equation $pv=RT$ be regarded as a first approximation to a true gas equation, J. D. van der Waals' equation can be regarded as a second, and C. Dieterici's as a third approximation towards a complete law. Most, if not all, the formulæ of physics and chemistry are in the earlier stages of such a process of evolution. As I have said elsewhere,

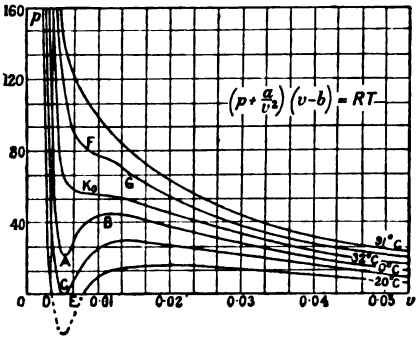

FIG. 3.—Graphs of J. D. van der Waals' Equation.

> There is a prevailing impression that once a mathematical formula has been theoretically deduced, the law embodied in the formula has been sufficiently demonstrated provided the differences between the calculated and the observed results fall within the limits of experimental error. With improved instruments, and better methods of measurement, more accurate data are from time to time available. The errors of observation being thus reduced the approximate nature of the original formula becomes more and more apparent. Ultimately the discrepancy between theory and fact becomes too great to be ignored. It is then necessary to "go over the fundamentals." New formulæ must be obtained embodying less of hypothesis, more of fact. Thus, from the first primitive guess, succeeding generations progress step by step towards a comprehensive and a complete formulation of the several laws of Nature.

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§ 5. J. D. van der Waals' Theory of Corresponding States

J. D. van der Waals' equation assumes the form of an equation of the third degree in v when it is multiplied out:

$$v^3-\left(b+\frac{RT}{p}\right)v^2+\frac{a}{p}v-\frac{ab}{p}=0 \quad . \quad . \quad . \quad (16)$$

In algebra, we are taught that such an equation must have three roots real or imaginary, equal or unequal; and of the real roots, there may be one or three equal or unequal—imaginary roots have no physical meaning. Otherwise expressed, there may be one or three different volumes corresponding with certain assigned values of p and T. If there is only *one real root*, *A*, Fig. 4, the equation furnishes only one value of v for every assigned value of p. The graph for carbon dioxide above the critical temperature is an example. If the equation has *three unequal roots*, *C*, Fig. 4, there ought to be three different values of v at the given pressure and temperature, but only two of these have been realized, since the middle portion of the curve is physically unstable. The line of constant pressure cuts the theoretical curve in three places as indicated at a, b, and c, Fig. 4, but, instead of the pressure increasing to a maximum α (Fig. 4), falling to a minimum β, and then increasing indefinitely, as the volume is diminished, the pressure increases to a certain value, and then remains constant until the gas has completely condensed to a liquid. The curve $C'a$ has been prolonged a very short distance towards β by undercooling; and the curve Cc prolonged a little towards a by supersaturation. The suggestion that the dotted line, Fig. 4, be substituted for the horizontal part of Andrew's curves was made by J. Thomson in 1862. For three unequal roots, the line of constant pressure cuts the theoretical curve in three places, as indicated at a, b, c, Fig. 4; but, when there are *three equal roots*—β, Fig. 4—there is only one numerical value for v for the assigned values of p and T. This occurs at the critical temperature K.

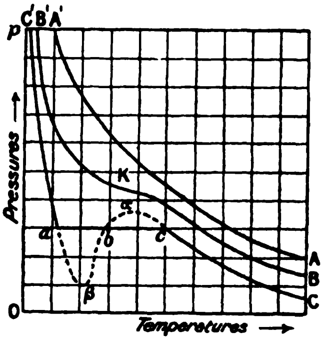

FIG. 4.—Graphs showing the Roots of J. D. van der Waals' Equation.

Let v_c, p_c, and T_c respectively denote the critical volume, critical pressure, and critical temperature; v_c will be the root of van der Waals' equation at the critical temperature, and $(v-v_c)^3=0$. Expand this equation, and the result is an identity with (16) above. Equate coefficients of like powers of v, and it follows that

$$v_c=3b\,;\ p_c=\frac{a}{27b^2}\,;\ T_c=\frac{8a}{27bR}\ . \quad . \quad . \quad . \quad (17)$$

These results enable the values of the constants a, b, and R to be calculated when the critical volume, pressure, and temperature are known, on the *assumption* that a, b, and R are constant. Corresponding values for C. Dieterici's equations are

$$v_c=2b\,;\ p_c=\frac{a}{29{\cdot}56b^2}\,;\ T_c=\frac{a}{4bR}\ . \quad . \quad . \quad . \quad (18)$$

Again, let $\mathbf{p}=p/p_c$; $\mathbf{v}=v/v_c$; and $\mathbf{T}=T/T_c$, then, by the substitution of these values in J. D. van der Waals' equation (18), there remains

$$\left(\mathbf{p}+\frac{3}{\mathbf{v}^2}\right)(3\mathbf{v}-1)=8\mathbf{T}\ . \quad . \quad . \quad . \quad (19)$$

The magnitude $\mathbf{v}$ is called the *reduced volume*; $\mathbf{p}$ the *reduced pressure*; $\mathbf{T}$ the *reduced temperature*; and (19), the *reduced equation of state*. The operation of reduction seems to have freed van der Waals' equation of specific constants peculiar to individual substances, and substituted numbers of universal application in their place. The result means that if the initial assumption be granted, different substances can exist in such states or conditions that their volume, pressure, and temperature are respectively the same fractions of their critical values. Hence, states characterized by the same values of $\mathbf{v}$, $\mathbf{p}$, and $\mathbf{T}$, were called **corresponding**

states—*übereinstimmende Züstande*—by J. D. van der Waals. This extraordinary conclusion means that **at the critical point the relation between the pressure, volume, and temperature is the same for all substances**; no matter what the substance, no matter what be the diameters of the particles, the range and magnitude of the molecular forces, or the potential energy of the particles, the same relation holds; any two of these variables being given, the third can be calculated.

J. D. van der Waals' theory of corresponding states was first regarded as being derived from the molecular theory, but it is now treated as being based on a purely empirical equation of state, like those of R. Clausius[1] and D. Berthelot, both of which were empirically devised to represent the facts more nearly than the state-equation of J. D. van der Waals. G. Meslin has shown that the theory of corresponding states follows directly from any equation of state with not more than three constants. *R. Clausius' equation of state* has four constants—namely a, b, c, R—and it gives a reduced equation with one constant λ:

$$\left(p+\frac{a}{T(v+c)^2}\right)(v-b)=RT\,;\quad\left(\mathbf{p}+\frac{1}{\mathbf{T}(\mathbf{v}+\lambda)^2}\right)(\mathbf{v}-1)=\mathbf{T}$$

If the constant c be removed, *D. Berthelot's equation of state* with three constants, and a reduced equation with no constants:

$$\left(p+\frac{a}{Tv^2}\right)(v-b)=RT\,;\quad\left(\mathbf{p}+\frac{1}{\mathbf{T}\mathbf{v}^2}\right)(\mathbf{v}-1)=\mathbf{T}$$

are obtained. P. Curie has also shown that at the critical point $(dp/dv)_T=0$, $(d^2p/dv^2)_T=0$, and any critical point so defined will serve for setting up reduced equations. For example, let p_0, v_0, and T_0 be critical points, then, from J. D. van der Waals' equation, $b=Bv_0$; $a=Ap_0v_0^2$; and $R=Cp_0v_0/T_0$, where A, B, and C represent pure numbers. Then $p/p_0=\mathbf{p}$; $v/v_0=\mathbf{v}$; and $T/T_0=\mathbf{T}$, so that

$$\left(\mathbf{p}-\frac{A}{\mathbf{v}}\right)(\mathbf{v}-B)=C\mathbf{T}$$

a reduced equation containing only numerical constants; J. D. van der Waals' form of the reduced equation is a special case of this. D. Berthelot has set up three reduced equations with special properties—in one, the unit of reference in the critical point is defined by $dp/dT=0$, where p is a maximum. As G. von Kaufmann has shown, the theory of corresponding states is quite independent of any critical point, for by assigning specific or special units for p, v, and T, for each substance, three specific constants can be eliminated from any equation of state.

S. Young[2] tested the law of corresponding states with a few substances; it seems to hold fairly well for a few groups of related compounds—hydrocarbons, esters, ketones, ethers, etc.—where the results are not disturbed by molecular association. It does not agree closely with water, the alcohols, and the fatty acids. The results with the monatomic gases argon and helium agree amongst themselves, but not with those of other groups. A few examples are indicated in Table VII. In S. Young's method the values of v_c, p_c, and T_c are measured and the different functions compared with equal values of $\mathbf{p}$ and $\mathbf{T}$. E. H. Amagat (1896) recommended a method in which no knowledge of the critical values is needed, because curves with the variables log p, log v, log T, etc. are plotted, and from the theory of corresponding states, the curves for different substances should be of identical shape and superposable by a parallel shifting of the axes. C. Raveau (1897) applied E. H. Amagat's method to ethylene and carbon dioxide. K. Meyer and D. Berthelot found that a fairly accurate correspondence of states exists if the reduced variables p/p_c, $(v-v_c)/(v_c-v_m)$, and $(T-T_c)/(T_c-T_m)$ be chosen, where T_n and v_n have specific values for each substance. G. von Kaufmann sums up the position:

Although in many cases a fairly approximate correspondence of states has been found to exist, the theory in its entirety has been proved without doubt inexact; it has not been found completely true for even a single pair of substances. There is therefore no general p, v, T-equation of state with only three specific constants. Nevertheless, a theory which is so far-reaching and fundamental as this, and which over a whole range of phenomena gives a good first approximation to the facts, will not be lightly discarded, and in the present position, attempts are being made to modify it in such a way as to bring it more into agreement with the truth.

The critical density.—P. A. Guye (1890) and S. Young (1892)[3] showed interesting consequences of combining the three equations (18). S. Young obtained $v_cp_c=\frac{3}{8}RT_c$. Let v denote the volume occupied by the substance in the gaseous state, and assume that it behaves like an ideal gas at the critical state when $vp_c=RT_c$. By division, $v_c=\frac{3}{8}v$. If d_c denotes the observed density of the gas in the critical state, and D_c the theoretical density required for an ideal gas, then, remembering that the density is the reciprocal of the volume, $d_c/D_c=\frac{8}{3}=2·67$, so that if J. D. van der Waals' equation accurately describes the behaviour of the gas in the critical state, the observed critical density of all gases ought to be 2·67 times the theoretical density of an ideal gas at the critical temperature and pressure. This is not the case. The actual results are larger, being somewhere near 3·67 for the hydrocarbons, esters, ketones, and ethers.

TABLE VI.—ILLUSTRATIONS OF THE LAW OF CORRESPONDING STATES.

Gases and vapours.	$\mathrm{v}=\frac{v}{v_c}$	$\mathrm{p}=\frac{p}{p_c}$	$\mathrm{T}=\frac{T}{T_c}$
Carbon tetrachloride	0·725	0·408	27·5
Stannic chloride	0·736	0·403	28·1
Ether	0·738	0·403	28·3
Benzene	0·728	0·407	28·3
Fluorobenzene	0·733	0·407	28·4
Ethyl alcohol	0·735	0·400	29·6
Acetic acid	0·762	0·410	25·4

	CCl_4	$SnCl_4$	CO_2	SO_2	CH_4	O_2	N_2
$\frac{d_c}{D_c}$	3·65	3·76	3·61	3·62	3·67	3·49	3·53

Abnormally high results are obtained with associated substances—*e.g.* the fatty acids and alcohols have values approximating 4 or 5. Argon has the value 2·71 (D. Berthelot, 1901), and hydrogen 2·69 (J. J. van Laar, 1904); and these gases alone approximate with any reasonable accuracy to the value required by van der Waals' hypothesis. According to C. Dieterici's values for the critical data, the critical density is 3·6945 times greater than the density of an ideal gas at the critical temperature and pressure. This is a much closer approximation to the actual results with normal substances than is obtained with the equation of J. D. van der Waals, for, according to S. Young (1892), the value of d_c/D_c is nearly 3·7 for all substances which can attain the critical state without chemical change.

Method of determining molecular weights from the critical constants.——If the pressure be expressed in atmospheres and the unit of volume be the volume occupied by a gram-molecule of the gas under normal conditions, J. D. van der Waals[4] has shown that the equation

$$\left(p+\frac{a}{v^2}\right)(v-b)=R\frac{T}{273}, \text{ becomes } (1+a)(1-b)=R\frac{T}{273}$$

so that the relative molecular volumes of the different gases at 0° and 1 atm. pressure, or the volumes of the different gases at 0° and 1 atm. which contain the same number of molecules, are proportional to

$$\frac{1}{(1+a)(1-b)},\ \frac{1}{(1+a')(1-b')},\ \ldots$$

and the volume in litres occupied by a gram-molecule of the gas under normal conditions, by Avogadro's rule, will be the same for all gases, so that $(1+a)(1-b)M/W=$a constant, where W denotes the weight of a litre of a gas under normal conditions:

$$M=\frac{22{\cdot}412W}{(1+a)(1-b)}$$

since P. A. Guye (1905) has shown Avogadro's constant to possess the same normal value 22·412 for all gases. The constants a and b vary with temperature, and Guye considers that the value of the critical constants at the temperature T can be represented by the equations:

$$a_0=a\left(\frac{T_c}{T}\right)^{\frac{3}{2}};\ b_0=b\left(1+\frac{T_c-T}{T_c}\right)\left(1-\beta\frac{p}{p}\right)$$

The numerical value of the constant $\beta=0{\cdot}0032229$ has been deduced from the critical constants, density, and molecular weight of carbon dioxide, consequently the molecular weight of the gas is given by the expression:

$$\text{Molecular weight }=\frac{22{\cdot}412W}{(1+a_0)(1+b_0)}$$

The following examples illustrate the application of the rule:

	Carbon dioxide.	Nitrous oxide.	Sulphur dioxide.	Hydrogen chloride.	Acetylene.
W . . .	1·9768	1·9774	2·9266	1·6407	1·1707
T_c . . .	303·98	311·8	428·4	325	308·25
p_c . . .	72·93	77·8	78·9	83	61·03
$a\times10^5$ . .	721	719	1345	726	879
$b\times10^5$ . .	191	185	251	180	231
$a_0\times10^5$ . .	847	878	2644	943	1055
$b_0\times10^5$ . .	161	156	255	153	207
M . . .	44·003	44·000	64·065	36·484	26·018

With gases which have a low critical temperature and which do not liquefy very readily, the correction of the constants a and b for temperature is not necessary, and

$$\text{Molecular weight }=\frac{(22{\cdot}412-mT_c)W}{(1+a)(1-b)};\text{ or }M=\frac{(22{\cdot}412-0{\cdot}0000623T_c)W}{(1+a)(1-b)}$$

is sufficiently accurate, where the value of the constant m has been fixed with respect to oxygen $=16$, at $m=0{\cdot}0000623$. For example,

	Oxygen.	Hydrogen.	Nitrogen.	Argon.	Carbon monoxide.
W . .	1·4290	0·089873	1·2507	1·7802	1·2504
T_c . .	154·2	32	128	152	133·5
$a\times10^5$.	266	28·8	275	260	284
$b\times10^5$.	139	73·7	174	138	172
M . .	32	2·0153	28·013	39·866	28·003

A. Leduc's[5] method of molecular volumes for determining the molecular or atomic weight of gases.—A. Leduc's method is related to D. Berthelot's method of limiting densities, but as experimental data it requires a knowledge of the densities and the critical constants. It is based on the theory of corresponding states. The variations of pressure p, molecular volume V, and absolute temperature T of a gas described by Boyle's and Charles' laws, are related by $pV=KT$, where K is a constant the same for all gases. All known gases deviate from this rule, and the relation is then represented by $pV'=K'T$, where K' is related with K so that $K'/K=V'/V$. Let V'/V, the ratio of the molecular volume V' of a gas to the molecular volume V of an ideal gas at the same temperature, be represented by $\phi=V'/V$. Consequently, it follows that $K'/K=\phi$, and $pV'=KT\phi$, where ϕ is variable quantity. If M denotes the molecular weight, and v the specific volume, it follows, since $Mv=V'$,

$$Mpv=KT\phi$$

For oxygen gas $M=32$; $v=v_1$; and $\phi=\phi_1$; accordingly, $32pv_1=KT\phi_1$; and by division, remembering that if D and D_1 respectively denote the densities of a given gas and oxygen, $D=1/v$ and $D_1=1/v_1$—all at the same temperature and pressure:

$$\frac{M}{32}=\frac{\phi D}{\phi_1 D_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If $1-E$ and $1-E_1$ be respectively substituted for ϕ and ϕ_1, this equation is identical with that used in D. Berthelot's method of limiting densities.

In order to evaluate ϕ and ϕ_1, it follows that the relation for zero pressure becomes $Mp_0v_0=KT\phi_0$, and by division $pv/p_0v_0=\phi/\phi_0$. A. Leduc then assumes that ϕ_0 may be regarded as unity at a common temperature, and at an indefinitely small pressure; this means that under these conditions all gases have the same molecular volume, consequently

$$\frac{pv}{p_0v_0}=\phi$$

A. Leduc further assumes that the compressibility of a gas over a range of a few atmospheres, can be represented by the expression $E=1-pv/p_0v_0$, or

$$1-\frac{pv}{p_0v_0}=mp+np^2$$

where m and n are small constants to be determined for each gas. Accordingly, $\phi=1-mp-np^2$, and therefore

$$\phi=1-mp_c\left(\frac{p}{p_c}\right)-np_c^2\left(\frac{p}{p_c}\right)^2 \quad . \quad . \quad . \quad . \quad (2)$$

A. Leduc measures p in cm. of mercury, and p_c in atm., and he denotes the ratio p/p by e.

To evaluate the constants m and n, A. Leduc assumes that the molecular volumes of gases are equal at the same reduced temperature T/T_c, and reduced pressure, p/p_c. At the same reduced pressure, different gases at the same reduced temperature give the same values of ϕ. Consequently, the coefficients mp_c and np_c^2 must each be functions of the reduced temperature only. A. Leduc finds that within the limits of experimental error, these functions are respectively:

$$mp_c=18{\cdot}85\frac{T_c}{T}\left(2\frac{T_c^3}{T^3}-\sqrt{2}\frac{T_c^3}{T^2}+2\sqrt{2}\frac{T_c}{T}-1\right)\times10^{-4}\,;\quad np_c^2=3{\cdot}5\frac{T_c^3}{T^3}\left(\frac{T_c}{T}-1\right)\times10^{-4}$$

The results represent his experiments on compressibility very closely, excepting with ammonia, phosphine, hydrogen sulphide, and methyl ether.

In applying this method, (i) the density D of the gas at the temperature T and pressure p; and (ii), the critical pressure p_c and temperature T_c, are supposed to be known. This enables the constants m and n to be evaluated. It is then necessary to calculate ϕ from equation (2). The value of ϕ_1 for oxygen is also supposed to be known; and the required molecular weight is then calculated from (1). In practice $T=273$ and $p=1$. A comparison of some results by these different physical methods gives:

Method of	Hydrogen.	Nitrogen.	Carbon.	Chlorine.
Limiting densities . .	1·0075	14·008	12·009	35·461
Critical constants . .	1·0075	14·010	12·003	35·436
Molecular volumes . .	1·0075	14·006	12·005	35·450

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§ 6. Summary of the Kinetic Theory of Molecules

The phenomena are our data, and behind them we cannot go except in imagination.—A. SCHOPENHAUER.

The fundamental assumptions of the kinetic theory in its simplest form, can now be summarized—the term "kinetic," by the way, is derived from the Greek κινέω, I move. (1) Matter is composed of a finite number of molecules. In gases, the volume of the molecules is very small compared with the space not occupied by the molecules. At great pressures, however, the relative sizes of the molecules must be taken into consideration. (2) The molecules of a gas are in a state of rapid perpetual motion in straight lines. The molecules are continually colliding against the walls of the boundary vessel and against one another. (3) The molecules are perfectly elastic and rebound after a collision without any loss of momentum. (4) The molecules of gases do not always move quite independently of one another, since some molecules have a slight attractive force one for the other. This becomes appreciable with increasing concentrations. (5) Two gases are in thermal equilibrium when the average kinetic energies of the molecules of both gases are the same.

A. D. Risteen in his *Molecules and the Molecular Theory* (Boston, 1895), has compared the results of observation with the deductions from the kinetic theory in double columns. The following is modified from his scheme:

TABLE VII.—COMPARISON OF THE KINETIC THEORY WITH FACTS.

Results of theory.	Results of observation.
1. The molecules of a particular gas are all alike. There are special cases of dissociation and polymerization.	1. Gases are homogeneous and show no signs of settling, nor can the molecules of any particular gas in general be separated, by diffusion, into different molecules.
2. Molecules are at relatively great distances apart, and in constant motion in straight lines.	2. The compressibility, permeability, and diffusivity of gases is great. The incompressibility of gases at high pressures is supposed to be due to the abnormal crowding of the molecules.
3. In a given mass of molecules, the product pv is proportional to the average kinetic energy per molecule.	3. In a given mass of gas the product pv is proportional to the absolute temperature, etc. This includes the laws of Boyle, Dalton, and Charles.
4. The average *kinetic energy* is constant for every set of molecules in a mixture of gases.	4. So far as we can tell, the *temperature* of each constituent of a mixture of gases is the same.
5. If two sets of molecules have the same kinetic energy, and the same pressure, they contain the same number of molecules per unit volume.	5. Avogadro's hypothesis, and hence also Gay Lussac's law. This is not a result of observation, but it has been inferred independently from purely chemical phenomena.
6. Diffusion.	6 Graham's law.

Molecular magnitudes.—The following Table VIII summarizes the results of some preceding calculations for a few common gases:

TABLE VIII.—MAGNITUDES IN THE MOLECULAR WORLD.

Gas.	Molecular weight, M	Mean velocity V, at 0°, in cm. per sec.	Number of collisions per sec.	Average free path, L, at 0° and 10^6 bars cm.	Molecular diameter, d cm.	Mass of the molecules, m grm.
Hydrogen, H_2 .	2·016	$1·838 \times 10^5$	$10·6 \times 10^9$	$16·00 \times 10^{-6}$	$2·403 \times 10^{-8}$	$13·33 \times 10^{-24}$
Oxygen, O_2 .	32·00	0·461	4·7	9·05	2·975	52·78
Nitrogen, N_2 .	28·02	0·493	5·3	8·50	3·146	46·53
Argon, A . .	39·88	0·413	4·2	8·98	2·876	65·79
Water, H_2O .	18·02	0·615	6·3	8·31	2·900	29·73
Carbon dioxide, CO_2	44·00	0·393	6·5	5·56	3·335	72·59

The following [1] also represent some constants which occur in calculations:

Volume of ideal gas per gram molecule at 0°, 760 mm. .	22,412 c.c.
Number of molecules per gram molecule at 0°, 760 mm.	$6·062 \times 10^{23}$
Number of molecules per c.c. at 0° and 760 mm. . .	$2·705 \times 10^{19}$
Kinetic energy of a molecule at 0° and 10^6 dynes . .	$5·621 \times 10^{-14}$ erg
Gas constant, R, 1·987 cals. per degree, or . . .	$83·15 \times 10^6$ ergs per degree
Boltzmann's gas constant, $R/N = k$	$1·372 \times 10^{-16}$ ergs per degree

It is sometimes convenient to use a millionth of a metre, *i.e.* a thousandth of a millimetre, as a unit of smallness, and to represent this unit by the symbol μ; this unit is called a **micron.** In illustration, 0·001 mm. or 10^{-3} mm. is μ; and thus 0·01 mm. or 10^{-2} mm. will be 10μ, and 0·0001 mm. or 10^{-4} mm. will be $0·1\mu$. Similarly, the double μ or milli μ, symbolized $\mu\mu$, and called a **millimicron,** represents a thousandth part or $0·001\mu = \mu\mu$ $= 0·000001$ mm.

In every explanation of natural phenomena, said H. von Helmholtz, we are compelled to leave the sphere of sense perceptions and to pass to things which are not the objects of sense, and are defined only by abstract conceptions. It is almost the same with magnitudes in the molecular world. Most of the numbers representing the motions and magnitudes of molecules convey no meaning to the mind because they are utterly beyond the range of our comprehension, and they might almost as well be abstract conceptions. The following considerations will serve to emphasize our inability to form a clear concept of the scale of magnitudes in the world of molecules. They have been employed by several writers.[2]

> *First*, A normal human eye, at a distance of 10 inches, can see objects $\frac{1}{250}$th inch in diameter; with a good microscope objects not much smaller than $\frac{1}{50000}$ inch in diameter can be clearly seen, but this is nearly 5000 times the magnitude of the molecule of an element. It would take about 40,000,000 molecules, touching one another, to make a row an inch long. *Second*, If all the molecules in a cubic inch of a gas were laid in a row, touching one another, although they are so inconceivably small, yet they are so very numerous that they would form a line about 35,000,000 miles long, and this line would extend more than 1000 times round the earth, and this in spite of the fact that only about one-three-thousandth of the volume is actually occupied by matter, the remainder being vacuous space. *Third*, If the gas were magnified on such a scale that a molecule was an inch in diameter, each cubic foot would contain about one molecule, and a molecule would then travel about 100 feet before it collided with another. *Fourth*, It would take about 53 years, counting at the rate of three per second, 24 hours a day, to count the number of collisions—5,000,000,000—made by a molecule with its fellows every second. *Fifth*, A molecule travels at the rate of nearly a quarter of a mile per second.

If the molecules occupy only a fractional part of the space taken up by a mass of matter, it is natural to inquire : Is there absolutely nothing in the intermolecular spaces ? Students of light, heat, electricity, and magnetism say that the intermolecular space, where no ponderable matter exists, is full of " an entity of a highly rarefied nature called æther." This hypothetical medium is continually crossing the path of the student of chemical theory.

Early history of the kinetic theory.—The first inkling of the idea that many of the observed properties of matter may be explained by the motion of its constituent particles without the introduction of separate adventitious hypotheses as to the nature of matter, has been traced back to the so-called atomic theory of Leucippus (*c.* 450 B.C.), Democritus (*c.* 420 B.C.), Epicurus (*c.* 300 B.C.), and Lucretius (*c.* 80 B.C.). Francis Bacon, in his *De principiis atque originibus* (London, 1612), said :

> Almost all the ancients—Empedocles, Anaxagoras, Anaximenes, Heraclitus, and Democritus—though they differed in other respects about the first matter, agreed in this, that they set down matter as active, as having some form, as dispensing with that form, and as having the principle of motion in itself. Nor can any one think otherwise unless he plainly deserts experience.

The theory that the properties of matter are dependent on the mode of motion of the constituent particles was taken up by P. Gassend, in his *Syntagma philosophicum* (Lugduni Batavorum, 1658), where he explained the three states of matter by postulating absolutely rigid atoms moving in all directions in empty space. Robert Boyle also, in his *Considerations and Experiments touching the Origin of Qualities and Forms* (London, 1664), assumed the existence of a continued motion of the primitive atoms. As previously indicated, Robert Hooke (1678) attributed the pressure of gases to the impact of similar particles ; and the same notion occurred independently to D. Bernoulli (1738), and to T. Herapath (1821). J. P. Joule (1848) also applied the principle to calculate the average speed of the particles of a mass of hydrogen. J. P. Joule's calculation is independent of the number of particles, as well as of their direction of motion and of their mutual collisions. These ideas did not develop into a satisfactory hypothesis until R. Clausius, in 1857 and subsequent years, took into consideration the mutual impacts, and the internal rotations and vibrations which the molecules communicate to one another. R. Clausius also discussed the bearing of the internal motions of the molecules on specific heat, and he explained the comparative slowness of the process of diffusion of one gas into another in spite of the swiftness of the motions of the molecules.

In 1860, J. C. Maxwell applied the statistical method or method of averages to the distribution of velocities among the molecules of a gas, and he made the first numerical estimate of the average length of the free path of a moving molecule between two collisions. The work of A. Krönig (1856), R. Clausius (1857), J. C. Maxwell (1859), L. Boltzmann (1868), and of others played an important part in the subsequent development of the hypothesis.

The kinetic theory and the corresponding molecular theory of liquids and gases have been of great service in helping chemists to form mental pictures of many processes which would be otherwise too difficult to conceive clearly. No one pretends that the picture corresponds with reality, but it has been of great assistance in applying the method of deduction and verification. The theory has its faults; at present, it throws no light on many of the properties of gases, while the applications to liquids and solids have scarcely been touched. A great deal of work remains to be done, but most of the outstanding difficulties relate to the nature of the atoms and molecules, and do not affect the main outline of the theory. A short time back there was a school of chemists which repudiated the kinetic theory as an exhausted moribund hypothesis—for instance, C. L. Speyers rather prematurely said in his *Textbook of Physical Chemistry* (New York, 1898): "The kinetic theory is a troublesome thing, and is becoming an object of ridicule." As a matter of fact, the kinetic theory of molecules may be a troublesome thing, but it still promises to live long when our mathematicians get strong enough to wrestle with its many difficulties; few have any doubts as to the validity of the essential features of the doctrine.

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§ 7. Ultramicroscopic Particles—Ultramicroscopy

The sun discovers atoms and makes them dance naked in his beams.—D. CULVERWELL.

In practice, a good microscope will not clearly resolve particles much smaller than 0·00025 mm. (0·25$\mu\mu$, or $2·5 \times 10^{-5}$ cm.) in diameter by direct illumination; with oblique illumination, using a naphthalene monobromide immersion lens, and violet light, particles 0·000012 mm. in diameter have been noted. The term **ultramicroscopic particles** is applied to granules smaller than the limits of a good microscope. The ultramicroscopic particles cannot be seen with a powerful microscope illuminated in the ordinary manner, because the light waves bend round the minute particles and enter the eye just as if the particle did not exist. If the particles be illuminated with a lateral beam of light, their very smallness enables them to scatter the light, so that their presence can be inferred from the fact that each particle is surrounded by visible diffraction rings, or halos of light, just as surely as the presence of smoke indicates fire. The motes dancing in a beam of sunlight would be invisible but for this phenomena. The diffraction rings which surround the particles in the track of a beam of sunlight make them appear as if they were self-luminous, and they are more clearly seen against a dark background.

Clear solutions with particles too small to be resolved by the most powerful microscope, appear more or less opalescent when a beam of converging light is focussed into the solution. A solution free from these particles would not produce the opalescence, and such a solution is said to be **optically empty.** This is the so-called **Tyndall's optical test.**[1] Air and gases generally, if quite free from suspended particles, are said to be optically empty because the track of a beam of light therein is invisible. Air can be made optically empty by allowing it to stand overnight in a glass box whose sides are smeared with, say, glycerol. The difficulty in removing fine particles suspended in a gas is well shown by trying to remove sulphur trioxide from air by passing air charged with this compound through a number of wash bottles charged with water for which sulphur trioxide has a great affinity. The sulphur trioxide will persist after passing slowly through half a dozen ordinary washing bottles. It is also exceedingly difficult to get a liquid optically empty so that the track of a converging beam of light in the liquid is not visible in a darkened room. Distillation and filtration will not do. If colloidal silicic acid be suspended in the water, and then precipitated by passing an electric current through the solution, or if colloidal ferric or aluminium hydroxides be precipitated in aqueous solution, the precipitate in settling catches and drags the suspended particles down; the supernatant liquid is then optically empty. Precipitates which settle in a crystalline form do not clarify the liquid in the same way as colloidal precipitates. Ordinary air must be excluded or it will again charge the liquid with suspended particles. The work of R. C. Tolman, and others, shows that for the range of particles in actual smoke (5×10^{-6} to 10^{-4} cm.) and for particles in suspension 10^{-4} cm. upwards, the Tyndall beam becomes more intense at a given concentration the greater the subdivision. W. Mecklenburg found that with particles less than 10^{-4} cm., the Tyndall beam increased in intensity with an increase in the size of particles—concentration constant.

The sensitiveness of J. Tyndall's optical test (1868) has been greatly developed by the use of the so-called **ultramicroscope** of H. Siedentopf and R. Zsigmondy.[2] In this microscope, an intense beam of light—arc light, or, better, a beam of bright sunlight—is focussed into the liquid under examination, so that the light enters the liquid at right angles to the direction in which it is viewed under the microscope. The positions of the particles then become visible as points of light against a dark background. If transmitted light be used, the eye is dazzled by the profusion of light, and it cannot distinguish the slight differences of brilliancy caused by the diffraction of light by the small particles; just as it is impossible to see the stars by daylight. The presence of particles about 6×10^{-5} or 7×10^{-5} mm. in diameter can be demonstrated by this mode of illumination. Although the *position* of the particles can be seen, their form or *shape* cannot be distinguished. The *relative sizes* of the particles can be roughly estimated from their relative brightness. The ultramicroscope is therefore a microscope in which particles are illuminated against a dark background with the strongest possible light. It does not give an image of the object in the microscopic sense of the term, but it does give proof of the existence of small particles with a refractive index different from the surrounding medium. The stronger the illumination, the smaller the particles which can be perceived, but the efficiency of the ultramicroscope is limited by the decrease in the brightness of the particles at a rate which is proportional to the sixth power of their diameter.

While the opalescence produced by Tyndall's optical test merely shows that a solution contains a number of distinct individual particles in suspension, the ultramicroscope enables the *individual* particles to be detected under conditions where the most powerful microscope would fail to reveal any sign of non-homogeneity. When viewed in the ultramicroscope, the ultramicroscopic particles appear as glittering discs of light with a dim or dark background. A solution may thus appear perfectly homogeneous when viewed under the most powerful microscope, and yet appear distinctly heterogeneous when viewed under the microscope with Tyndall's illumination.

W. Ostwald suggested that in the two-phase system, the one phase which is finely subdivided and discontinuous is called the **disperse phase**; the other phase which is usually continuous is called the **dispersion medium**; the disperse phase may also extend through the dispersion medium as a kind of reticulum or network. The **degree of dispersion** or the dispersity of a colloid refers to the state of subdivision to which the disperse phase has been carried; the dispersion medium may be I. A *gas*, and the disperse phase (*a*) a liquid (*e.g.* cloud or mist), or (*b*) a solid (*e.g.* dust or smoke); II. A *liquid* and the disperse phase (*a*) a gas (*e.g.* foam), (*b*) a liquid (*e.g.* emulsion), or (*c*) a solid (*e.g.* suspensions); III. A *solid*, and the disperse phase is then (*a*) a gas (*e.g.* solid foam and scoriæ), (*b*) a liquid (*e.g.* certain liquid inclusions and gels), or (*c*) a solid (*e.g.* certain solid mixtures). When the dispersion medium and the disperse phase are both liquids, **emulsions** are formed if the degree of dispersion is not high, and **emulsoids** if the degree of dispersion is large; while if the dispersion medium is a liquid and the disperse phase is solid, **suspensions** are formed if the dispersity is not high, and **suspensoids** if the degree of dispersion is large. The general term **dispersoids** covers both emulsoids and suspensoids. H. Siedentopf and R. Zsigmondy proposed to call dispersoids which are visible under the microscope **microns,** and those which can be seen only by the application of ultramicroscopic methods **ultramicrons** or submicrons; ultramicroscopic particles which cannot be seen by ultramicroscopic methods are called **amicrons.** The limiting sizes are as follows:

Visible under microscope—*Microns*			$0{\cdot}25\mu$, or $2{\cdot}5\times10^{-5}$ cm.
Ultramicroscopic particles	*Submicrons*	Electric arc light	$15\mu\mu$, or 15×10^{-7} cm.
		Strong sunlight	$1{\cdot}0\mu\mu$, or 10^{-7} cm.
	Amicrons		$<1{\cdot}0\mu\mu$, or $<10^{-7}$ cm.

Early in the nineteenth century, the products obtained by reducing solutions of the salts were generally regarded as solutions although several investigators believed them to be suspensions of the metals, and not solutions at all, and those formed by cathodic reduction were considered to be hydrides, although R. L. Ruhland (1815)[3] and J. C. Poggendorff (1848) believed them to be metals in a very fine state of subdivision. J. J. Berzelius (1844) said that the arsenious sulphide obtained by the action of hydrogen sulphide is for the present to be regarded rather as a suspension of transparent particles than a solution, for arsenious sulphide gradually separates out as a precipitate; similarly, H. W. F. Wackenroder (1846) found that the reaction between solutions of sulphur dioxide and hydrogen sulphide furnishes a liquid from which the suspended sulphur can be separated by thawing and freezing; but it immediately separates out in large flocks if a neutral salt of an alkali like sodium chloride be added to the acid liquid. A. Sobrero and F. Selmi (1850) also gave an elaborate account of the same suspension of sulphur, and stated that sulphur belongs to a class of substances which possess the power of dispersing and dividing themselves in a liquid without completely dissolving therein—*e.g.* soap, starch, and Prussian blue, and which F. Selmi (1844) classed together under the name *pseudo-solutions*. J. L. Gay Lussac (1810) and W. Crum (1853) noted the formation of a suspension during the hydrolysis of aluminium acetate; L. Péan de St. Gilles (1854), the hydrolysis of ferric acetate; J. J. Berzelius (1833), E. Fremy (1853), and H. Kühn (1853), the formation of a solution of silicic acid by the hydrolysis of silicon sulphide by water, and the coagulation of the solution by alkalies. Then followed T. Graham's researches on dialysis in 1861–64.

T. Graham found that substances like potassium hydroxide, potassium sulphate, sugar, and alcohol diffuse much more rapidly in aqueous solution than hydrated silicic acid, dextrin, tannin, gelatin, and albumin. He found also that the former diffuse much more rapidly than the latter through a parchment membrane. Since the slow diffusing substances are apt to occur in the gelatinous or non-crystalline form. T. Graham suggested calling them **colloids**—from κόλλα, glue; on the other hand, since the crystalline salts are typical of those substances which diffuse rapidly, T. Graham called them **crystalloids.** In illustration, potassium chloride, cane sugar, magnesium sulphate, hydrochloric acid, sodium chloride, and barium chloride are crystalloids; while albumin, gums, starch, gelatinous aluminium hydroxide, gelatinous ferric hydroxide, and gelatinous silicic acids are colloids. It must not be supposed that the colloids do not pass through the parchment at all.

T. Graham found that when the time of diffusion of hydrochloric acid—HCl—was taken as unity, the rate of diffusion of an equal quantity of sodium chloride was 2·3, cane sugar 7, egg albumen 49, and caramel 98. On account of these great differences, T. Graham proposed the useful method of separating substances in the colloidal and crystalloid states. The crystalloid is removed by diffusion through a membrane of parchment, bladder, or some similar substance. The process is called **dialysis**—from the Greek διά, through; λύω, I loosen. The operation will be understood from the following description:

> A piece of parchment or bladder is bound across one end of a glass or guttapercha hoop so as to form a kind of shallow dish, Fig. 5, narrower at the base than the open top. A mixed solution of albumin (the white of an egg) and potassium chloride in water is poured into the dish. This vessel is placed in another dish, *B*, containing distilled water. The water in the outer vessel is renewed every few hours. The dish containing the mixed solution is covered by a clock-glass to protect it from dust. In about three days, practically all the potassium chloride will have passed through the membrane into the outer vessel, while the egg albumin will remain in the inner compartment. The whole apparatus is called a **dialyzer.**

FIG. 5.—Dialyzer.

T. Graham held the opinion that the distinction between a crystalloid and colloid was due to a difference in molecular conditions, for, he said:

> Crystalloids and colloids . . . appear like different worlds of matter and give occasion to a corresponding division of chemical science. The distinction between these kinds of matter is that subsisting between the material of a mineral, and the material of an organized mass.

It is now believed that crystalloids and colloids are not different *kinds* of matter, but rather different *states* of matter. W. Ostwald emphasized the idea that we should speak rather of a colloidal state than of a colloidal substance, and that if the phase is sufficiently subdivided it is to be regarded as **colloidal phase** or **colloidal state**; and he defines *colloidal chemistry* not as the study of colloid materials but as that of the colloidal state of materials. T. Graham's classification of substances into colloids and crystalloids left the wrong impression that a colloidal substance must be amorphous, whereas it is now believed that a phase is colloidal when it is in a sufficiently fine state of subdivision whether it be crystalline or amorphous, and that every substance may appear under different circumstances either in the colloidal or in the crystalline nature of the substance concerned. P. P. von Weimarn has shown that a mere change in the concentration of the components of a reacting system suffices to precipitate a substance in either the crystalline or the colloidal states. W. D. Bancroft accordingly says that colloidal chemistry differs from ordinary chemistry through variations resulting from the increasing dispersity of one or more phases. T. Graham also distinguished between colloids in solutions and colloids in the gelatinous form, and he applied the term **sol** to the colloids when the system appeared to be liquid, and **gel** when the colloids assigned a jelly-like condition. If the one component was water, he employed the terms *hydrosol* and *hydrogel*; if alcohol, *alcosol* and *alcogel*; etc. The terms sol and gel are in fairly common use. J. Perrin (1905)[4] proposed the term **lyophile**—from λύειν, to loosen; φίλος, loving—for those systems in which there is a marked affinity between the two phases of a colloidal solution, and **lyophobe**—φόβος, fear—to the others; if the colloidal dispersion medium is water, **hydrophile** and **hydrophobe**—ὕδωρ, water—are used. If the degree of dispersion of a dispersoid can be increased or decreased by reversing the conditions which brought about the change, the dispersoid is said to be a **reversible colloid,** and if this cannot be done, an **irreversible colloid.** These terms were introduced by W. B. Hardy in 1900.

The particles which can be perceived in the ultramicroscope are more or less approximately the same order of magnitude as the molecules themselves. For instance, ultramicroscopic particles of colloidal gold, 1·7$\mu\mu$, have been measured, and, according to C. A. Lobry de Bruyn, the estimated size of a molecule of soluble starch in solution is 5$\mu\mu$; a molecule of chloroform is roughly 0·8$\mu\mu$, according to G. Jäger; a molecule of carbon dioxide approximates to 0·285$\mu\mu$; a molecule of water vapour, 0·113$\mu\mu$; and a molecule of hydrogen gas is between 0·067 and 0·159$\mu\mu$, according to an estimate of O. E. Meyer.[5] Hence particles smaller than the complex molecule of soluble starch have been perceived.

The definition of solutions.—Solutions are usually defined as "homogeneous mixtures which cannot be separated into their constituent parts by filtration." This definition forces us back to the distinction between homogeneous and heterogeneous mixtures; and this, in turn, upon the sensitiveness of the tests for homogeneity.

S. E. Linder and H. Picton [6] filtered arsenious sulphide suspensions through porous earthenware; and found that while particles over a certain size were arrested, others passed through unchanged. C. Barus tried to estimate the size of the disperse phase in a silver suspension from the pore size of the plate which just permitted filtration, and H. Bechhold elaborated the principle by preparing a graduated series of filters by impregnating filter paper, wire gauze, or fabric with a solution of collodion in acetic acid or gelatin in water, and subsequently hardening the solid. The filters for *ultrafiltration*, as it is called, were then standardized with a solution of hæmoglobin.

A solution may appear clear and homogeneous; the particles in solution may not be separable by the ordinary methods of filtration; and the substance in the solution may remain suspended an indefinite time; and yet when Tyndall's optical test is applied, an opalescence will prove that minute particles are in suspension; and the ultramicroscope will enable the particles to be recognized as distinct individuals. Perfect solutions, said T. O. Bergmann (1779), should be transparent, but there are all possible gradations between liquids carrying rapidly settling particles in suspension, and liquids which carry particles in suspension an indefinite time without settling, and in which the particles are so small that they can only just be perceived by the ultramicroscope. Consequently, if the above definition of a solution be accepted, every time the sensitiveness of the method for detecting non-homogeneity is increased, a certain number of solutions previously classed as homogeneous will probably appear heterogeneous or colloidal. This difficulty can be partially overcome by restricting the term solution, by an arbitrary convention: **Solutions are mixtures which appear clear and homogeneous with Tyndall's illumination, and which cannot be separated into their constituent parts by ordinary mechanical processes of filtration through paper or settling.**

J. W. Gibbs' concept of phase and component helps to clarify and generalize the distinction between chemical and physical action and between colloidal and true solutions. The idea underlying J. W. Gibbs' concept of a phase involves a distinction between molecular magnitudes and matter *en masse*, and it certainly holds good for matter which is homogeneous so long as it is not reduced in bulk to molecular dimensions. J. W. Gibbs' phase-concept serves as a criterion for a sharp classification of systems until the colloidal solution is reached, and then difficulties occur. In order to emphasize his opinion that the study of colloidal solutions renders it impracticable to draw even an arbitrary line between molecular and molar magnitudes, W. Ostwald advocates the use of the term **dispersoid system** in place of solution, and he applies the general term **dispersoids** in the following manner:

	Size of particles.	Examples.
Dispersoids .	Over 0·1μ	Suspension, emulsions, etc.
	Between 0·1μ and 1$\mu\mu$ . .	Colloidal solutions
	About 1$\mu\mu$ or less . . .	Molecular (and ionic) solutions

because he also believes that suspensions, colloidal and true solutions, represent varying degrees of dispersion of the solute. Although colloidal solutions are usually considered to be two-phase systems, and ordinary solutions one-phase systems, there appears to be an unbroken continuity between the heterogeneity of suspensions and the homogeneity of true solutions. Hence W. Ostwald tried to emphasize this by calling dispersoids with a degree of dispersion greater than 6×10^7 *molecular dispersoids*; and molecules may ionize—ionically disperse—to form *ionic dispersoids*. The evidence is therefore pointing to the inference that **the distinction between colloidal two-phase solutions and ordinary one-phase solutions turns on the relations between the dispersoids or solute and the solvent rather than on the size of the particles.**

Colloids have but a slight influence on the vapour pressure, freezing point, and boiling point of the dispersion medium. Indeed, when the colloid has been purified to a high degree, the colloid has no influence on these properties at all. For example, E. Paterno found that tannic and gallic acids form colloidal solutions with water and do not appreciably influence the freezing point of the solvent, but in glacial acetic acid, a true solution is formed, and the freezing point is depressed in the regular manner. The *molecular weights of colloidal solutions* have quite a different meaning from the results obtained with the so-called true solutions. Apart altogether from disturbances due to absorbed impurities, and possible hydrolytic changes, the different results obtained with systems having the same composition but varying degrees of dispersion, show that a series of progressively varying molecular weights can be obtained for one and the same substance which, in the systems with a low degree of dispersion, would approach infinity. In some cases where a change has been observed, we are by no means sure that some compounds other than the assumed colloid are not producing the change. For instance, it is highly probable that hydrolysis in aqueous solutions of sodium palmitate, or oleate, results in the formation of some sodium hydroxide. It must also be remembered that it is exceedingly difficult to get rid of impurities which are associated with colloids during their preparation. Again, said W. D. Bancroft, if the suspended colloidal particles are insoluble in the dispersion medium, there will be no change of surface tension, no osmotic pressure, and no diffusion except what is due to the Brownian movements; and conversely, if the particles are slightly soluble, there will be a slight change of surface tension, some osmotic pressure, and some diffusion other than that due to the Brownian movements.

Many attempts have been made to calculate the molecular weight of colloids from the osmotic pressure calculated in this and analogous methods, and numbers like these have been reported, Table IX, for example.

TABLE IX.—OSMOTIC PRESSURE AND MOLECULAR WEIGHTS OF COLLOIDS.

	Concentration grams per litre.	Osmotic pressure mm. of mercury.	Molecular weight.
Egg albumin	12·5	20	11,000
Gelatin	12·5	6	36,000
Starch iodide	30·0	15	34,000
Dextrin	10·0	165	1,000
Gum arabic	10·0	72	2,400

Some confusion is here prevalent because the term molecular weight is imparted to two totally different concepts. Molecular weight means something quite different in the case of gas or a solute, and in the case of a suspended particle. The molecular weight of a lump of, say, metal is not generally supposed to be high because the metal does not diffuse and is visible; why then should it be permitted to assign a high molecular weight to the finely divided metal? The mere fact of grinding cannot increase its molecular weight. This has been emphasized by W. D. Bancroft[7]:

> The molecular weight of a suspended particle, if it means anything at all, means something entirely different from the molecular weight of a solute or gas. We can determine the molecular weight of benzene approximately from the measurement of the surface

tension, but it is absurd to say that suspending fine drops of benzene in water causes the molecular weight of benzene to become . . . very large. We are talking about entirely different things in the two cases. What we mean is that liquid benzene has a molecular weight of 78, and that liquid benzene suspended in water behaves, or may behave, as if it were a dissolved substance having a . . . very large . . . molecular weight. As a matter of fact, the experiments bring out clearly the enormous difference between a solution and a suspension.

Many colloids show a small osmotic pressure, and measurements of the *osmotic pressure of colloidal solutions* have been made by W. Pfeffer,[8] H. Picton and S. E. Linder, C. E. Linebarger, etc. The results show that the osmotic pressure of most colloids is a complex function not only depending on the number of particles in unit volume but also on the degree of dispersion, and the state of the system. The theoretical investigations of A. Einstein and M. von Smoluchowsky show that the osmotic pressures—P_1 and P_2—of two equally concentrated but differently dispersed phases are inversely proportional to the cubes of the radii—r_1 and r_2—of their particles; or $P_1 : P_2 = r_2^3 : r_1^3$. Observations on the *vapour pressure of colloidal solutions* have been made by A. Smits,[9] F. Guthrie, C. Lüdeking, etc.; on the *boiling points of colloidal solutions* by F. Guthrie,[10] C. Lüdeking, etc.; and on the depression of the *freezing points of colloidal solutions* by H. F. Brown and C. H. Morris,[11] F. Krafft, etc.

The *compressibilities of colloidal solutions* have been determined by G. de Metz,[12] H. Gilbaut, etc. The compressibility of a colloidal solution is in general smaller than that of the dispersion medium, and it decreases as the concentration increases. The *specific gravities* and the *specific volumes of colloidal solutions* do not follow the mixture rule. The relations are somewhat complicated, but approach the mixture law the less the degree of dispersion of the disperse phase. W. Ostwald[13] showed that the capillary pressure causes the specific gravity of water to increase the smaller the size of the globulets—for the water in droplets 3 in diameter has a density 0·005 per cent. greater, and the droplets 0·03μ in diameter, 0·5 per cent. greater than water *en masse*. Observations have been made by G. Rose, J. P. Cholodny, etc.

The internal friction or *viscosities of colloidal solutions* is very marked. The concentrations of inorganic colloidal solutions of the metal and sulphides are small and the viscosities are but little different from that of water; the case is different with organic colloids like gelatin and albumin, and inorganic colloids like silicic acid and hydrated alumina, where the viscosity becomes relatively large such that T. Graham called the viscosimeter a *colloidoscope*. The viscosities have been measured by J. Friedländer,[14] H. W. Woudstra, etc., and the effects of changes in concentration, temperature, and age have been investigated. The effect of the addition of other substances in the solution has also been determined. A. Einstein deduced the viscosity formula $\eta = \eta_0(1 + 2{\cdot}5v)$, where v is the volume of colloidal matter per unit volume of medium. It is assumed that the volume v is not too large, that is, the concentration is not too great; the radius of the particles assumed to be rigid spheres is also supposed to be large compared with the range of molecular attraction. Values for the constant ranging from 1·5 to 4·75 have been obtained. The *surface tensions of colloidal solutions* have been measured by Lord Rayleigh,[15] G. Quincke, etc. The *diffusibility of colloidal solutions* was measured by T. Graham,[16] T. Voightländer, etc. The *dialysis of colloidal solutions* has been examined by T. Graham,[17] G. Malfitano, R. P. van Calcar, etc. The *coefficients of thermal expansion of colloidal solutions* have been investigated by H. Rodenwald.[18]

The settling of particles suspended in water.—It is well known that the finer the grain-size of a given substance the slower the settling in still water. G. G. Stokes[19] has shown that in a medium of specific gravity D', and viscosity η, the rate of settling V of a spherical grain of measurable size and of radius r and specific gravity D,

$$\text{Rate of settling, } V = \frac{2}{9} \cdot \frac{r^2 g(D - D')}{\eta}$$

where g is the gravitation constant. This formula assumes that the resistance a fluid opposes to the descent is proportional to the radius of the sphere and to the coefficient of viscosity of the fluid. E. Cunningham showed that with microscopic or ultramicroscopic particles, the resistance no longer depends exclusively on the coefficient of viscosity, and it is necessary to take into consideration resistance elements borrowed from the kinetic theory of gases; he uses the same factor as G. G. Stokes multiplied by $1+Al/r$, where l is the average length of path of the molecules of gas, and r is the radius of the spherule. Hence, the Stokes-Cunningham formula is:

$$\text{Rate of settling, } V=\frac{2}{9}\cdot\frac{gr^2(D-D')}{\eta}\left(1+\frac{Al}{r}\right)$$

The coefficient A depends on the nature of the shocks between gaseous molecules and the surface of the sphere, and it has to be evaluated experimentally, it has values ranging between 0·815 and 1·63. This formula has been verified by M. Knudsen and S. Weber, R. A. Millikan, J. Roux, M. Keehan, A. Schidlof, O. W. Silvey, etc.

A particle of radius μ settles in still water at the rate of 2·4 mm. per minute, and a particle of radius $10\mu\mu$ and specific gravity 3, settles at the rate of one mm. per month. The formula does not apply to angular grains, nor to excessively fine grains. P. Ebell found that ultramarine particles, when reduced to a very fine state of subdivision by grinding, remain suspended in water for months; O. Mühlhäuser found that similar remarks apply to carborundum powder; and some clays freed from soluble salts will remain in suspension an indefinitely long time. There is then some disturbing factor which neutralizes the action of gravity; the clue to this was given by some observations by the botanist R. Brown in 1827. He said:

> While examining the form of the pollen grains from *Clarckia pulchilla* suspended in water, . . . I observed many of them very evidently in motion. . . . Their motions were such as to satisfy me, after frequently repeated observation, that they arose neither from currents in the fluid nor from its gradual evaporation, but belonged to the particle itself . . . smallest moving particles observed and which I have termed *Active Molecules*, appear to be spherical, or nearly so, and to be between $\frac{1}{20000}$th and $\frac{1}{30000}$th of an inch in diameter (about 0·001 mm.). The molecules were not limited to organic bodies. . . . In every mineral which I could reduce to a powder, sufficiently fine to be temporarily suspended in water, I found these molecules more or less copiously, and in some cases, more particularly in siliceous crystals, the whole body submitted to examination appeared to be composed of them. . . . By reducing a drop of water to microscopic minuteness . . . by shaking or triturating water with almond oil . . . the motion of the smaller particles (of water) takes place with undiminished activity.

The bearing of R. Brown's observations on the phenomenon was not appreciated for many years. The phenomenon is named **the Brownian movement** after its discoverer R. Brown.[20] If water in which a little lycopodium—that is, the spores of the club moss—is suspended be examined under the microscope, the small particles appear to be incessantly vibrating with a slow trembling motion.

The phenomenon is demonstrated as follows: Rub a fragment of gamboge for a moment on an ordinary 3 × 1 glass slip, and place a couple of drops of water on the slip where the gamboge has been rubbed. Gently push a cover-glass up to the edge of the gamboge. The brisk motion of the particles can now be readily seen through a $\frac{1}{2}''$ objective and a dark-ground illumination; it is easy to seal up the liquid in little capillary tubules about half an inch long. These tubules can be mounted in Canada balsam under a cover-glass in the usual manner, and they are then available for showing the phenomenon at any time.

There are references to the "dancing particles of rudimentary animalcules" in the writings of some of the earlier naturalists, which show that the phenomenon had been noticed before Brown's time, but without a clear idea of the nature of the particles. Fig. 6 gives a sketch from a photograph of the Brownian movement[21] prepared by moving a photographic film at a uniform rate across the field of the microscope from left to right. Experiment has shown that the motion cannot be due to convection currents set up by small differences of temperature or pressure, to light effects, to the electrical state of the particles or of the liquid, nor indeed to any known influence outside the liquid. The cause of the motion must be sought in the liquid itself.

The kinetic theory of molecular motion seems to furnish the only admissible explanation of the phenomenon. It is supposed that, owing to the perpetual movements of the molecules of the fluid, the moving molecules are continually striking the particles, thus driving them irregularly, to and fro, up and down, in the liquid. As might be expected, the incessant movements become more and more vigorous the smaller the particles. There is a big contrast between the apparently sluggish movements of lycopodium and the vivacious motions of the ultramicroscopic particles of, say, M. Faraday's gold.[22] So much so that R. Zsigmondy once thought the two were really different phenomena. The movements of the particles of gold are described by R. Zsigmondy somewhat as follows: "The particles move with astonishing rapidity. A swarm of gnats in a sunbeam will give an idea of the motion. The particles hop, dance, and jump, and they dash together and fly away from one another so that it is difficult to get one's bearings." To this must be added the fact that if the composition of the liquid remains unchanged, the motion in the liquid seems to continue an indefinite time without ceasing, for the Brownian movements have been observed in the fluid in cavities of quartose rocks, showing that the motion has in all probability been maintained for enormous periods of time—ever since the fluid was sealed up in the rocks. By studying the movements of the fine particles of gamboge—that is, the dried latex of the *Garcinia morella*—suspended in water; and of extremely fine particles of silver dust obtained by striking an electric arc between silver poles—suspended in air; it has been proved by direct observation[23] that **the distribution of the particles, their velocities, and the frequency of their collision is the same as the kinetic theory assumes to be the case with the particles of a gas.** F. M. Exner found that particles larger than 4μ do not show the Brownian movement in water; particles smaller than 0·1μ show vigorous movements; and particles with a diameter 10$\mu\mu$ have trajectories up to about 20$\mu\mu$. The movement takes place in all fluids, though more actively the less the viscosity. J. Perrin detected it with particles suspended in the film of a soap bubble. It is just perceptible in glycerol, and very active in gases. All attempts to find an explanation of the Brownian movement outside the fluid have failed. As C. Wiener[24] stated in 1863, the agitation does not originate either in the particles themselves or in any cause external to the fluid, but must be attributed to internal movement characteristic of the fluid state; and J. Perrin adds that the apparent repose of a fluid in equilibrium is an illusion due to the imperfection of our senses; in reality the constituent particles of a fluid are in a state of spontaneous, unco-ordinated, and never-ceasing agitation. A particle of a solid suspended in a fluid is being continuously bombarded by the neighbouring molecules. W. Ramsay (1876), G. Gouy (1888), H. Siedentopf (1900), and J. Delsaulx and J. G. G. Carbonelle (1877) had a clear view of the mode in which the molecular bombardment of the fine particles suspended in a fluid can produce the Brownian movement:

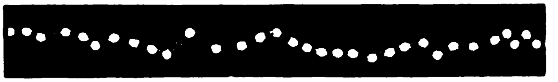

FIG. 6.—Sketch from a Photograph of the Brownian Movement (T. Svedberg, 1912).

> The internal movements of the molecules which determine the heat content of a fluid, is well able to explain the facts. . . . In the case of large surfaces, the molecular impacts which cause pressure produce no displacement of the suspended body because the resultant tends to move the body in all directions at once; but if the surface of the suspended body be smaller than the area necessary to ensure that all the irregular motions will be compensated,

> the pressures from different sides will be unequal, and continually shifting from point to point; these pressures will not be equalized by the law of averages, and their resultant being no longer zero, they will vary continuously in intensity and direction.

A. Einstein (1905) and M. von Smoluchowsky (1906) developed a quantitative theory of the phenomenon. The former showed that an emulsion diffuses like a solution, so that if x^2 denote the mean square of the projection of the displacement along a horizontal axis, the quotient x^2/t is constant when t denotes the time, so that the mean displacement is doubled when the time is increased four-fold; and increased ten times when the time is increased a hundred-fold. The quotient x^2/t is called the *activity* of the Brownian movement of the granules. A. Einstein next showed that the *coefficient of diffusion*, $\delta=\frac{1}{2}x^2/t$; and further, if N denotes Avogadro's number, the

$$\text{Coefficient of diffusion, } \delta=\frac{RT}{6N\pi r\eta}; \text{ or, Activity of movement, } \frac{x^2}{t}=\frac{RT}{3N\pi r\eta}$$

but the mean kinetic energy K of the molecules is $\frac{3}{2}RT/N$, and therefore $x^2/t=\frac{2}{9}K/\pi r\eta$. This means that the activity of the agitation (or the rate of diffusion) is proportional to the molecular energy or the absolute temperature, and inversely proportional to the viscosity and absolute temperature of the grains. This formula has been verified by L. Bancelin for sugar solutions, and for emulsions of gamboge in solutions of glycerol. V. Henri has discussed the different methods available for determining the grain size of the colloidal particles.

T. Svedberg showed that the amplitude A or the distance between the extreme and mean positions of the particle, and the period of oscillation t or the time taken by the particle to make a complete oscillation or excursion from one extreme position and back again, is related with the velocity V, by the equation $V=4A/t$. T. Svedberg found that as the amplitude increases the period of oscillation increases in such a way that $4A/t$ is nearly constant,

	Acetone.	Ethyl acetate.	Amyl acetate.	Water.	*n*-propyl alcohol.
A	3·1	2·0	1·5	1·1	0·7μ
t	0·032	0·028	0·026	0·013	0·009 sec.
$4A/t$	390	290	230	340	310

F. M. Exner showed that with particles 0·4μ in diameter, the velocity was 3·8μ per sec.; with particles 1·3μ in diameter, the velocity was 2·7μ per sec.; with particles 3μ in diameter the velocity was just perceptible, and with particles 4μ in diameter no movement was discernible; and R. Zsigmondy showed that the amplitude depends on the size of the particles; with particles 6, 10, and 35$\mu\mu$ in diameter, the amplitudes were over 10μ, 3 to 4μ, and 1 to 7μ respectively. T. Svedberg further showed that if the sizes are constant the viscosity of the medium is alone of importance; and that neither the nature of the particles nor the other properties of the medium are of importance. For any given size of particles, the amplitude is approximately inversely proportional to the viscosity of the dispersion medium.

	Acetone.	Ethyl acetate.	Amyl acetate.	Water.	*n*-propyl alcohol.
A	3·1	2·0	1·5	1·1	0·7μ
$\eta\times10^3$	3·2	4·6	5·9	10·2	22·6
$A\eta\times10^3$	9·9	9·2	8·9	11·2	15·8

J. Perrin[25] experimented on the arrangement of the particles of a colloid suspended in water under the action of gravity and its own osmotic pressure. If n and n_1 respectively denote the number of particles in unit volume at heights 0 and h; w, the mass; D, the density of the granules; D', that of the liquid; g, the gravitation constant; and P, the osmotic pressure of a single particle in unit volume, then, according to J. Perrin,

$$\log\frac{n}{n_1}=\frac{wgh}{P}\left(1-\frac{D'}{D}\right)$$

The agreement of the calculated with the observed results led J. Perrin to conclude that *the concentration of the granules in a uniform emulsion decreases in an exponential manner as a function of the height* in the same way as the barometric pressure does as a function of the height. Once this relation is established, the same equation affords a means of evaluating **Avogadro's constant,** N—for example, the number of molecules per gram-molecule of gas at 0° and 760 mm. Assuming that the pressure exerted by the particle is analogous with that as a gas obeying Boyle's law, $P=RT/N$, numbers ranging from $N=5\times10^{23}$ to 8×10^{23} were obtained —the generally accepted value determined by other independent methods is $N=6\times10^{23}$.

The perpetual agitation which is illustrated by the Brownian movement proceeds ceaselessly without external cause; it has therefore been asked if this motion contradicts the principle of the conservation of energy. The principle would be satisfied if every increment in velocity acquired by a granule is accompanied by the cooling of the liquid in its immediate vicinity, and every diminution in velocity is accompanied by local heating. J. Perrin tried to get round the difficulty by pointing out that J. C. Maxwell, W. Gibbs, and L. Boltzmann have robbed Carnot's principle of its claim to rank as an absolute truth, and reduced it to the mere expression of a very high probability. He adds that on the scale of magnitudes that are of practical interest to us, perpetual motion of the second kind is in general so insignificant that it would be foolish to take it into consideration. The impression left by this argument is that the principle is valid on the scale of magnitudes that are practical to us, but not in the realm of molecular magnitudes.

The Brownian movement is an expression of the molecular movements usually attributed to the molecules of matter. The molecular bombardment of the particles suspended in an emulsion tends to give a uniform distribution. Now, said J. Perrin, in his *Les preuves de la réalité moléculaire,*

> Let us suppose that it is possible to obtain an emulsion, with the granules all identical, an emulsion which I shall call, for shortness, *uniform*. It appeared to me at first intuitively, that the granules of such an emulsion should distribute themselves as a function of the height in the same manner as the molecules of a gas under the influence of gravity. Just as the air is more dense at sea-level than on a mountain-top, so the granules of an emulsion, whatever may be their initial distribution, will attain a permanent state where the concentration will go on diminishing as a function of the height from the lower layers, and the law of rarefaction will be the same as for the air.

J. Perrin confirmed this hypothesis with suspensions of gamboge and mastic in water; with the former, particles $0{\cdot}3\mu$ in diameter, a rise of 30μ sufficed to lower the concentration to one-tenth its value. J. Perrin found that unless the mixtures are aseptic, they may be invaded by elongated and very active protozoa, which, by stirring up the emulsion like fishes agitating the mud of a pond, much diminish the inequality of distribution between the upper and lower layers. H. Zangger[26] likewise confirmed the theory for drops of mercury; L. M. Brillouin, for emulsions of gamboge in glycerol; and B. Iljin, for emulsions of gamboge in water or castor oil, and an aqueous solution of gum arabic. B. Iljin also found that the movements of a given particle are quite independent of the movements of other particles.

A. Einstein and M. von Smoluchowsky worked out a mathematical kinetic theory of the process, and as a result of the close agreement between theory and observations, J. Perrin was led to say in his *Les atomes* (Paris, 1913), and in his *Les preuves de la réalité moléculaire* (Paris, 1909):

> The objective reality of the molecules becomes difficult to deny. At the same time, molecular movement has not been made visible. . . . The Brownian movement offers us on a different scale the faithful picture of the movement possessed, for example, by the molecules dissolved in the water of a lake which, encountering one another only rarely, change their direction and speed by virtue of the impacts with the molecules of the solvent. . . . The Brownian movement is a faithful reflection of molecular movement, better, it is a molecular movement in itself, in the same sense that the infra-red vibration is still light. From

the point of view of agitation, there is no distinction between nitrogen molecules and the visible molecules realized in the grains of an emulsion, which have a gramme molecule of the order of 100,000 tons. Thus, as we might have supposed, an emulsion is actually a miniature ponderable atmosphere; or, rather, it is an atmosphere of colossal molecules, which are actually visible. The rarefaction of this atmosphere varies with enormous rapidity, but it may nevertheless be perceived. In a world with such an atmosphere, Alpine heights might be represented by a few microns, in which case individual atmospheric molecules would be as high as hills.

In fine, **the experimental facts go very near towards establishing the validity and essential reality of the molecular kinetic theory as an explanation of the properties of matter.** In the words of E. E. Fournier d'Albe:

> We are face to face with this extraordinary situation: the molecule has ceased to be a theoretical abstraction—it has become a visible and tangible reality; for we can not only see it, but also "manipulate" it—not, indeed, with our hands, but by means of heat, and electricity, and the air pump.

Fine particles—say less than $0{\cdot}5\mu$—will remain in suspension an indefinitely long time, presumably because the Brownian movements tend to distribute the particles through the liquid against the action of gravity. If, however, enough particles agglomerate or coalesce so as to form large aggregates, settling may ensue. The aggregation, flocculation, or clotting of the fine particles and the converse dispersion, or deflocculation of aggregates is of great importance in many chemical processes, and will be discussed later—see purple of Cassius, and colloidal gold.

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§ 8. The Kinetic Theory of Atoms

There are countless worlds in countless heavens each revolving about its sun.—G. BRUNO.

The curve described by a single atom is as fixed as the path of a planet, and between the two cases no other difference exists save that resulting from our ignorance.—L. MEYER.

Many philosophers—E. Kant, G. W. E. Hegel, T. S. Hunt, etc.—have laboured in vain to demonstrate by abstract reasoning that chemical combination is an interpenetration of masses or a juxtaposition of molecules. According to G. W. E. Hegel, the chemical process is either an identification of the different, or a differentiation of the identical. The characteristic mark of a chemical species or individual is homogeneity. Is this homogeneity merely relative ? Can it be truly said : *Tota in minimis existit natura ?*

Do the atoms of the molecules of a compound retain their individuality ?—It may be quite true that the properties of a compound are mainly determined by the character of the constituent elements, yet, it is not to be supposed that there is necessarily any resemblance between the properties of the elements and of their compounds. It is not yet possible for the chemist to infer *a priori*, nor explain *a posteriori* the properties of a compound from the properties of the constituent elements. For instance, no one would have suspected the peculiar properties of cyanogen from the qualities of its constituent elements carbon and nitrogen, or of sodium chloride from the constituent elements sodium and chlorine. Chemists generally consider that the atoms preserve a kind of individuality throughout their existence, and when associated with other atoms, change their habit but not their nature. The change in the habits of an atom depends entirely on its associates. For instance, the properties of a molecule of water are very different from the properties of either of the constituents hydrogen or oxygen; the atoms of oxygen are magnetic when associated together in pairs or triplets, but they are non-magnetic when compounded with many other elements; iron too is intensely magnetic, some if its compounds are also magnetic, yet there are others which are non-magnetic, and still others which are diamagnetic—*e.g.* the iron carbonyls. Although the atoms of a compound molecule do not enjoy a separate external existence, yet, *within* the molecule, the atoms are probably distinct individuals, self-contained and self-existent. As Lucretius would have expressed it, they are *solida pollentia simplicitate*, or strong in their solid singleness; but the individual properties of the atoms are not always unrecognizable in the properties of the molecules of their compounds. J. Larmor (1908) [1] has well said :

> It becomes increasingly difficult to resist the simple view that chemical combination involves an arrangement of the atoms alongside each other under steady cohesive affinity, *the properties of each atom being somewhat modified, though not essentially, by the attachment of the others:* and that the space formulæ of chemistry have more than an analogical significance. The many instances in which the physical properties of the compound molecule can be calculated additively with tolerable approximation from those of the constituent atoms, are difficult to explain otherwise.

Those qualities which depend upon the nature of the atom in the molecule are called *additive properties* when each atom exerts its own specific influence whatever its state of combination. The following is selected from the evidence which might be cited to show that the atom retains its individuality in all its migrations no matter how many of its properties might be disguised by association with other atoms: (i) The weight of an atom remains intact whatever be its associated partners. (ii) The atom emits a peculiar type of Röntgen ray when stimulated in a suitable manner, and this property can neither be changed nor disguised by association with other atoms. (iii) The absorption of Röntgen and cathode rays is an atomic property, for each atom has its own specific absorptive power which is independent of the nature of the partners, with which it may be associated. There are numerous other examples—specific heat, crystalline form, etc.—not quite so decisive.

Are the atoms of a molecule at sensible distances apart?—It is sometimes asserted that the atoms are at insensible distances apart and that the atoms of a molecule are accordingly very close together. These statements have given rise to a misconception, for if the size of the atom be taken as a standard of reference it is probable that in the molecule the distances of the atoms from one another are comparatively great. Nothing is great or small unless it be considered in relation to other things regarded as standards of comparison.

Are the atoms of a molecule at rest or in motion?—The molecules are in motion, and therefore the atoms which make up the molecules must also be in motion just as a train waiting at the station is said to be at rest, although it is moving with the earth about the sun, at a great velocity. Accordingly, the term rest here refers to the position of the atom with respect to the molecule regarded as a standard of comparison. J. B. A. Dumas (1837),[2] S. Brown (1843), and D. I. Mendeléeff (1868), like many previous philosophers—notably C. L. Berthollet (1803)—picture a complex molecule to be analogous with a kind of miniature solar system with the atoms whirling rhythmically about one another at great speeds. Like the planets and their satellites, the atoms are supposed to be "endowed with an everlasting motion." The atoms are further supposed to be held in position, and to move in definite orbits owing to their attraction for one another, just as the planets and satellites move in definite orbits owing to the action of gravitational forces. D. I. Mendeléeff, like S. Brown, was an enthusiast; he said:

> Chemically, the atoms may be likened to the heavenly bodies, the stars, sun, planets, satellites, etc. The building up of the molecules from atoms, and of substances from molecules is then conceived to resemble the building up of systems, such as the solar system, or that of twin stars, or constellations from individual bodies. This is not a simple play of words in modern chemistry, nor a mere analogy, but a reality which directs the course of all chemical research, analysis, and synthesis.

Molecular models.—M. Berthelot (1875) [3] said that a complete representation of chemical compounds must involve the notion of rotatory and vibratory movements by which each particular atom, and each group of atoms in the molecule are animated. Although many chemists have similarly expressed their belief in a kinetic theory of atoms based upon a supposed analogy between atomic and planetary systems, they would yet recoil from any attempt to represent the idea pictorially or by mechanical models; but what Lord Kelvin said of himself applies to most: "I never satisfy myself until I can make a mechanical model of a thing. If I can make a mechanical model, I can understand it." So long as we are not seduced by a prepossessing analogy, there is no harm in constructing a model or diagrammatic picture because the strength and weakness of the analogy may be then better apprehended. Following up the analogy between planetary systems and the constitution of molecules, a two-atom molecule of hydrogen, H_2; iodine, I_2; or oxygen, O_2, can be regarded as a binary star—that is, as a pair of stars—in which each atom in the molecule rapidly revolves about the other in a regular orbit. A molecule of water, H_2O, would be represented by three atoms revolving in a similar manner; ammonia, NH_3, said D. I. Mendeléeff (1889), may be represented in the simplest manner by supposing the sun, nitrogen, to be surrounded by three planets, hydrogen atoms; and a molecule of sulphuric acid, H_2SO_4, might be depicted as a complex system with a central revolving sulphur atom around which the other atoms whirl in definite orbits:

> Each orb, the smallest in its motion sings.

First would come one sulphur or two oxygen atoms representing the nucleus, SO_2, outside these would encircle two oxygen atoms each with a revolving hydrogen atom as satellite. The imaginary picture so obtained would be a kinetic model of the formula $(HO)_2{=}SO_2$. E. Frankland and F. R. Japp [4] explained the constitution of acetic acid, $CH_3.CO.OH$, in a similar manner in 1884. The chemist determines the constitution of these tiny systems by a process which G. Martin has compared with the plucking of, say, the earth and moon from the solar system, or by replacing one planet by another and observing the disturbing effects of the transposition on the whole system; for, said C. Daubeny (1850), it is probable that any of the planets in the solar system could be replaced by a ball of matter with totally different properties, provided its gravitational mass were the same, without disturbing in the least the conditions of mechanical equilibrium. A kind of orrery would therefore give a better idea of the structure of a molecule than the crude plane formulæ usually employed. By this analogy, the planets Mercury and Venus represent single atoms, the Earth, Jupiter, and Saturn with their moons represent radicles—each composed of several distinct atoms so as to form a small sub-system complete in itself. All these individuals and sub-systems are linked to one another so as to form a balanced or stable molecular system, in some respects analogous with the solar system.

Valency.—Supposing that the above speculations were to be established by unassailable evidence, that would not alter the value of graphic or constitutional formulæ. E. Molinari (1893) considered that the constitution of compounds is rather dependent upon the intramolecular movements of the atoms in relation to each other, than on the relative positions of the atoms in space; and that the so-called valency bonds denote the nature of the motion or energy of the atoms with regard to each other. Hence, so far as graphic formulæ are concerned, it really makes little difference whether the atoms are actually attached to one another, or whether they are held in position by their mutual attractions while they are revolving about a centre of stability. Indeed, some assume that the conditions of temperature, light, or electricity necessary for the formation of a stable system determine whether a given atom can form a stable system with 1, 2, 3 . . . other atoms; otherwise stated, **the valency of an element is determined by the necessity for harmonizing the peculiar motions of the combining atoms to form stable molecular systems.** When J. Dalton was asked why an atom of carbon would take up one or two atoms of oxygen, but not three or four, he replied:

> The reason I would assign is that in the state of CO_2 there are two atoms of oxygen combined with one of carbon, and a third or fourth oxygen atom, however it may be attracted by the carbon, cannot join it without repelling one or more of the atoms of oxygen already combined. The attraction of carbon is able to restrain the mutual repulsion of two atoms of oxygen but not that of three or four.

S. Brown expressed the same idea in 1843: " The conception can perhaps be made still more lucid by the counter statement in astronomy that a sun cannot be overloaded with planets." S. Brown's view of valency shows that it is not necessary to postulate a distinct force emanating from the atoms in order to explain how, say, HCl forms a stable system, while HCl_2 and H_2Cl do not form stable molecular systems. If such systems were momentarily formed, the supernumerary atoms would be immediately flung off. After trying motions and unions of every kind, the atoms no doubt fall into those favourable arrangements which can persist as stable configurations. There may, of course, be a number of different stable systems corresponding with the different stable molecules of, say, iron and chlorine, $FeCl_2$ and $FeCl_3$. L. Meyer (1884),[5] E. Molinari (1893), F. P. Venable (1899), and others have advocated similar views. The plausibility of this hypothesis, of course, is not a proof that it is true.

The energy of atoms.—Each elementary atom presumably has its own definite charge of energy. The energy possibly exists in the form of rhythmical atomic motions, so that when one atom unites with another atom, each atom possibly gives up a part of its energy or absorbs energy from some external source, so that the motions of the one atom may be co-mingled with the motions of the other atoms to form a stable molecular system. The hypothesis thus suggests a plausible explanation of selective affinity.

Selective chemical affinity.—Lucretius frequently affirmed that it was absolutely decreed from the beginning what each thing can and cannot do; and to-day it is assumed that the molecules of matter are endowed with certain peculiar qualities, for the physicist explains gravitational phenomena by investing all the molecules of matter with a *common* property which he calls **gravity,** even though he may say with Isaac Newton (1717): "Gravity is not to be taken as an essential property of bodies." The chemist too explains chemical action by endowing the atoms with a *selective* power which he calls **affinity.** Gravitation is purely a physical relation common to all molecules of all known kinds of matter, while affinity is a very specialized chemical relation characteristic of specific types of matter. The kinetic theory of selective affinity assumes with W. M. Wundt (1897) that all the qualitative properties of matter are derived from the different modes of motion assumed by the atoms; the atoms themselves are completely devoid of quality. It is supposed that when two molecules meet, they can react chemically only when the motions of the atoms of the one molecule can be co-mingled with the motions of the atoms of the other molecules, so that instead of "shattering, confounding, and dispersing" one another's motions, they move in cadence and form harmoniously working systems called molecules. Two atoms moving in unison support and sustain one another's attractions; two atoms moving in discordant periods, despite their mutual influence, cannot form a stable combination because they offer a certain resistance to conjugation. As it has been otherwise expressed, "Every atom according to its nature is always striving to get into harmonious relations with other atoms." The idea recalls Democritus' view that the atoms are attracted to one another on account of their whirling motions; paraphrasing Lucretius, "the atoms unite in all manner of ways, and thoroughly test motions and combinations of every possible kind;" consequently, it is not at all strange that the atoms have at last formed arrangements which can be maintained more or less permanently. These speculations may give the impression that chemical phenomena will be ultimately referred to fundamental mechanical laws; but we have passed in imagination beyond the region of demonstrated fact, and are dimly conscious of an illimitable expanse where hypothesis and conjecture can but wander aimlessly and blindly. Here Newton paused: "The whole frame of nature may have been wrought into various forms, at first by the immediate hand of the Creator, and ever after by the power of nature."

What makes the atoms and molecules move?—We do not know! How can matter of itself initiate motion,[6] and particularly motion in a harmoniously working system? *Ignoramus!* In the words of C. Kingsley, "Everywhere skin-deep below our boasted science we are brought up short by mystery impalpable, and by the adamantine gates of transcendental forces and incomprehensible laws." We are profoundly ignorant of the cause of the specific activities of atoms, molecules, and planets. Immortal Newton could get no further than this: "The motions which the planets now have could not spring from any natural cause." It seems as if

> Full many a secret in her sacred veil
> Hath Nature folded. She vouchsafes to knowledge
> Not every mystery, reserving much
> For human veneration, not research.—Anon. (1851).

Consequently, the kinetic theories of the Brownian movements, of atoms, of molecules, of the planetary systems, and indeed of the solar system itself, are all compelled to prescribe or postulate an initial state of motion which is self-sustained and self-regulated. Guesses at the birth-history of these motions has been whispered only by the poets. *Deus mundum ædificavit,* said Cicero; and, in the oft-quoted lines of Virgil:

> Know first, the heaven, the earth, the main,
> The moon's pale orb, the starry train,
>   Are nourished by a soul,
> A bright intelligence, whose flame
> Glows in each member of the frame,
>   And stirs the mighty whole.

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§ 9. The Two Specific Heats of Gases

The kinetic theory of molecules assumes that the temperature of a gas is proportional to the average speed of translation of the moving molecules—an increase of the speed is accompanied by a rise of temperature, and conversely.

It will be remembered that specific heat is a term employed to represent the amount of heat required to raise the temperature of one gram of a substance 1°. A gas can be heated by simple compression, its specific heat then appears to be zero; but, in reality, a certain amount of energy, equivalent to the specific heat, is needed for the work of compression. Again, a gas, if it be expanded, is cooled; if the cooling effect of expansion just counterbalances the heat added to the gas, the temperature remains constant; and the specific heat appears to be indefinitely large. Here work, equivalent to the heat supplied, is performed by the expanding gas. These facts show that the condition of the gas must be stated before it is possible to define its specific heat. It is conventionally agreed that if the gas be allowed to expand during a change of temperature so that its pressure remains constant, the amount of heat required to raise the temperature of one gram-molecule of the gas 1° shall be called the **specific heat under constant pressure,** and symbolized by C_p. If the pressure be increased so that the volume remains constant when the gas is heated, the amount of heat required to raise the temperature 1° of a gram-molecule of the gas is likewise called the **specific heat under constant volume,** and symbolized C_v.

The heat imparted to a gas is not spent merely in raising the temperature of the gas; that is, in speeding up of the motions of the molecules. Energy is spent in—(1) *Augmenting the speed of the moving molecules.* The heat required actually to increase the kinetic energy of the moving molecules so as to produce a rise of temperature is the same for all gases. Let K denote this quantity. (2) *Performing external work.* Heat energy is needed to overcome the pressure of the atmosphere when the gas is allowed to expand. Call this quantity W. Since the coefficient of thermal expansion of all gases is the same, this quantity is practically constant for equal volumes or equimolecular weights. (3) *Performing internal work.* Heat energy is required to produce changes within the molecule which may alter the motions or orientation of the constituent atoms of the molecule, or raise the kinetic energy of the atoms moving with the molecule. Let ϵ denote the energy spent within the molecule per degree rise of temperature. A certain amount of energy must also be spent in overcoming the effects of intermolecular attractions. This can be neglected for the time being. Consequently, the ratio of the two specific heats may now be written, after J. J. Waterston (1845) : [1]

$$\frac{C_p}{C_v}=\frac{K+W+\epsilon}{K+\epsilon} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The specific heat of a gas at constant volume.—We have seen, (1) that $pv=\frac{1}{3}MV^2$, where M denotes the mass, and V the average velocity of the molecules. But the kinetic energy of a body of mass M moving with a velocity V is $\frac{1}{2}MV^2$; hence $pv=\frac{2}{3}\times\frac{1}{2}MV^2$; or the kinetic energy of the molecular motions is $\frac{3}{2}pv$, since $pv=RT$, the kinetic energy of molecular motion is $\frac{3}{2}RT$. If one gram-molecule of gas be heated 1°, the kinetic energy becomes $\frac{3}{2}R(T+1)$. Hence if the gas be heated 1° at constant volume, the thermal value of the increased kinetic energy is $\frac{3}{2}R(T+1)-\frac{3}{2}RT=\frac{3}{2}R$ cals. This result represents the specific heat of the gas at constant volume per gram-molecule ; or, $C_v=\frac{3}{2}R$.

The specific heat at constant pressure.—Again, if a gram-molecule of gas expands against atmospheric pressure when its temperature is raised 1°, the gas, in consequence, does work by pressing back the atmosphere, so to speak. The equivalent of this work must be supplied in the form of heat. This work is equivalent to the product of the pressure against the change in volume. Let x denote the change in volume when the gas is heated 1°, under a constant pressure ; then, $p(v+x)=R(T+1)$, and $pv=RT$. By subtraction $px=R$. This means that when a gram of gas is heated 1°, the resulting expansion against atmospheric pressure does work equivalent to R cals. ; or *the gas constant R, is numerically equal to the work done by a gas expanding against a constant atmospheric pressure, when the temperature is raised* 1°. Hence, R cals. must be added to the previous result to obtain the thermal equivalent of the energy supplied to one gram of gas in the form of heat when its temperature is raised 1°. Otherwise expressed, if one gram-molecule of gas be heated 1°, at constant pressure, an amount of heat equivalent to $\frac{3}{2}R+R=\frac{5}{2}R$ is required. This result represents the specific heat of the gas at constant pressure per gram-molecule or $C_p=\frac{5}{2}R$. In passing, it is interesting to note that *the difference between the two specific heats of a gas is numerically equal to the work done by the gas expanding against a constant atmospheric pressure when the temperature is raised* 1°, *or in symbols,*

$$C_p-C_v=R$$

a relation sometimes called **Mayer's equation,**[2] because it was used by him in 1842 to calculate the mechanical equivalent of heat, for the difference in the two specific heats represents the external work done during the expansion of 1 c.c. of air (*i.e.* 0·001293 grm.) against atmospheric pressure (*i.e.* 1,031,000 dynes per sq. cm.) when heated 1°. In Mayer's equation, when the work R is measured in calories, R is approximately 2 cals. The same value of R can be obtained another way—one gram of oxygen occupies 699·8 c.c. at standard pressure 1,013,200 dynes per sq. cm. and at 273° K. Hence, for one gram of oxygen, $R'=pv/T=2{\cdot}6\times10^6$ ergs ; and for 32 grams, or one gram-molecule, $R=2{\cdot}6\times10^6\times32=8{\cdot}3\times10^7$ ergs$=8{\cdot}3$ joules$=2$ cals. (nearly). Instead of representing gram-molecules of a gas, the specific heats C_p and C_v can be referred to one gram. In that case, R. Mayer's equation becomes $C_p-C_v=R/M$, where M denotes the molecular weight of the gas, and, for oxygen, $R/M=2\div32=0{\cdot}063$ cal.

EXAMPLES.—(1) The specific heats of oxygen at constant pressure and constant volume are respectively 0·217 and 0·155. The difference in the molecular specific heats is therefore $32(0{\cdot}217-0{\cdot}155)=2$ cals. nearly.

(2) Compute the mechanical equivalent of heat when for air $C_v=0{\cdot}1685$ and $C_p=0{\cdot}2375$. The mechanical equivalent of heat J is equal to the ratio W/Q, where Q denotes the amount of heat in calories required for performing W ergs of work. The work of

expansion when 1 c.c. of gas expands $\frac{1}{273}$ c.c. is $\frac{1}{273}\times1,013,000=w$, and the heat Q is equivalent to 0·001293(0·2375 − 0·1685) cal. Hence $J=41{\cdot}6\times10^6$ ergs per calorie.

The ratio of the two specific heats of a gas.—Returning to the ratio of the two specific heats, which is usually symbolized γ, we can now write $K=\frac{3}{2}R$, and $W=R$, or,

$$\gamma=\frac{C_p}{C_v}=\frac{\frac{5}{2}R+\epsilon}{\frac{3}{2}R+\epsilon} \quad . \quad . \quad . \quad . \quad . \quad (2$$

The magnitude of ϵ will vary with different gases, for it will naturally be related somehow with the complexity of the molecule. The greater the value of ϵ the less the value of the ratio of the two specific heats. For a monatomic gas, ϵ probably approaches zero, and the numerical value of the ratio becomes $\gamma=\frac{5}{3}$, or 1·67. The greater the complexity of the molecule, the greater the value of ϵ, and the smaller the value of the ratio of the two specific heats. This is illustrated by Table X.

TABLE X.—RATIO OF THE TWO SPECIFIC HEATS OF GASES.

Gas.	Molecule.	Atoms per molecule.	γ	Gas.	Molecule.	Atoms per molecule.	γ
Mercury . .	Hg	1	1·67	Carbon dioxide .	CO_2	3	1·31
Argon . . .	A	1	1·65	Nitrous oxide .	N_2O	3	1·31
Hydrogen . .	H_2	2	1·41	Hydrogen sulphide	H_2S	3	1·31
Nitrogen . .	N_2	2	1·41	Ammonia . .	NH_3	4	1·30
Oxygen. . .	O_2	2	1·40	Methane . .	CH_4	5	1·27
Carbon monoxide .	CO	2	1·40	Ethylene . .	C_2H_4	6	1·24
Hydrogen chloride .	HCl	2	1·39	Ethane . .	C_2H_6	8	1·18
Chlorine . .	Cl_2	2	1·32	Alcohol . .	C_2H_5OH	9	1·13
Bromine . .	Br_2	2	1·29	Benzene . .	C_6H_6	12	1·09
Iodine . . .	I_2	2	1·29	Ether . .	$C_4H_{10}O$	15	1·06
Iodine chloride .	ICl	2	1·31	Turpentine. .	$C_{10}H_{16}$	26	1·03

The effect of variations of temperature and pressure on γ.—The ratio of the two specific heats of gases decreases as the temperature rises. Thus, A. Wüllner[3] found the ratio of the specific heats of the following gases to fall as the temperature rose from 0° to 100:

γ for	Air	CO	CO_2	N_2O	NH_3	C_2H_4
0° . . .	1·4052	1·4032	1·3113	1·3106	1·3172	1·2455
100° . . .	1·4051	1·3970	1·2843	1·2745	1·2791	1·1889

and E. H. Stevens found the value for air to fall from 1·4006 at 0°, to 1·3993 at 100°, to 1·3400 at 950°; and M. Trautz obtained for water vapour saturated at 100°, γ=1·3290, and saturated at 110°, 1·3301; at 120°, 1·3129; and at 130°, 1·3119. Conversely, the ratio of the two specific heats of gases increases as the temperature falls from about 20° to −180°. For instance, M. Trautz (1913) has shown:

	Nitrogen, N_2	Carbon monoxide, CO	Oxygen, O_2	Hydrogen, H_2	Helium, He
γ from 18° to 20° . .	1·400	1·398	1·399	1·407	1·660
γ from −180° to −181°	1·468	1·472	1·447	1·597	1·673

A. Witkowsky obtained analogous results with air, and he also found that the ratio of the two specific heats increased when the pressure is augmented from 10 to 100 atm. both at 0° and at −78·5°, and attains a maximum value at −120°, as indicated in Table XI.

The ratio of the two specific heats and molecular weights.—The numbers in Table XI mean that if the ratio of the two specific heats of a gas be about 1·6, the gas will usually have one atom per molecule; with a ratio about 1·4, two atoms per molecule; and with a ratio of about 1·3, three atoms per molecule. The kinetic theory would have no explanation to offer if the value of γ were greater than $1\frac{2}{3}$; but no cases are known. There are a number of discrepancies. This must be expected owing to differences in molecular attraction, tendencies to polymerization, dissociation, etc., which affect the value of ϵ. The coloured gases—chlorine, bromine, iodine, and iodine chloride, with two atoms per molecule—give lower values than is usually obtained with the colourless diatomic molecules; and gases which are readily condensed to liquids give rather lower values than those less readily liquefied. Hence, **if the ratio of the two specific heats of a gas falls into one of these groups—1·6, 1·4, 1·3—this fact may be taken as circumstantial evidence, but not conclusive proof, that the molecule has a corresponding number of atoms per molecule.** There is, however, no unimpeachable relation connecting the specific heat of a complex molecule with the *number* of the constituent atoms which is independent of their nature. The ratio of the two specific heats of argon and the inert gases appears to be about 1·6, and hence it is supposed that the molecules of these gases are monatomic, like mercury. This means that the density ($H=2$), the molecular weight, and the atomic weight will probably have the same numerical value. Hence, the determination of the ratio of the two specific heats provides an independent method of ascertaining the number of atoms in the molecules of a gas without reference to the compounds of the element. In the case of mercury, the monatomicity of the gas has been established altogether apart from this reasoning.

TABLE XI.—THE EFFECTS OF TEMPERATURE AND PRESSURE ON THE RATIO OF THE TWO SPECIFIC HEATS OF AIR.

Temperature.	10	30	60	100
− 0°	1·43	1·44	1·53	1·60
− 60°	1·42	1·49	1·58	1·72
−100°	1·44	1·53	1·71	2·10
−120°	**1·45**	**1·56**	**1·79**	—
−140°	1·38	1·46	1·54	1·80

This subject cannot be passed by without bringing a weak step in the above reasoning into prominence. The low molecular heats of the inert gases are assumed to prove that these gases have one-atom molecules. But it is easy to see that **if little or no heat is expended in doing internal work when the temperature of a gas is raised, a gas with polyatomic molecules might be reported to have monatomic molecules.** Unlike mercury, the inert gases do not form chemical compounds, and hence the number of atoms in the molecule cannot be determined by the usual methods based upon Avogadro's hypothesis. The inference that the molecules of the inert gases are monatomic involves an assumption which is less readily granted than is the case with mercury, cadmium, etc., because these elements form volatile compounds which enable their atomic weights to be evaluated. Hydrogen at very low temperatures behaves in this respect like a monatomic gas.

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§ 10. The Relation between the Two Specific Heats of a Gas and the Degree of Freedom of its Molecules

> Invisible movements, invisible particles—these and kindred assumptions have supplied the window through which the human mind has sought to spy into the inner machinery of phenomena.—T. GOMPERZ (1912).

R. Clausius [1] has shown that a value for the total heat energy contained in a gas can be obtained by assuming that the gas has been brought into its present condition by being warmed at constant volume from absolute zero to the temperature T. The density D of the gas represents the mass of the gas, and, if C_v be the specific heat at constant volume assumed for convenience not to vary with temperature, the total heat energy of the gas will be C_vDT. From (5), § 2, the kinetic energy of the translatory motions of the molecules of a gas is $\frac{3}{2}p$, a magnitude which also increases proportionally with the absolute temperature. The ratio of the total heat energy to the total kinetic energy is therefore a constant independent of temperature—provided C_v is independent of the temperature. Both magnitudes are proportional to the density D of the gas, and accordingly, the kinetic energy of the molecules of a perfect gas stands in a constant ratio to the total energy of the gas. From J. R. Mayer's equation, the kinetic energy of translatory motion is $\frac{3}{2}p=\frac{3}{2}(C_p-C_v)DT$, and accordingly, the ratio of the two forms of energy is :

$$\frac{\text{Energy of translatory motion}}{\text{Total energy}}=\frac{3(\gamma-1)}{2} \quad . \quad . \quad . \quad (3)$$

which shows that the ratio of these two forms of energy is determined by the two specific heats.

The kinetic energy of the molecules of a gas is supposed to be divided between the kinetic energy of the translatory motions, and of the various rotatory motions of the molecules. The former is sometimes called the external, and the latter the internal energy of the gas. During a collision there is probably a rapid exchange of kinetic energy between the external and internal motions. There are probably also elastic vibratory internal motions which are scarcely affected by molecular collisions, although a gain or loss of this form of internal energy may become appreciable after countless collisions. The vibratory energy may be dissipated as radiant heat, etc., and if the gas were not exposed to an external source of energy, it would be cooled by the loss of radiant vibratory energy, since the kinetic energy of the translatory and rotational motions would be gradually transformed into vibrational energy. Conversely, if a gas be exposed to a source of radiant energy, the vibrating motions are accelerated owing to the absorption of vibrational energy, and the energy so gained is but slowly converted into kinetic energy of translatory motion whereby the gas is warmed. The difficulty of heating gases by simple radiation shows that radiant energy is not rapidly absorbed by the molecules of a gas. From equation (3) it follows that if Q be the total energy of a gas, and K the kinetic energy of translatory motion, $Q-K$ represents the internal energy, or the

$$\frac{\text{Internal energy}}{\text{Total energy}}=\frac{3}{2}\left(\frac{5-3\gamma}{3}\right)=\frac{5-3\gamma}{2} \quad . \quad . \quad . \quad (4)$$

The energy of the translatory motions of the molecules has been shown to be equal to $\frac{3}{2}R$. Consequently, the ratio

$$\frac{\text{Internal energy of the molecules}}{\text{Energy of translatory motion}}=\frac{5-3\gamma}{3(\gamma-1)} \quad . \quad . \quad (5)$$

The constancy of the ratio γ for certain gases thus shows that the ratio of the internal or vibratory energy to the energy of translatory motion is likewise constant for these gases at ordinary temperatures ; or the internal energy of a gas is proportional to the kinetic energy of the gas.[2] The ratio of the vibratory to the translatory energy increases with the number of atoms in the molecule. With monatomic gases this ratio (5) is zero, and Table XII shows the value of the ratios (3) and (5) for a number of other gases as well as for ratio (5) divided by the number of atoms in the molecule.

TABLE XII.—MOLECULAR AND ATOMIC ENERGIES.

	$\frac{C_p}{C_v}=\gamma$	$\frac{\text{Kinetic energy}}{\text{Total energy}}$	$\frac{\text{Internal energy}}{\text{Kinetic energy}}$	$\frac{\text{Internal energy}}{\text{Kinetic energy}}$ per atom.
Oxygen	1·403	0·604	0·656	0·328
Nitrogen	1·405	0·607	0·646	0·323
Hydrogen	1·394	0·591	0·692	0·346
Carbon monoxide, 0°	1·403	0·605	0·653	0·327
Carbon monoxide, 100°	1·397	0·595	0·679	0·340
Nitric oxide	1·394	0·591	0·692	0·346
Hydrogen chloride	1·392	0·586	0·706	0·353
Chlorine iodide, ClI	1·317	0·475	1·103	0·551
Chlorine	1·323	0·485	1·064	0·532
Iodine	1·294	0·441	1·268	0·634
Carbon dioxide	1·300	0·449	1·226	0·409
Nitrous oxide	1·270	0·405	1·469	0·490
Water vapour, 103°	1·277	0·415	1·407	0·469
Ammonia	1·262	0·393	1·543	0·386
Methane	1·316	0·474	1·110	0·222
Ethylene	1·243	0·364	1·740	0·291
Ethylchloride	1·126	0·189	4·300	0·537
Ethylether	1·029	0·043	22·200	1·480

For moderate temperatures, the ratio of the molecular and atomic energies is nearly constant for diatomic molecules, but varies with temperature and other circumstances for more complex molecules. While the ratio of the two specific heats usually decreases a little with a rise of temperature, the ratio between the internal and kinetic energies, per atom, increases with a rise of temperature, and this increase appears to be the greater, the larger the number of atoms per molecule. This has been explained by assuming that some of the energy is consumed in work against the chemical affinity which hold the atoms of the molecule together.

In his *Ueber Molekularphysik* (Königsberg, 1888), F. Lindemann [3] assumes that the development of heat during chemical action consists merely in the transfer of the internal vibratory energy into translatory energy so that the products of the action possess less internal energy than before. If this be true, the internal vibratory energy of the initial products of the reaction between, say, hydrogen and chlorine must be enormously greater than the translatory energy, because of the great development of heat which occurs, and this is quite incompatible with the observed ratios of the two specific heats of the gases. Attempts [4] to correlate the specific heat ratio with the numbers of atoms in the molecule have not been very successful. J. C. Maxwell [5] sought a relation between the ratio of the two specific heats and the number of ways a system of particles is movable—*Beweglichkeitsarten*—or the so-called number of degrees of freedom of the molecules.

Degrees of freedom.—At any instant, the position of a particle compelled to oscillate to and fro on a given *straight line* is completely described by its distance from a fixed point in that line ; if the particle moves in a *plane*, its position will be described by its distance from two intersecting straight lines in that plane ; while if the particle moves in *space*, its position can be described by its distance from three fixed intersecting planes. In the first case, the particle is said to have *one degree of freedom* ; in the second, it is said to have *two degrees of freedom*, because two relations are needed to define its position, and each of the two relations can change independently of the other ; in the third case, the particle is said to have *three degrees of freedom*, because three independent relations are needed to define its position. The degree of freedom of an object is the number of facts which must be specified in order to define completely its position or state ; more precisely, **a degree of freedom is an**

independent mode in which the condition or state of a body can be altered. Consequently, the number of degrees of freedom of a particle in space cannot be less than three. If a short straight indefinitely thin rod be substituted for the particle, then, the position of the rod in space can be defined by indicating the distances of the two ends of the rod from the three intersecting planes. Hence, six relations are then used in defining the position of the rod. The rod, it is to be remembered, has a fixed definite length, and one of the six relations can be eliminated because it is related with the other five; as a result, the position of the rod can be completely defined by five independent relations. The rod is therefore said to have five degrees of freedom. If a rigid body, ABC, be fixed in space, its position can be defined by the relations of any three points, taken as the apices of a triangle drawn on the body, to the three intersecting planes of reference. Each point is defined by three relations, making nine in all; but the relation of A to B, of B to C, and of C to A are fixed distances, and hence three of the nine relations are not independent. A rigid body in space has therefore six degrees of freedom. A pair of compasses has seven degrees of freedom, but six if the joint is "ankylosed."

If a molecule has n atoms which have a definite and fixed relation with one another, the number of degrees of freedom cannot exceed $3n$. If a gas has but one atom per molecule, then the molecule will have three degrees of freedom; if two atoms at a fixed distance apart—dumb-bell fashion—five degrees of freedom; and if the atoms are so arranged such that (i) the atoms are at the apices of an imaginary triangle, there will be $3n-3=6$ degrees of freedom; (ii) if the three atoms are situated as if they were in one fixed line, there will be five degrees of freedom; and (iii) if the atoms are fixed so that two of the atoms can oscillate about a central atom, there will be $3n-2=7$ degrees of freedom. For more complex molecules, and for more complex movements, the number of degrees of freedom will be greater. The six degrees of freedom of a rigid body, free to move in space, can be resolved into three translatory movements parallel to three fixed and intersecting planes of reference, and three rotations about the same axes.

The kinetic energy of the translatory motions of the molecules of a gas is measured by the pressure, and is analogous with Helmholtz's free energy. The molecule itself, however, may be a complex system of two or more atoms capable of rotation about their centres of mass; and possibly also each is capable of rotation about its centre of mass; and possibly also each is capable of rotatory motion. The kinetic energy absorbed by the motions of this secondary system is usually called the *internal energy*, and is analogous with Helmholtz's bound energy, although a small proportion of the internal kinetic energy of gases is also vibratory or oscillatory energy.

The ratio of the two specific heats of gases makes it probable that during the collisions between the molecules, there is a constant exchange and re-distribution of the energy between the translatory and the internal energy; but for every gas, a constant ratio is preserved between the two forms of energy, namely, that portion of the energy which is manifested in the translatory motions of the molecules between their encounters, and that portion which is concerned in the rotatory and other motions. The energy distributed between each form of motion probably preserves a constant ratio to the total energy. An important assumption can now be introduced: **During the fortuitous collisions of the molecules of a gas, the total kinetic energy K is divided equally among the n degrees of freedom of the molecules,** so that the kinetic energy of translatory motion for each degree of freedom is $3K/n$; and for monatomic molecules, each with three degrees of freedom, $n=3$, the total kinetic energy is k. This hypothesis is sometimes called **Maxwell's distribution theorem,** because J. C. Maxwell (1859) applied the proposition to systems of rigid particles. L. Boltzmann (1861) extended the principle to particles which were not rigid, but which were regarded as complex systems having great numbers of degrees of freedom, and hence the hypothesis is also called **Maxwell-Boltzmann's distribution theorem.** L. Boltzmann showed that this is the most probable distribution of the energy in an aggregate of a large number of molecules, provided that all the values for the coordinates and corresponding momenta of a single molecule are equally probable. This hypothesis has been the subject of much discussion,[6] and even though the hypothesis is not now considered to be of general application, it has been an important stimulus to investigation.

Since translatory motion involves only three degrees of freedom, it follows from

Maxwell-Boltzmann's theorem, that if a molecule has n degrees of freedom, the *translatory energy* of the molecules of the gas with mean velocity V, will be equal to $3K/n$, where K is the *total kinetic energy* $\frac{1}{2}mNV^2$. Hence, the kinetic energy of the translatory motion can be written $3K/n=\frac{1}{2}mNV^2$, and since the kinetic energy, $pv=\frac{1}{3}mNV^2$, it follows, $\frac{2}{3}(\frac{1}{2}mNV^2)$, or $pv=2K/n$. The work which a gas can do when it expands adiabatically—that is, without receiving or giving out heat—is equal to its total kinetic energy, which in turn is equal to $pv/(\gamma-1)$, where γ represents the ratio of the two specific heats of the gas. Since $K(\gamma-1)=pv$ and $pv=2K/n$, it follows that by substituting for pv,

$$\gamma=1+\frac{2}{n} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This expression enables (i) the ratio of the two specific heats of a gas to be computed when the degree of freedom of the molecules is known; and conversely, (ii) the degree of freedom when the ratio of the two specific heats is known. The simplest possible case of a gas with monatomic molecules, each with three degrees of freedom, furnishes a gas with $\gamma=1\frac{2}{3}$. The value found for mercury by A. Kundt and E. Warburg (1876)[7] is 1·66; and the constant has the same value for members of the argon family. If the three degrees of freedom concerned in the translatory movements of a molecule between each encounter, be deducted from n, the total number of degrees of freedom, then n—3 will represent the number of degrees of freedom of the internal motions. The following table shows the result with a few gases:

TABLE XIII.—RELATION BETWEEN SPECIFIC HEATS AND DEGREES OF FREEDOM OF THE MOLECULES OF SOME GASES.

Gas.	Observed γ	n	n-3
Mercury	1·67	3·00	0·00
Helium	1·65	3·07	0·07
Oxygen	1·40	4·98	1·98
Carbon monoxide	1·41	4·94	1·94
Hydrogen chloride . .	1·39	5·06	2·06
Carbon dioxide	1·30	6·67	3·67
Carbon disulphide . .	1·24	8·40	5·40
Ethane	1·18	11·10	8·10
Carbon tetrachloride . .	1·13	15·40	12·40

With diatomic molecules, $n=5$ and $\gamma=1{\cdot}4$. This corresponds with a molecule whose shape and structure are symmetrical about one axis. Such a molecule would be formed by the union of two spherical atoms, or of two atoms not necessarily spherical, but each spherical about one axis and both axes corresponding with the axes of the molecule. This conclusion agrees with the observed values of γ for oxygen=1·4, as well as for the diatomic gases, nitrogen, hydrogen, carbon monoxide, nitric oxide, and hydrogen chloride. For superheated steam, the observed value of γ is 1·3, which virtually corresponds with a molecule with six degrees of freedom. There are some objections against a rigid application of the hypothesis:

(*a*) Intermolecular attraction has been neglected in developing the theory. With gases like steam, this attraction may reach some magnitude, and it would reduce the specific heat ratio, because instead of n, it would be necessary to substitute $n+d$ in equation (6), where d is a small positive quantity.

(*b*) If some of the molecules of a gas are dissociated, a gas with diatomic molecules would have a value of γ ranging between that appropriate for a diatomic gas with five, and that for a monatomic gas with three degrees of freedom. The gradual rise of the specific heat ratio with temperature also agrees with the assumption that a greater and greater proportion of the molecules decrease in complexity owing to dissociation with rise of temperature. The converse of this applies to molecular aggregation which would give rise to molecules with a more complex structure, and thus increase the value of n and decrease that of γ.

(*c*) If the bond which holds the atoms of a molecule together behaves as if the atoms are held together neither with perfect rigidity nor with perfect freedom, the degrees of freedom may not all have the same value, and moreover another degree of freedom would have to be added for, say, a diatomic molecule in which the atoms do not remain at an invariable distance apart. The comparison of the ratio of the two specific heats for transparent and coloured diatomic gases—Table XIV—shows that the former have values of γ in the neighbourhood of 1·4 corresponding with five degrees of freedom, while with the latter, the value of γ is 1·3, corresponding with seven degrees of freedom, and it is possible that molecular aggregation or the so-called loose-jointing of the molecules accounts for the discrepancy.

TABLE XIV.—COMPARISON OF THE RATIO OF THE SPECIFIC HEATS OF TRANSPARENT AND COLOURED GASES.

Transparent gases.				Coloured gases.			
	γ	n	n-3		γ	n	n-3
Hydrogen . .	1·40	5·0	2·1	Chlorine . .	1·33	6·1	3·1
Hydrogen chloride	1·39	5·1	2·1	Bromine . .	1·29	6·9	3·9
Hydrogen bromide	1·42	4·8	1·8	Iodine . .	1·29	6·9	3·9
Hydrogen iodide .	1·40	5·0	2·0	Iodine monochloride	1·31	6·5	3·5

(*d*) The addition of heat may also set up motions other than those described by the degrees of freedom of the molecules indicated above. Other kinds of motions may be set up by, say, a reaction with the æther as indicated by the emission of radiant energy. Even the atoms of monatomic gases may be capable of internal oscillatory motions as is made probable by the complexity of their spectra; but these motions require so small an expenditure of energy that its amount may be neglected in comparison with the kinetic energy of translatory motion Further, adds O. E. Meyer,[8]

> It does not appear impossible that the ratio $\gamma=1·67$ should be found in the case of chemically compound molecules also, if the connection of the atoms is so firm that internal motions are excluded.

Attempts to connect the values of γ or n with the number of atoms in the molecule have not been successful. A. Naumann (1867)[9] suggested that n—3 is identical with the number of atoms in the molecule; and J. J. Thomson (1893) added that only when the atoms are symmetrically arranged will n—3 be proportional to the number of atoms per molecule. J. W. Capstick (1894-5) found that the *nature* as well as the *number* of atoms is of importance. Thus, with the chloro-derivatives of methane, CH_4, J. W. Capstick found

	CH_4	CH_3Cl	CH_2Cl_2	$CHCl_3$	CCl_4
γ	1·313	1·279	1·219	1·154	1·130
n	6·4	7·2	9·0	13·0	15·4

This shows that the substitution of atoms of chlorine for atoms of hydrogen, step by step, produces a perceptible rise in the value of n, although the number of atoms remains unchanged; and K. Strecker (1881-2) pointed out that while one halogen can replace another in the hydrogen haloids without any change in value of n, the substitution of a second halogen for the hydrogen raises the value of n.

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§ 11. The Molecular Heats of Gases

It follows that if n denotes the number of degrees of freedom per molecule of a gas, and if K denotes the increase in the kinetic energy when the temperature is raised from $T°$ to $T°+1°$, the total increase in the kinetic energy for N molecules will be $\frac{1}{3}nNK$. If C_v denotes the specific heat of a gas, and M the molecular weight, it follows that if the change of temperature be accompanied by no other than a change in the kinetic energy of translatory motion, $\frac{1}{3}nNK=NMC_v$, and hence, $\frac{1}{3}nK=MC_v$. From J. J. Waterston's hypothesis, if two gases be raised through the same range of temperature, the increase in the kinetic energy of each gas will be the same, and remembering that K is a constant, $MC_v=(\frac{1}{3}K)n$, which means that the product of the specific heat and the molecular weight of a gas is proportional to the number of degrees of freedom of its molecules, and equal to the product of the number of degrees of freedom of the molecules of a gas and a constant. The constant K is evaluated by substituting known values of C_v, M, and n in the equation ; and $\frac{1}{3}K$ works out to be very nearly unity, as indicated in Table XV. Accordingly,

$$\text{Molecular heat}=C_vM=n \quad . \quad . \quad . \quad . \quad (7)$$

The degrees of freedom calculated from this equation agree with those obtained for a number of gases in other ways. This relation makes the atomic heats of the monatomic gases equal to 3.

The constancy of the molecular heats over a range of different gases implies that their molecules have the same number of degrees of freedom ; and conversely, the approximate number of degrees of freedom of the molecules of a gas is given by the product of the specific heat and molecular weight. That is, **the molecular heat of a gas is almost numerically equal to the degree of freedom of its molecules,** or about one calorie per degree of freedom. The observed value for all monatomic gases excepting helium agrees with theory. The two-atom molecules with five degrees of freedom seem to behave like a rigid dumb-bell when the gas is heated, in that the possible vibratory motion of two atoms along the line joining them does not appear to represent a degree of freedom, for the motions appear to be distributed solely in two rotational and three translational movements. The results are confirmed by the molecular heats of the diatomic permanent gases. The molecular heats of chlorine and bromine are about a calorie too high for agreement with the hypothesis. This possibly corresponds with to-and-fro vibrations of the atoms along an axis joining the two atoms.

TABLE XV.—RELATION BETWEEN MOLECULAR HEATS AND DEGREES OF FREEDOM.

	Specific heat, C_v	Molecular weight, M	C_vM	Degrees of freedom, n	Constant, $\frac{1}{2}K$
Argon	0·0731	39·92	2·92	3	0·97
Mercury	0·0147	200	2·94	3	1·00
Helium	0·7465	3·96	2·95	3	0·98
Hydrogen. . . .	2·4263	2	4·85	5	0·97
Nitrogen	0·1721	28	4·82	5	0·96
Oxygen	0·1544	32	4·95	5	0·99
Carbon monoxide . .	0·1746	28	4·89	5	0·97
Hydrogen chloride . .	0·1392	36·5	5·08	5	0·95
Nitric oxide, NO . .	0·1650	30	4·95	5	1·01
Chlorine . . .	0·0873	71	6·20	6	1·03
Bromine	0·0428	160	6·84	6	1·14
Iodine	0·0257	254	6·52	6	1·09
Ammonia . . .	0·3803	17	6·46	6	1·08
Carbon dioxide . .	0·1486	44	6·54	7	0·94

L. Boltzmann[1] expresses these results another way, the thermal capacity of a gas is equal to the product of its mass by its specific heat C_v; consequently, if w denotes the atomic weight, *i.e.* the molecular weight of a monatomic gas, the thermal capacity or the atomic heat will be wC_v. It has been shown that the mean kinetic energy of a gram-molecule of a gas is equal to $\frac{3}{2}pv$ or $\frac{3}{2}RT$, and if the gas at $-273°$ has no kinetic energy of translatory motion, the kinetic energy of a gram-molecule of the gas at 0° will be $273\ wC_v=\frac{3}{2}RT$; but $R=2$ cals. nearly; accordingly, the atomic heat of a monatomic gas per 1° will be nearly 3. This agrees with the results in Table X. In raising the temperature of a polyatomic gas from $-273°$ to 0°, intramolecular work may be done. Accordingly, if M denotes the molecular weight of the gas, MC_v will be equal to $\frac{1}{2}R(1+\epsilon)$, where ϵ denotes the fractional part of the kinetic energy which is spent in doing intramolecular work. For a diatomic gas, $\epsilon=\frac{2}{3}$, and $MC_v=5$ nearly, or the atomic heat of a diatomic gas is nearly 2·5; similarly, L. Boltzmann has shown that for triatomic gases, $\epsilon=1$, or $MC_v=6$, or $wC_v=2$ nearly.

The effect of temperature and pressure on molecular heats.—The specific heat of a gas at constant pressure, C_p, increases with a rise of temperature such that the mean specific heat C_p between 0° and $\theta°$ is $C_p=a+b\theta$; or $C_p=a+b\theta+c\theta^2$, where a, b and c are constants. E. Wiedemann's[2] value for carbon dioxide between 0° and 200° is $0·1952+0·000229\theta$; and L. Holborn and F. Henning's value between 0° and 800° is $0·0208+0·0001384\theta+0·00000005\theta^2$. H. V. Regnault thought that pressure had no effect on the thermal capacity of hydrogen, carbon dioxide, etc., but J. Joly and S. Lussana[3] have shown that the specific heat increases with increasing pressure when the temperature is constant. Thus, the value for carbon dioxide increased 38 per cent. when the pressure rose from one atm. to 41 atm. The observed results can be represented by analogous formulæ, $C_p=a+b(p-1)$ or $C_p=a+b(p-1)+c(p-1)^2$. Thus, for carbon dioxide, S. Lussana found that $C_p=0·20130+0·0019199(p-1)$. The specific heat at constant volume varies with temperature and pressure somewhat similarly to the results for the specific heat at constant pressure

W. Nernst's measurements (1911) show that the molecular heat of chlorine rises from 5·85 at 0° to 7·0 as the temperature rises to 1200°, and still another calorie higher at about 2000°. This corresponds with the addition of two new degrees of freedom. The gases with a molecular heat approaching 6 are easily dissociated, and therefore the number of degrees of freedom of molecules whose atoms are joined by strong chemical forces is less than when the atoms are united by weaker forces. The effect of temperature on the molecular heats of a few gases is further illustrated by Table XVI.

TABLE XVI.—THE EFFECT OF TEMPERATURE ON THE MOLECULAR HEATS OF GASES AT CONSTANT VOLUME.

Gas.	Theoretical value for rigid molecules.	Temperature (°C.).					
		0°	100°	300°	500°	1200°	2000°
Argon	3	2·98	2·98	2·98	2·98	2·98	2·98
Hydrogen	5	4·75	4·78	5·02	5·20	5·80	6·50
Nitrogen	5	4·90	4·93	5·17	5·35	6·00	6·70
Steam	6	5·93	5·97	6·45	6·95	8·62	13·10
Carbon dioxide	6	6·80	7·43	8·53	9·43	11·00	11·50
Ammonia	6	6·62	6·82	7·41	8·52	—	—

Similar values were obtained for oxygen, hydrogen chloride, and carbon monoxide as those indicated in the table for nitrogen; and sulphur dioxide furnished numbers similar to those for carbon dioxide. According to A. Eucken (1912),[4] the molecular heat of hydrogen falls from 5 to 3 calories as the temperature falls to —213°, and diatomic gas then behaves as if it were monatomic. At still lower temperatures, —238°, the molecular heat of hydrogen and helium at constant volume fall still lower than 3. M. Trautz (1913) has shown that the molecular heat at constant pressure decreases as the temperature diminishes from 20° to —180°. For instance,

	Nitrogen.	Carbon monoxide.	Oxygen.	Hydrogen.	Helium.
18° to 20°	6·983	7·006	6·980	6·860	4·993
—180° to —181°	7·162	7·244	7·300	5·330	4·934

The molecular heat of helium thus exhibits a positive temperature coefficient, whereas, if helium were a monatomic gas, and nothing has been overlooked, its molecular heat should not be affected by variations of temperature. The decrease with hydrogen at low temperatures is explained by M. Trautz (1913) by assuming that the hydrogen is converted into another modification with the properties of a monatomic gas whereby it loses one or more degrees of freedom. A. H. Compton (1915) made a similar assumption for solids.

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§ 12. The Specific Heats of Elementary Solids—Dulong and Petit's Rule

> Les atomes de tous les corps simples ont exactement la même capacité pour la chaleur.
> —P. L. DULONG and A. T. PETIT (1819).

In 1819, P. L. Dulong and A. T. Petit published an account of their *Recherches sur quelques points importants de la théorie de la chaleur ;* [1] they found that while different substances have different capacities for heat, the atomic heats of nearly all the elements then known were the same. **Atomic heat** is a convenient term for the thermal capacity of a gram atom of an element ; it is the product of the specific heat and the atomic weight of the element. P. L. Dulong and A. T. Petit determined the specific heats of different solid elements, at constant pressure, and obtained this remarkable result : **The product of the atomic weight and the specific heat of an element has nearly always the same numerical value—Dulong and Petit's rule.** This means that the atomic heats or the thermal capacity of the atoms of the elements are approximately the same ; it requires the same amount of heat to raise every atom, no matter of what kind, one degree of temperature. The relation is usually expressed :

Atomic heat, $Cw=6$ approximately . . . (8)

where w denotes the atomic weight of the element, and C its specific heat—at constant pressure. The rule is remarkably near the truth for the solid elements at ordinary temperatures, but it fails with the gaseous elements and a very small number of solid elements. In illustration, a few examples selected at random from a list containing nearly 50 elements for which data are available, are indicated in Table XVII.

TABLE XVII.—ATOMIC HEAT OF ELEMENTS.

Element.	Specific heat.	Atomic weight.	Atomic heat.
Lithium	0·9408	6·94	6·53
Silver	0·0559	107·88	6·03
Gold	0·0304	197·2	6·25
Copper	0·0923	63·57	5·88
Bismuth	0·0305	208·0	6·34
Lead	0·0315	207·10	6·52
Aluminium . . .	0·2143	27·1	5·81
Iron	0·1098	55·85	6·12
Uranium . . .	0·0277	238·5	6·61

H. V. Regnault extended and confirmed P. L. Dulong and A. T. Petit's observation. The average value of the constant is 6·36 or 6·4. The atomic weights range from 6·94 to 238·5. and yet, when multiplied by the respective specific heats, the products are nearly constant. Rigorous agreement cannot be expected. The divergencies are too large to be accounted for by the inevitable errors of observation involved in measuring the specific heats, but the very irregularity of the divergencies leads to the view that Dulong and Petit's law approximates to a truth, and that the observed differences are due to disturbing effects which are not functions of the atomic weight. According to H. Kopp (1865) the atomic heats (determined indirectly) of the following elements in the solid state are exceptionally low :

	O	H	F	B	C	Si	S	P
Atomic heat . .	4·0	2·3	5·0	2·7	1·8	3·8	5·4	5·4

Beryllium also gives a low value. The atomic heats of the other forty elements examined by H. Kopp were nearly all in the vicinity of 6. **The elements with exceptionally low atomic heats usually form gaseous or readily volatile compounds,**

and they have small atomic weights. Of these, those which exhibit the greatest deviation usually have the smallest atomic weights, while those with the largest atomic weights approximate most nearly to the normal value. Magnesium and aluminium have small atomic weights, and though their atomic heats are considered to be normal, they are on the low side. Sodium and lithium are exceptional in possessing low atomic weights and normal atomic heats.

Attempts have been made to explain the divergencies (i) as a result of the fact that the temperatures at which the specific heats have been determined stand in a different relation to their fusion temperatures. Lead, for instance, at the temperature of boiling water, is much nearer its fusion temperature (327°) than iron is to its fusion temperature (1530°); but in the case of many elements, the specific heat does not change very much with changes of temperature not far removed from atmospheric. Another explanation assumes (ii) that the divergencies are due to differences in the configuration or orientation of the molecules or atoms of the solid elements. According to F. Richarz,[2] the fact that solid bodies with low atomic volumes—beryllium, boron, and carbon—have low values for the atomic heats shows that, on a rising temperature, the displacement of the atoms, relatively to their mutual distances apart, is large. This would make the thermal capacities of these elements more sensitive to changes of temperature than when the displacements are relatively small. This is also confirmed by the observation that the allotropic forms of an element with the smaller atomic volume or the larger specific heat have the lowest specific gravity.

The influence of pressure on atomic heats.—Measurements of the specific heats of solids, C_p, are made at a constant pressure, and the results are probably not very different from the specific heat, C_v, at constant volume at very low temperatures, but at higher temperatures the difference is significant. For instance, the observed value of C_p for silver at 100° K. is 4·86, the computed value for C_v is 4·72; and at 589° K., C_p is likewise 6·64, and C_v is 5·92. As in the case of gases, the difference between the two depends upon the amount of work required to compress the heated solid back to the volume it occupied before it was heated.

The internal energy U of compressed gases, or the heat developed during expansion without doing external work has an appreciable value, and is usually negative, and when work W is done against an external pressure p, during an expansion from a volume v_1 to v_2, $W=(v_2-v_1)p$, and, regarding the volume as constant, $dW=(v_2-v_1)dp$. Consequently, the heat Q developed during the change, follows from Helmholtz's equation, $Q=W-U=(v_2-v_1)T.dp/dT$; and the heat dQ developed during an infinitesimal change, $v_2-v_1=dv$, will be $dQ=T(dp/dT)dv$, or

$$\left(\frac{dQ}{dv}\right)_T=T\left(\frac{dp}{dT}\right)_v \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Again,[3] by the partial differentiation of Q, p, v, and T,

$$dQ=\left(\frac{dQ}{dT}\right)_v dT+\left(\frac{dQ}{dv}\right)_v dv\text{; or, }\left(\frac{dQ}{dT}\right)_p=\left(\frac{dQ}{dT}\right)_v+\left(\frac{dQ}{dv}\right)_v\frac{dv}{dT}$$

These results obtain as a purely mathematical operation like multiplication or division, and altogether apart from any meaning the symbols may have. Since dQ/dT denotes the specific heat at constant pressure or constant volume,

$$C_p-C_v=\frac{dQ}{dv}\cdot\frac{dv}{dT}\text{; or, }C_p-C_v=T\left(\frac{dp}{dT}\right)_v\frac{dv}{dT} \quad . \quad . \quad (10)$$

by substituting for dQ/dv from equation (9). E. H. Amagat applied this relation to his data on highly compressed gases, and his results with carbon dioxide at 50° are shown in Table XVIII.

TABLE XVIII.—VALUES OF $\frac{dp}{dT}\cdot\frac{dv}{dT}$ FOR CARBON DIOXIDE.

Pressure.	$\frac{dp}{dT}$	$\frac{dv}{dT}$	$\frac{dp}{dT}\cdot\frac{dv}{dT}$
50	0·265	0·0001300	0·1353
60	0·370	0·0001250	0·1815
70	0·505	0·0001428	0·2831
80	0·689	0·0001687	0·4563
90	0·960	0·0002133	0·8040
100	1·460	0·0002020	1·1105

The numbers in the last column have been divided by the mechanical equivalent of heat to convert them into gram-calories. On multiplying and dividing the right member of (10) by v_0dv, it furnishes

$$C_p-C_v=T\frac{v_0\left(\frac{1}{v_0}\cdot\frac{dv}{dT}\right)^2}{-\frac{1}{v_0}\frac{dv}{dp}} \quad . \quad . \quad . \quad . \quad (10)$$

where the coefficient of cubical expansion, $3a=dv/v_0dT$; and the compressibility, $\beta=-dv/v_0dp$, and v_0 is the volume in c.c. at 0°. These equations have been employed by M. Margules (1888), E. H. Amagat (1896), E. Grüneisen (1906), and others.[4] The preceding discussion reduces to

$$C_p-C_v=\frac{(3a)^2}{\beta}v_0T \quad . \quad . \quad . \quad . \quad . \quad (11)$$

which is a well-known relation in thermodynamics. All the magnitudes—specific heat at constant pressure, C_p; coefficient of linear expansion, a; the volume at 0°, v_0; and the coefficient of compressibility, β—, can be determined experimentally. If C_p and C_v represent the corresponding atomic heats, v_0 will represent the atomic volume; and if the unit of pressure be megadynes per sq. cm., and the unit volume is 1 c.c., the calculated values of C_p and C_v will be in mega-ergs per degree. Since $41·82\times10^6$ ergs, or 41·82 mega-ergs are equivalent to one calorie,

$$C_p-C_v=\frac{(3a)^2}{\beta}Tv_0 \text{ mega-ergs}; \quad C_p-C_v=\frac{(3a)^2v_0T}{41·82\beta} \text{ cals.}$$

The data in Table XIX were compiled by G. N. Lewis, and they show that within the limits of experimental error, the atomic heats of these elements at constant volume and 20°, are the same for all the solid elements whose atomic weights are greater than potassium. The mean of these values of the atomic heats at constant pressure (Dulong and Petit's constant) is 6·2, and at constant volume 5·9. The average deviation for the former is 0·26, and excluding the first four elements, 0·18; the average deviation for the latter is 0·15, or, excluding the first four elements, 0·09. F. Bürki found that the differences C_p-C_v for chemically related elements are nearly the same; and that for the halides of the elements of group I. in the periodic table, the requirements of H. Kopp's rule are more nearly fulfilled by C_p than by C_v.

When the coefficients of compressibility and of cubical expansion at the desired temperature are not known, the empirical expression of E. Grüneisen, $C_v=C_p-0·0214C_p^2T/T_m$, can be used when T_m denotes the melting point of the solid. Here v_0/β of (28) is assumed to be constant, and a^2 to be proportional to the atomic heat. Still further, the empirical expression of A. Magnus and F. A. Lindemann,[5] $C_v-C_p-aT^{\frac{3}{2}}$, gives results of sufficient accuracy for many purposes. The constant a is evaluated by putting $C_v=3R$ at sufficiently high temperatures.

The influence of temperature on atomic heats.—Silicon, boron, beryllium, and carbon at ordinary temperatures, have atomic heats represented respectively by 3·8, 2·7, 3·4, and 1·8. From the point of view of Dulong and Petit's rule, these numbers are low. H. F. Weber (1874) found that the atomic heats of carbon, boron, and silicon approximate closer and closer to the normal value, the higher the temperature; and A. G. Worthing has shown that the atomic heat of carbon rises to $wC_p=5{\cdot}35$ at 1200° K., and to 6·05 at 2000° K. L. F. Nilson and O. Pettersson (1880), and T. S. Humpidge (1886) obtained a similar conclusion for beryllium.[6] This is illustrated by the diagram, Fig. 7, which represents the effect of a rising temperature on the atomic heats of the elements in question. The specific heats of these elements increase with temperature until a point is reached at which they are nearly constant. W. A. Tilden's examination of the influence of temperature on atomic heats led him to conclude that *there is no one condition or set of conditions under which Dulong and Petit's rule is true for all the elements.* If carbon, boron, silicon, and beryllium be regarded as exceptional, the mean specific heats between 0° and 100° may be arbitrarily selected as a standard for the best results. E. H. and E. Griffiths suggest that the empirical relation $Cw^{0\cdot95}=4{\cdot}804$ fits the specific heats of the metals at 0° better than Dulong and Petit's rule; and by extrapolation, they infer that the atomic heats of the elements at absolute zero will have the mean value 4·813, but this induction does not fit the facts. There does not appear to be a true upper limiting value in the sense indicated by Dulong and Petit's rule, for several substances possess greater atomic heats even at 1000°; for example, A. G. Worthing has shown that while the atomic heat of tungsten at constant volume is 5·95 at moderate temperatures, the value is 6·25 at 1200° K., and 7·35 at 2400° K. As a rule the temperatures at which the elements exhibit the same atomic heats decrease as the atomic weights increase.

TABLE XIX.—THE TWO ATOMIC HEATS OF THE ELEMENTS AT 20°.

Element.	Atomic weight.	Atomic volumes, V_0	$3\alpha\times10^6$	$\beta\times10^6$	C_p-C_v	C_p	C_v
Sodium . .	23·0	23·7	15·4	72	0·5	6·9	6·4
Magnesium .	24·32	13·3	2·7	25	0·2	6·0	5·8
Aluminium .	27·1	10·1	1·3	23	0·2	5·8	5·6
Potassium .	39·1	45·5	31·5	83	0·6	7·1	6·5
Iron . .	55·84	7·1	0·40	10	0·1	6·0	5·9
Nickel . .	58·68	6·7	0·27	13	0·2	6·1	5·9
Copper . .	63·57	7·1	0·54	16	0·2	5·8	5·6
Zinc . .	65·37	9·5	1·5	29	0·3	6·0	5·7
Palladium .	106·7	9·3	0·38	11	0·2	6·1	5·9
Silver . .	107·88	10·3	0·84	19	0·3	6·1	5·8
Cadmium .	112·40	13·0	1·9	28	0·3	6·2	5·9
Tin . .	118·7	16·2	1·7	22	0·3	6·4	6·1
Antimony .	120·2	17·9	2·2	11	0·1	6·0	5·9
Iodine . .	126·92	25·7	13·0	84	0·9	6·9	6·0
Platinum .	195·2	9·1	0·21	9	0·2	6·1	5·9
Gold . .	197·2	10·2	0·47	14	0·3	6·2	5·9
Thallium .	204·0	17·2	2·6	28	0·3	6·4	6·1
Lead . .	207·2	18·2	2·2	29	0·4	6·3	5·9
Bismuth .	208·0	21·2	2·8	13	0·1	6·3	6·2

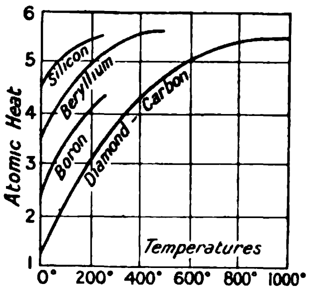

FIG. 7.—Atomic Heat Curves of Beryllium, Boron, Carbon, and Silicon.

U. Behn[7] (1898) found that there is a decrease in the atomic heats with falling temperatures, so that when the observed results are plotted, the curves appear as if they would intersect at low temperatures, but T. W. Richards and F. G. Jackson determined the specific heats of many elements between the temperature of liquid air and ordinary atmospheric temperatures, and found that with the exception of the elements of low atomic weight, they conform to Dulong and Petit's rule. Further observations[8] by W. Nernst and his co-workers, J. Dewar and H. K. Onnes, have confirmed Behn's conclusion; for while **the atomic heats of the elements with abnormally low values increase approximately to about the theoretical value with a rise of temperature, the atomic heats of all the elements converge towards zero as the temperature approaches absolute zero.** For instance, with silver:

Temperature .	−238°	−228°	−196°	−173°	−73°	−58°	−30·6°
Atomic heat .	1·58	2·47	4·07	4·86	5·78	6·01	6·64

The results with carbon (diamond), aluminium, and lead are illustrated by the graphs in the diagram, Fig. 8. H. K. Onnes and G. Holst found that the specific heat of mercury is 0·00142 between 4·26° K. and 6·48° K., and 0·000534 between 2·93° K. and 3·97° K. J. Dewar's determinations of the specific heats of fifty-three elements at temperatures between the boiling points of hydrogen and nitrogen when plotted with the atomic weights, gave a periodic curve closely resembling the atomic volume curve of L. Meyer; the specific heats at ordinary temperatures give a hyperbolic not a periodic curve—Fig. 5, Cap. VI.

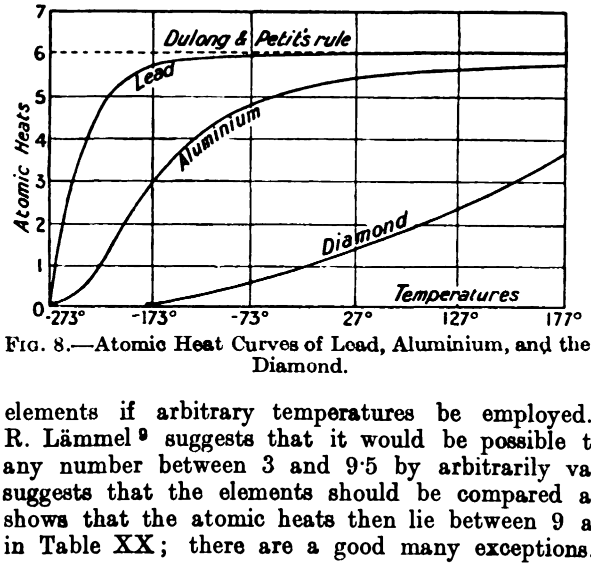

FIG. 8.—Atomic Heat Curves of Lead, Aluminium, and the Diamond.

These results make it clear that Dulong and Petit's rule is a limiting rule to which these elements approximate when the temperature is high enough, but, in virtue of the marked relation between the thermal capacity and temperature, Dulong and Petit's constant can be obtained for diverse elements if arbitrary temperatures be employed. By the same procedure, R. Lämmel[9] suggests that it would be possible to use for the atomic heat any number between 3 and 9·5 by arbitrarily varying the temperature. He suggests that the elements should be compared at their melting points and shows that the atomic heats then lie between 9 and 10 calories as indicated in Table XX; there are a good many exceptions. As a matter of fact, the

TABLE XX.—ATOMIC HEATS OF THE ELEMENTS AT THEIR MELTING POINTS.

Elements.	Atomic weight.	Melting point, T_m.	Specific heat at T_m.	Atomic heat.
Lithium . . .	7	190°	1·3	9·45
Aluminium . .	27	700°	0·35	9·45
Sodium . . .	23	100°	0·36	8·28
Sulphur . . .	32	120°	0·25	8·00
Copper . . .	64	1100°	0·145	9·28
Nickel . . .	59	1600°	0·166	9·79
Zinc . . .	65	420°	0·142	9·23
Bromine . . .	80	7°	0·114	9·12
Silver . . .	108	1040°	0·082	8·87
Cadmium . . .	112	315°	0·066	7·39
Lead . . .	207	330°	0·0413	8·55

atomic heat indicates how rapidly heat, dQ/dT, is added per atom per degree rise of temperature, and a high value for this constant means that the potential energy of the molecules is being rapidly increased, possibly owing to the dissociation or approaching dissociation of complex into simpler molecules. At low temperatures where the specific heats are small, S. Pagliani (1915) has pointed out that the atomic heats of the elements at a given temperature, tend to increase with increasing atomic weight; and this is not the case at temperatures near atmospheric. The temperatures at which different elements show the same atomic heats decrease as the atomic weights become larger, presumably because usually the larger the atomic weight of the element the less is the strength of the union between the atoms.

The influence of the state of aggregation on atomic heats.—According to the kinetic theory, the heat required to raise the temperature of a body is spent (1) in raising the kinetic energy of the molecules; (2) in raising the kinetic energy of the constituent atoms—*e.g.* in doing chemical work, etc.; (3) in increasing the volume of the body against atmospheric pressure; (4) in overcoming molecular attractions, etc. The coefficient of thermal expansion of solids is small, and therefore also the work of expansion of solids against atmospheric pressure is small, but the work done against molecular cohesive forces is probably large with liquids and solids. This is illustrated by the comparative large difference in the specific heats of solid, liquid, and gaseous elements. As a rule, the specific heat of a substance in the gaseous state is less than it is in the liquid state. Thus, the specific heat of liquid alcohol is 0·5475 and for the vapour 0·4534: for ether, the numbers are respectively 0·5290 and 0·4797. The atomic heat of solid iodine is 6·9, and of the gas, 3·3; liquid bromine, 8·56, and bromine gas, 4·7. There are exceptions—for instance, the specific heat of ice is 0·500, liquid water, 1·000, and steam, 0·477; the specific heat of solid mercury is 0·0314, of the liquid, 0·0333, and of the vapour, 0·0147; the numbers for liquid and solid tin are 0·0637 and 0·0559, and for liquid and solid lead, 0·0470 and 0·0314 respectively. H. Mache[10] has worked out a demonstration that the thermal capacity of a liquid ought to be nearly double the true thermal capacity of its vapour, so that if C_v is the true thermal capacity of a vapour, the value for the corresponding liquid should be $2C_v$. This applies to a number of liquids and gases. According to J. D. van der Waals' theory, the specific heat at constant volume of any unassociated substance would be the same in the liquid and gaseous states of aggregation, but the deduction has not been tested experimentally.

The discontinuity in the atomic heat of metals at their melting point is usually positive, but, according to I. Iitaka, the magnitude is generally smaller than corresponds with the energy of one degree of freedom, *i.e.* 1 cal. In the case of lead and tin, the change is negative. In the case of these metals, therefore, it seems very probable that the molecules are not free to rotate during melting, or at least that the rotation of the molecules in the liquid state does not increase with the rise of temperature, *i.e.* these metals are to be considered as monatomic, even in the liquid state.

The difference in the specific heats of liquid and solid may not be solely determined by differences in the states of aggregation, because during the transition, the molecules may become more or less complex. This is known to be very probably the case with water. Variations in the complexity of the molecules of an element in one state of aggregation may determine differences in the atomic heats. Thus H. V. Regnault (1866)[11] found the specific heat of amorphous carbon to be 0·2609; graphitic carbon, 0·2000; and the diamond, 0·1470. R. Bunsen also found the specific heat of ordinary tin to be 0·0559 and of allotropic tin, 0·0545. No difference was observed between the specific heats of aragonite and calcite. According to F. Richarz (1893), with carbon, silicon, boron, phosphorus, sulphur, arsenic, selenium, tellurium, and tin, **the allotropic modification of an element with the smaller specific gravity has the larger specific heat—Richarz's rule**; otherwise expressed, the modification with the smaller atomic volume has the smaller specific heat. Illustrations in support of this rule are indicated in Table XXI.

TABLE XXI.—EFFECT OF SPECIFIC GRAVITY ON SPECIFIC HEAT.

Element.	Specific gravity.	Specific heat.
Carbon (diamond)	3·52	0·113 (10°)
Carbon (graphite)	2·25	0·160 (10°)
Carbon (retort)	1·89	0·204 (68°)
Boron (crystalline)	2·49	0·165 (21°)
Boron (amorphous)	2·45	0·307 (100°)
Phosphorus (red)	3·30	0·183 (51°)
Phosphorus (yellow)	1·83	0·202 (36°)
Arsenic (grey)	5·87	0·082 (100°)
Arsenic (black)	4·78	0·086 (100°)
Sulphur (rhombic)	2·06	0·173 (54°)
Sulphur (monoclinic)	1·96	0·181 (52°)
Sulphur (amorphous insoluble)	1·89	0·190 (53°)
Sulphur (amorphous soluble)	1·86	0·248 (50°)
Selenium (crystalline)	4·80	0·084 (62°)
Selenium (amorphous)	4·30	0·113 (57°)
Tellurium (crystalline)	6·30	0·048 (100°)
Tellurium (amorphous)	6·00	0·053 (100°)
Tin (white)	7·30	0·054 (21°)
Tin (grey)	5·85	0·059 (18°)

O. Richter (1913) found F. Richarz's rule applicable to binary alloys of lead and bismuth, and bismuth and tin, excepting for alloys in the vicinity of BiPb, where it is assumed the formation of the compound BiPb renders the rule inapplicable. Similar differences have been noticed with the specific heats of metals in different physical conditions—*e.g.* according to H. V. Regnault (1843), the specific heat of hard tempered steel is 0·1175, and of soft tempered steel, 0·1165; while hard bronze has a specific heat 0·0858, soft bronze has a specific heat 0·0862. Consequently, it must be inferred that the heat does important work other than merely raising the kinetic energy or temperature of the molecules; and it therefore appears strange that the relation pointed out by Dulong and Petit does not exhibit greater divergencies.

The rectification of atomic weights by Dulong and Petit's rule : $Cw = 6{\cdot}0$ to $6{\cdot}4$, where w denotes the atomic weight of the element. It will be obvious that if the specific heat of an element be known, it is possible to compute an approximate value for the atomic weight. The number so obtained may be useful in deciding between two numbers which are multiples of a common factor. The method is obviously only applicable to elements whose specific heat can be determined. In view of the variation of specific heats with temperature, the usual application of this law to the rectification of atomic weights "is a rough empirical rule, which, setting aside silicon, boron, beryllium, and carbon, is only available when the specific heats have been determined at temperatures, usually and most conveniently, between 0° and 100°." The specific heat method of fixing the atomic weights is not so much used as formerly, because so many other methods which are more exact are available.

EXAMPLES.—(1) What is the atomic weight of silver assuming that the specific heat is 0·0559? Here, $6{\cdot}0 \div 0{\cdot}0559 = 108$ nearly. This is close to the accepted value for the atomic weight of this element.

(2) Platinum chloride, on analysis, furnished 35·5 grams of chlorine per 48·6 grams of platinum. The specific heat of platinum is 0·0324, and the atomic weight is approximately $6{\cdot}0 \div 0{\cdot}0324 = 197$ nearly. Hence, since $197{\cdot}5 \div 48{\cdot}6 = 4$ nearly, it follows that if the atomic weight of chlorine is 35·5, the atomic weight of platinum must be nearly $48{\cdot}6 \times 4 = 194$.

(3) When indium was first discovered, the analysis of its chloride furnished indium, 37·8; chlorine, 35·5. The equivalent of indium is therefore 37·8. The formula of the

chlorine was thought to be $InCl_2$, and the atomic weight was accordingly represented 75·6. The specific heat of the metal was found to be 0·057. Hence, $75·6 \times 0·057 = 4·5$. If 75·6 be the correct atomic weight, the product would approximate more closely to 6, and hence it was inferred that 75·6 is not the correct atomic weight of indium; rather does the atomic weight approximate to $6 \div 0·057 = 112$ nearly. If $InCl_3$ be the formula of the chloride, the atomic weight will be $37·8 \times 3 = 113·4$, which is the number usually adopted for the atomic weight of this element.

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§ 13. Molecular Heats—Neumann's and Joule's Rules

Es verhalten sich bei chemisch ähnlich zusammengesetzten Stoffen die specifischen Wärmen ungekehrt, wie die stöchiometrischen Quantitäten.—F. E. NEUMANN (1831).

The **molecular heat**, or thermal capacity of the molecules of a substance, is defined as the product of its specific heat and its molecular weight. The molecular weight of but few solids are known, and the simplest formula consistent with the valency of the component elements is provisionally regarded as representing the molecule. In the course of his *Untersuchungen über die specifische Wärme der Mineralien*,[1] in 1831, F. E. Neumann noticed that **the product of the specific heats and the molecular weights of compounds of similar composition is nearly constant—Neumann's rule.** This was confirmed by H. V. Regnault in 1841. Two illustrations of Neumann's rule for molecular heats are indicated in Table XXII.

If *R* represents the symbol of the basic element, with the RO-oxides, the constant is 11·0; with the RO_2-oxides, 14·0; with the RO_3-oxides, 18·8; with the R_2O_3-oxides, 26·9; with the RS-sulphides, 11·9; and 18·1 with the RS_2-sulphides; with the RCl-chlorides, the constant is 12·75; and 18·7 with the RCl_2-chlorides. With the RCO_3-carbonates, the constant is 21·4; and 29·1 with the R_2CO_3-carbonates. With RSO_4-sulphates the constant is 25·4; with the R_2SO_4-sulphates, 32·9; with the RNO_3-nitrates, 24·0; and with the $R(NO_3)_2$-nitrates, 38·2.

TABLE XXII.—MOLECULAR HEATS OF SOLIDS.

Carbonates.	Mol. wt.	Sp. heat.	Mol. heat.	Chloride.	Mol. wt.	Sp. heat.	Mol. heat.
$CaCO_3$	100·09	0·206	20·6	$BaCl_2$	208·29	0·090	18·7
$SrCO_3$	147·62	0·145	21·3	$SrCl_2$	158·54	0·120	19·0
$BaCO_3$	197·37	0·109	21·4	$PbCl_2$	277·02	0·066	18·3
$PbCO_3$	277·02	0·080	21·3	$HgCl_2$	270·92	0·069	19·2

J. P. Joule, in 1844, brought forward some evidence indicating that **the molecular heat of a solid compound is approximately the sum of the atomic heats of the constituent elements—Joule's rule.** Consequently, if M and C_p respectively denote the molecular weight and specific heat of the compound; $m_1, m_2, m_3, \ldots$ the atomic weights of the constituent elements; $c_1, c_2, c_3, \ldots$ the specific heats, and $n_1, n_2, n_3 \ldots$ the number of atoms of the respective elements,

$$\text{Molecular heat, } MC_p = n_1m_1c_1 + n_2m_2c_2 + n_3m_3c_3 + \ldots$$

This rule is sometimes called *Woestyn's rule*, after A. C. Woestyn (1848), and *Kopp's rule*, after H. Kopp (1865), since they each expressed the same idea by saying that **each element has the same atomic heat in compounds as it has in the free state,** so that if $a_1, a_2, a_3, \ldots$ denote the atomic heats of the respective elements,

$$\text{Molecular heat} = n_1a_1 + n_2a_2 + n_3a_3 + \ldots$$

or, if 6·4 be the atomic heat of each element, and the compound contains n atoms, the molecular heat of the compound will be approximately $6·4n$. Otherwise expressed, **the quotient obtained by dividing the molecular heat of a compound by the number of elementary atoms in one molecule is approximately equal to 6·4.** This rule was also favoured by J. J. J. Garnier and S. Cannizzaro; but H. Kopp showed that it is not universally applicable. Hydrogen, nitrogen, oxygen, fluorine, and chlorine give discordant results. There is obviously a difficulty with the carbonates. This may possibly be connected with the difficulty previously found for carbon. In the case of the lighter elements the atomic heats must be taken less than 6·4. Some atomic heats of the elements when in combination have been previously indicated. Further, if the atomic heats of all but one of the elements in a compound be known, the unknown atomic heat can be computed; thus, the atomic heat of chlorine in lead chloride is $\frac{1}{2}(18·3-6·4)=5·95$. A comparison of the results of experiment with calculations based upon Neumann's and Joule's laws is indicated in Table XXIII.

TABLE XXIII.—MOLECULAR HEATS OF SOLIDS.

Compound.	Formula.	Sp. heat.	Mol. weight.	Molecular heat.	
				Observed.	Calculated.
Mercuric chloride	$HgCl_2$	0·0689	270·92	18·67	18
Mercuric iodide	HgI_2	0·0420	253·84	19·06	18
Mercurous chloride	HgCl	0·0520	235·46	12·25	12
Mercurous iodide	HgI	0·0385	326·92	12·91	12

W. A. Tilden found the specific heats of solids show variations with temperature analogous to those exhibited by the elements; but in general, the molecular heat of a compound or alloy did not differ greatly from the sum of the atomic heats of the component at the same temperature. S. Meyer[2] has drawn attention to the fact that the additive law of mixtures is more nearly followed with molecular heats than it is with molecular volumes. A. Winkelmann found the additive law applicable to glasses; H. V. Regnault, R. Durrer, W. Spring, and L. Schüz applied it to alloys; and P. Bachmetjeff and M. Wascharoff, to amalgams. According to W. Spring, the additive rule fails with alloys of tin and lead. M. Trautz found that in the majority of cases the additive rule with the internal atomic heats, $C_v-\frac{3}{2}R$, either holds good exactly, or very approximately. J. J. J. Garnier confirmed the additive rule for hydrated salts on the assumption that the combined water has nearly the same thermal capacity as solid ice, 9·85 cals. per gram-molecule of H_2O. There are many discrepancies, as might be expected, and for the reasons stated in connection with the atomic heats of the elements.

EXAMPLES.—(1) Calculate the specific heat of solid oxygen given the specific heat of potassium chlorate, $KClO_3$, 0·194; and that of potassium chloride, 0·171. Here the molecular heat of potassium chlorate (molecular weight × specific heat) is 25·7; and of potassium chloride, 12·8. The difference $25·7-12·8=12·9$ represents the molecular heat of O_3, hence the atomic heat of oxygen will be $\frac{1}{3}$ of $12·9=4·3$. By definition, atomic weight × specific heat of solid = atomic heat of solid = 4·3. Hence, the specific heat of solid oxygen will be $4·3\div16=0·27$.

(2) The specific heat of silver chloride is 0·0911 and that of silver, 0·057: assuming the atomic weight of silver to be 107·9, what is the specific heat of solid chlorine? The molecular heat of silver chloride is 13·1, and the atomic heat of silver is 6·2. The difference $13·1-6·2=6·9$ represents the atomic heat of solid chlorine. The specific heat of solid chlorine is therefore $6·9\div107·9=0·064$.

The molecular heats can be employed to rectify the atomic weights of elements which do not form volatile compounds. Thus, the analyses of mercurous and mercuric salts indicate that the atomic weight of mercury may be 100, 200, . . . If the atomic weight be 100, the formula of mercurous chloride will be Hg_2Cl, and of mercuric chloride, HgCl; while if the atomic weight be 200, the formulæ will be those indicated in the above table. There are some discrepancies as is illustrated by the fact that E. Donath (1788) deduced the value 120 for the atomic weight of uranium from the specific heat of uranoso-uranic oxide, where C. Zimmermann's value (1881), from the observed specific heat of the metal, was twice E. Donath's value—viz. 240.

EXAMPLES.—(1) The analysis of barium chloride furnishes 35·5 parts of chlorine per 68·7 parts of barium. The specific heat of barium is 0·0465. What is the atomic weight of barium, when the atomic weight of chlorine is 35·5? The formula of barium chloride may be written Ba_xCl, where x is to be determined. The atomic weight of barium, by Dulong and Petit's rule, will be of the order $6·4\div0·0465=137$. Taking 35·5 as the atomic weight of chlorine, the fraction x must be of the order $68·7\div137=\frac{1}{2}$. Hence the formula of barium chloride is $Ba_{\frac{1}{2}}Cl$, that is, $BaCl_2$, or some multiple of this. Hence the atomic weight of barium (chlorine, 35·5) must be $2\times68·7=137·4$.

(2) The percentage composition of platinum chloride is: Platinum, 57·7; chlorine, 42·3. The specific heat of platinum is 0·0324. What is the atomic weight of platinum? Hint, see (2) in the last but one set of examples. The ratio of the constituent elements is as 48·6 : 35·5; the atomic weight is of the order 197·5; the ratio x is nearly $\frac{1}{4}$; and hence the formula of the chloride is $PtCl_4$ or some multiple of this. Hence, assuming the atomic weight of chlorine is 35·5, the atomic weight of platinum will be $4\times48·6=194·4$.

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§ 14. The Meaning of Dulong and Petit's Rule

The fact that the atomic heats of all elements are approximately the same, led Dulong and Petit to infer that **the thermal capacity of all atoms is the same.** This means that every atom of a solid—no matter of what kind—requires the same amount of heat to raise its temperature 1°. J. P. Joule's rule means that **each elementary atom retains the same capacity for heat when it is combined as it had when free.** The number and kind of other atoms present and their mode of combination seem to have no influence on the numerical value of this property. The observations of Neumann and Joule indicate that **the constituent atoms of a solid compound behave as if the solid were a mechanical mixture of its component atoms, and each atom were free to vibrate independently of the others.**[1]

According to the kinetic theory, temperature is proportional to the kinetic energy of the molecules; and consequently, Dulong and Petit's rule points to a similar relation. It must be added that we can form no real conception of the "temperature of an atom" or of the "temperature of a molecule." All our conceptions of temperature are based on the properties of atoms and of molecules *en masse*. R. Clausius [2] supposes the specific heat of an element to be made up of two magnitudes (i) the heat c_v required to raise the kinetic energy of the molecules; and (ii) the heat ϵ required to perform internal work. Clausius calls c_v the true specific heat of the solid. Hence if M be the atomic weight of an element, the observed atomic heat MC is equal to $M(c_v+\epsilon)$. It is often stated that at the absolute zero of temperature, $-273°$, all atomic motion must cease. This is a mere assertion, of no intrinsic value, and probably wrong. The statement *might* be true of the translatory motion of the molecules—such that R. Clausius' Mc_v is zero —because of the convergence of the specific heats of the elements to zero as the temperature approaches absolute zero. The same fact also shows that the internal work ϵ becomes very small at absolute zero, and the fact that Dulong and Petit's rule is so nearly exact at ordinary temperatures coupled with the assumption that at the same temperature the kinetic energy of the molecules is the same, leads to the inference that when the temperature of elementary solids is raised from absolute zero, the internal work per atom is approximately the same.

W. Jankowsky [3] argued that the heat of a chemical reaction is developed for the most part by the conversion of potential energy into heat, and that at the absolute zero, the energy content of a substance is entirely potential, and that there must be an absolute upper limit or maximum temperature where the energy content of a substance consists entirely of heat.

Among the evidence which indicates that the atoms of a solid even at absolute zero, probably oscillate about a position of equilibrium, the following may be cited: (i) The low coefficient of thermal expansion of solids shows that the volume would be very little changed if the solids were cooled to absolute zero; (ii) it is not probable that solids would lose their compressibility at absolute zero; (iii) the natural frequency of the vibrations of the atoms of a solid calculated by different methods shows no signs of ceasing at absolute zero. (iv) *P. Debye's effect*, in which the intensity of the higher orders of the X-ray spectrum of crystalline solids increases as the temperature of the crystal is lowered, points in the same direction.

L. Boltzmann, in a paper *Ueber die Natur der Gasmoleküle* (1876), has shown that

the kinetic and potential energies of the molecules of a monatomic solid vibrating about a position of equilibrium are equal in magnitude. Consequently, the total energy of a vibrating system—called for convenience an *oscillator*—is shared equally between the average kinetic and potential energies, and is twice the value of either alone.[4]

This interesting result follows by considering the motion of a particle under the influence of a central attractive force moving on an orbit about its position of equilibrium. If the particle were at rest in any part of its orbit, it would tend to move to its centre of attraction, and in so doing, would acquire such a velocity that its kinetic energy would be the same as it possessed when oscillating in its former orbit. Hence, a particle oscillating about a centre of rest possesses both kinetic and potential energy, and on the average, the one is equal to the other, provided that the time average of its kinetic energy is equal to that of the potential energy. This is the case if the potential energy is zero as the particle passes through its position of equilibrium. In reality, the equipartition theorem applies only to the kinetic energy, but if the average kinetic and potential energies are equal, each will make the same contribution to the specific heat.

L. Boltzmann assumed that the atoms of a solid have natural periods of vibration, so that if a monatomic gas be in contact with a solid, the bombardment of the gaseous molecules produces a state of thermal equilibrium when the mean kinetic energy of vibratory motion of the atoms of the solid is equal to the mean kinetic energy of the translatory motions of the molecules of the gas. With a solid, the average kinetic energy of the atoms in each state will be the same; but the average kinetic energy per atom of a monatomic gas is $\frac{3}{2}KT$ per atom, hence, the sum of the kinetic and potential energy of the solid will be $2\times\frac{3}{2}KT$, or $3KT$ per atom; and if there are N atoms in a gram-atom of the solid, the total kinetic and potential energy will be $3NKT$ or $3RT$ per gram-atom, where $NK=R$ is nearly equivalent to two calories per gram-atom per degree. Accordingly, the atomic heat, wC_v, must be $3R=6$ nearly, or with a more exact value of R, 5·95. This interesting argument shows how the atomic heats of the monatomic solids are nearly twice the molecular heats of the monatomic gases; and it furnishes a brilliant deduction of Dulong and Petit's rule for solids.

The agreement between the result of Boltzmann's assumption and Dulong and Petit's observation, shows that the atoms of a monatomic solid probably vibrate so that their energy is equally divided between the kinetic and potential energy. If the oscillations of the atoms are not harmonic in character, the time averages of the kinetic and potential energies will not generally be equal. The agreement in question also shows that the opposing forces—attraction and repulsion—between the atoms just balance one another so that as two atoms approach one another the attractive forces gradually diminish, and the repulsive forces gradually increase until the latter predominate.

The discrepancies between Boltzmann's $3R$ and Dulong and Petit's constant.—There must be a flaw somewhere, because the theory does not explain (i) how the solid elements with a low atomic heat—carbon, silicon, and boron—have normal atomic heats at high enough temperatures; nor (ii) how all solids give abnormally low values at low temperatures. Many attempts have been made to explain the discrepancy between theory and fact. It may be necessary to consider:

(*a*) *The time required for the atoms to adjust themselves to a change of temperature.*—L. Boltzmann assumed that the atoms take a long time to adjust themselves to the temperature—but no corresponding variation of specific heat with temperature has been detected; and the specific heats of solids are so related with the melting points that if the specific heat changed with time, the melting point ought likewise to change. Such a phenomenon has not been observed even in the case of artificial minerals and natural minerals formed æons ago. While the translational energy may be rapidly distributed between the internal motions of a molecule during a collision, yet, if the distribution is slow, so that it becomes appreciable only after millions of collisions, the number of collisions per second is so great—a million occurs in about one-seven-thousandth of a second according to G. J. Stoney—that even when the exchange is slow, a second of time is a comparatively long interval.

(*b*) *The oscillations of the atoms are not harmonic.*—L. Boltzmann assumes that the vibrations of the atoms is harmonic; and this assumption is probably valid for most metals far from their melting points; but if the amplitudes of the vibrations of the atoms are large, oscillations may be no longer harmonic. I. Langmuir[5] has emphasized the fact that if the oscillations of the atoms are not harmonic, the time averages of the kinetic and potential energies will not be equal. The average kinetic and potential energies will be equal, only when the motion is harmonic, in which case, the restoring force acting on the atom is proportional to the displacement from the position of equilibrium. If the restoring force increases more slowly than the displacement, the potential energy will be greater than the kinetic, and from the principle of equipartition, the atomic heat will be greater than $3R$; conversely, if the restoring force increases more rapidly than the displacement, the atomic heat will be less than $3R$. The remarkable closeness of the atomic heats of the elements to the value $3R$, is taken to show that the forces to which the atoms of a solid are subjected vary approximately with the displacement of the atoms from their position of equilibrium.

There must then be both attractive and repulsive forces acting between the atoms. On the average, these opposing forces must just balance each other. As one atom approaches another the repulsive force must *gradually* increase and the attractive force decrease until the repulsive force greatly predominates. We cannot consider that the repulsive forces in solids are exerted only during collisions between atoms, for under these conditions there would be no potential energy and the atomic heat would be $\frac{3}{2}R$.

(*c*) *The congealing of molecules to more rigid systems.*—R. A. Millikan (1912)[6] considers that it may possibly be assumed that as the temperature is reduced, the atoms of the solid are frozen, so to speak, into rigid systems of continually increasing size—where each system is endowed with the kinetic energy of agitation appropriate to its temperature—before absolute zero is attained, it might be possible for the total energy of the whole mass to become that of a single molecule of the surrounding gas. C. Benedicks (1913) has also shown that the equipartition law is avoided by assuming that the solids are not always monatomic, but at low temperature form atomic complexes, which change the number of degrees of freedom. The equipartition law applies only to free atoms. However, from Joule's law, it appears probable that the rule for atomic heats applies to atoms in combination as well as free.

(*d*) Another explanation of the reduction in the atomic heats below $3R$ when the temperature is low was suggested by A. Einstein (1907). It is based on the so-called quantum theory of energy; and has been remarkably successful.

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§ 15. The Quantum Theory of Energy and Dulong and Petit's Rule

> An observer who does not allow himself to be led in his work by any hypothesis, however cautious and provisional, renounces beforehand all deeper understanding of his own results.—M. Planck (1914).
>
> An attempt to imagine a universe in which action is atomic leaves the mind in a hopeless state of confusion.—J. H. Jeans (1914).

J. H. Jeans, in his *The Dynamical Theory of Gases* (Cambridge, 1904), shows that Maxwell-Boltzmann's theorem of the equipartition of energy is based upon the assumption that there is no interaction between matter and æther, whereas every ray of light which reaches the eye is evidence against the truth of the assumption. With ordinary diatomic transparent gases two (rotational) degrees of freedom appear to be directly affected by the translational motions during a collision; with the coloured gases there appear to be motions which consume energy in the production of æthereal vibrations. In 1906, M. Planck, in his *Vorlesungen über Theorie der Wärmestrahlung* (Leipzig, 1906), assumed that the interchange of energy between the æther and a vibrating atom is not a continuous process, but takes place *per saltum*—that is, discontinuously—by jumps in definite amounts $h\nu$, where ν represents the *Schwingungszahl* or the frequency of the atomic vibrations, and h is a universal constant in the same sense that e, the unit of electrical change, is a universal constant. The constant h—called **Planck's constant**—seems to be a fundamental unit which regulates and controls the ceaseless ebb and flow of energy in the world of matter. For brevity, write $\epsilon = h\nu$. This means that for any given temperature, a certain amount of energy is associated with the vibrating atom, and that this amount is a function of the vibration-frequency ν of the atom; and energy can be absorbed or emitted by a vibrating system spasmodically, and only in amounts ϵ or in integral multiples of this magnitude such as $\epsilon, 2\epsilon, 3\epsilon, \ldots$, but not in intermediate quantities, say, $\frac{1}{4}\epsilon, \frac{1}{2}\epsilon, \frac{3}{4}\epsilon, \ldots$ This virtually means, said H. Poincaré (1911),[1] that a physical system can exist only in a finite number of states, it leaps from one of these states to another without passing through a continuous series of intermediate states; and, adds M. Planck:[2]

> The continuity of all dynamical effects was formerly taken for granted as the basis of all physical theories and in close correspondence with Aristotle, was condensed in the well-known dogma—*natura non facit saltus*—nature makes no leaps. However, present-day investigation has made a considerable breach even in this venerable stronghold of physical science. This time it is the principle of thermodynamics with which that theorem has been brought into collision by new facts, and unless all signs are misleading, the days of its validity are numbered. Nature does indeed seem to make jumps—and very extraordinary ones.

The ration or unit of energy ϵ is called a **quantum**, and hence this hypothesis is called the **quantum theory of energy.** According to this remarkable hypothesis, the vibrating atoms radiate definite loads $h\nu$ of energy which, for any given vibration frequency, ν, are indivisible. M. Planck inferred that the average energy ϵ possessed by an oscillating unit, with two degrees of freedom,

$$\text{Average energy} = \frac{h\nu}{e^{\frac{h\nu}{kT}}-1}\text{; or, Average energy} = \frac{h\nu}{e^{u}-1} \quad . \quad . \quad (12)$$

per degree of freedom; and three times this value for a monatomic oscillator with three degrees of freedom instead of the average value $3kT$ per atom deduced by an application of Maxwell-Boltzmann's theorem which assumes that the evolution or absorption of energy is a continuous process. Here u is written in place of the fraction $h\nu/kT$.

M. Planck follows the theory of probability in deducing his formula; D. L. Chapman starts from J. H. van't Hoff's well-known expression $Q/RT^2 = (d \log k)/dT$. From the quantum law, if the resonators of vibration period ν are attached to the molecules of a gas, then there will be vibrators possessing amounts of energy 0, $h\nu$, $2h\nu$, . . . , but no vibrators with intermediate amounts of energy. Let the number of vibrators with 0, $h\nu$, $2h\nu$, . . . amounts of energy be respectively $n_0, n_1, n_2, \ldots n_m$. Then, from J. H. van't Hoff's rule, $mh\nu dT/kT^2=d \log (n_m/n_0)$, and by integration between T and ∞, and writing u in place of $h\nu/kT$, it follows that $n_m=n_0e^{-mu}$. Consequently, the mean energy of a vibrator is $(h\nu e^{-u}+2h\nu e^{-2u}+3h\nu e^{-3u}+ \ldots)/(1+e^{-u}+e^{-2u}+ \ldots)$, which, by division, reduces to (30) above. It might also be added that F. R. von Bichowsky[3] has shown that (i) Planck's radiation law, (ii) the quantum theory, and (iii) the equipartition law are not independent, because if any two be assumed the third will follow; and further, S. Ratnowsky has shown that if J. W. Gibb's assumption (that the free energy of a system cannot be generated until the magnitude of the co-ordinates fixing the energy of the system has reached a certain value, and is thereafter given off continuously) be made, Planck's radiation law follows directly without the assumption of the quantum hypothesis. Other attempts to establish a theory of radiation without quanta have been made by M. Brillouin, A. Byk, H. L. Callendar, and R. C. Tolman.

In one modification of the hypothesis, the oscillator is supposed to absorb energy continuously until an amount $h\nu$ has been absorbed, when it has a chance of emitting the whole of this unit. Otherwise, energy will continue being absorbed until it reaches $2h\nu$, $3h\nu$, . . . Only when the amount of energy reaches an exact multiple of $h\nu$ is the oscillator in a condition to emit the whole of its energy.[4]

It is an open question what are the receptacles of energy in a solid. As H. A. Lorentz (1913)[5] has shown, the phenomena of light make it highly probable that energy quanta can have no individual and permanent existence in the æther, and cannot be regarded as accumulations of energy in minute spaces travelling about with the velocity of light. It seems more probable that the energy of solids is localized in the elastic vibrations of the solid, and that the mean energy of an oscillator is equal to the mean energy of an æther vibration of the same frequency. No reason can be assigned why the electric charge e always acts as if it were atomic, or why electrons, each with a fractional charge—say, $\frac{1}{2}e$—do not exist; so also no reason can be assigned why energy can change only by complete quanta.

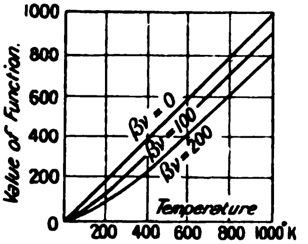

FIG. 9.—Values of the Function $\beta\nu/(e^u-1)$ at Different Temperatures.

In 1907, A. Einstein,[6] in his paper *Die Plancksche Theorie der Strahlung und die Theorie der spezifischen Wärme*, extended Planck's atomic theory of radiation to the radiation of heat. He assumed that the longer heat waves emitted and absorbed by solids are due to vibrations of the constituent atoms about a mean position of rest. A. Einstein further assumed that the energy of the solid does not reside solely in the kinetic energy of the atoms, but the vibration-frequency ν of each atom has three degrees of freedom, and the energy of these vibrations is governed by M. Planck's law, and A. Einstein thus deduced a formula analogous with that of M. Planck:

$$\text{Average energy} = 3R\frac{\beta\nu}{e^u-1} \quad . \quad . \quad . \quad . \quad (13)$$

for the energy of the vibrating atoms of a solid. If $\beta\nu$ is very small, the function is approximately $3RT$, and the expression corresponds with Dulong and Petit's law, which requires the atomic heat of monatomic solids to be proportional to the temperature. For all other values of $\beta\nu$ the function is less than $3RT$. The values of the function are plotted in Fig. 9. At any given temperature, the value of the function differs more and more from the value of T as the value of $\beta\nu$ is increased. Differentiating for dE/dT, the atomic heat, C_v, he obtained:

$$\text{Atomic heat} = 3R\frac{u^2e^u}{(e^u-1)^2} \quad . \quad . \quad . \quad . \quad (14)$$

where u, for convenience, has been written in place of $\beta\nu/T$, and β is written in place of h/k; k is the atomic gas constant represented by R/N, when R is the ordinary gas constant, and N (approximately $6·06\times10^{23}$) denotes the number of atoms per gram-atom. It will be evident that when the fraction $u=\beta\nu/T$ is very large, ν will either be very large, or T very small, and C_v will be virtually zero; and when u is small, $C_v=3R$. For example, if $\beta\nu/T$ be greater than 10, $C_v=3R\times0·004$; and if it be less than unity, C_v will be less than $3R\times0·92$. In the former case, the specific heat approaches unity, and in the latter case, C_v is nearly normal.

The numerical values of the constants *h* and *β*.—Seven different lines of argument [7] show that Planck's constant h, is equivalent to $(6·5543\pm0·0025)\times10^{-27}$ ergs per second, and is the same for all substances. For the yellow D-sodium line with a wave-length $0·5896\mu$, it follows that ν is $3\times10^{10}/0·5896\times10^{-4}$ or $5·088\times10^{14}$, so that $h\nu$ for this radiation is $6·62\times10^{-27}\times5·088\times10^{14}=33·7\times10^{-13}$ ergs per second. The numerical value of β is $4·865\times10^{-11}$.

W. Nernst and F. A. Lindemann (1911) [8] have shown that Einstein's equation is in fair agreement with their observations of specific heats at low temperatures, although discrepancies appear as the temperatures approach absolute zero; and they tried to rectify Einstein's equation by introducing a new term. So that the atomic heat C_v becomes

$$\text{Atomic heat}=\frac{3}{2}R\frac{u^2c^u}{(e^u-1)^2}+\frac{(\frac{1}{2}u)^2e^{\frac{1}{2}u}}{(e^{\frac{1}{2}u}-1)^2}\quad.\quad.\quad.\quad(15)$$

on the assumption that the solid is a mixture of oscillating atoms half of which have the vibration frequency ν and half the frequency $\frac{1}{2}\nu$. M. Planck and A. Einstein assumed that all the oscillating atoms had a frequency ν; and W. Nernst and F. A. Lindemann's assumption is a first approximation to a summation extending over an infinite number of values of ν. W. Nernst and F. A. Lindemann's equation represents the observed atomic heats of solids—aluminium, copper, silver, lead, mercury, zinc, iodine, and the diamond—down to the lowest temperatures. A few numbers selected from Nernst's tables for silver and the diamond are indicated in Table XXIV.

TABLE XXIV.—THE ATOMIC HEATS OF SILVER AND THE DIAMOND AT DIFFERENT TEMPERATURES.

Silver. $\beta\nu=221$.			Diamond. $\beta\nu=1940$.		
Temperatures.	C_p (calc.).	C_p (obs.).	Temperatures.	C_p (calc.).	C_p (obs.).
35·0	1·59	1·58	30	0·00	0·00
53·8	2·98	2·90	92	0·01	0·03
100	4·77	4·86	205	0·62	0·62
200	5·77	5·78	243	0·97	0·95
273	6·02	6·00	306	1·59	1·58
331	6·12	6·01	358	2·08	2·12
535	6·45	6·46	413	2·55	2·66
589	6·57	6·64	1169	5·41	5·45

According to the form of quantum hypothesis now under consideration, oscillating atoms cannot absorb energy unless it comes to them with a certain degree of intensity equal to $h\nu$, or some whole multiple thereof. As the temperature rises, the number of molecules which take up loads of energy from the low intensity heat waves increases rapidly in accord with the equipartition law, and the need for absorbing energy in integral multiples of $h\nu$. Molecules of chlorine and bromine begin to absorb this energy at a lower temperature than the transparent diatomic gases because (i) the bond of union between the respective atoms is weak, and their frequency ν—and consequently also their quantum $h\nu$—is small; hence (ii) the quanta or loads of energy $h\nu$ absorbed by these oscillators are correspondingly small; and (iii) the temperature at which the kinetic energy of the diatomic oscillators attain the value $h\nu$ is correspondingly low. Diatomic hydrogen molecules at a low temperature act like monatomic molecules because the rotatory motions at any given temperature correspond with a definite frequency ν, and when the energy of impact falls below this value of $h\nu$, no energy can go into these rotations, and energy is solely distributed among the three degrees of freedom corresponding with translatory motion.

The quantum hypothesis gives a qualitative explanation: (i) how the atomic heats of the elements approach zero as the temperature falls, and (ii) how abnormally low values appear at a higher temperature with the elements of low atomic weight. From measurements of atomic heats, it seems as if, as the temperature rises, different kinds of atoms can take on their normal load at different stages, the heaviest atoms take it on first, the lighter atoms last. With a given rise of temperature there is a corresponding increase in the vibratory energy of the atoms of an element, and at a sufficiently low temeprature, only a definite fraction of the atoms can take on the normal quota $h\nu$. The higher the vibration frequency ν, the higher the temperature at which energy can be absorbed. Again, other things being equal, with a falling temperature, the greater the vibration frequency ν, the sooner will atomic heats lower than $3R=6$ calories begin to appear.

Observations do not agree with the assumption that at absolute zero the atoms of hydrogen have no latent energy. Consequently, A. Einstein and O. Stern (1913)[9] have examined the hypothesis that the rotating molecules have $\frac{1}{2}h\nu$ units of energy at the absolute zero, and instead of M. Planck's expression (30), they write:

$$\text{Average energy} = \frac{h\nu}{e^u-1} - \frac{h\nu}{2} \quad . \quad . \quad . \quad . \quad (16)$$

The photoelectric effect and the emission of electrons by the action of the X-rays are also in accord with the assumption that the latent energy of the electrons on a metal is $\frac{1}{2}h\nu$ per degree of freedom. The average energy plotted according to the equipartition law, where the average energy $=kT$ per degree of freedom, is shown by the curve I, Fig. 10; according to M. Planck's formula (30), by II, Fig. 10, and according to A. Einstein and O. Stern's formula (35), by III, Fig. 10. The formula for the specific heats of gases at different temperatures derived by differentiating the above formula, agrees well with A. Eucken's observations. It might be added, however, that P. Ehrenfest (1913) obtained almost as good an agreement without their assumption. W. H. Keesom (1913) applied an argument similar to that used by P. Debye, and deduced a formula for the specific heats of gases similar to that obtained for solids. It was found generally that while the rate at which the specific heat (or the energy per degree) decreases to zero as the temperature is lowered, the total energy does not necessarily become zero at absolute zero—rather does there exist at this low temperature a latent energy whose magnitude is $\frac{1}{2}h\nu$.

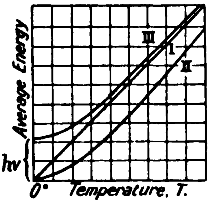

FIG. 10.—The Effect of Temperature on the Energy of Solids.

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§ 16. Debye's Theory of Atomic or Specific Heats

The final object of mathematical research is a knowledge of the principles of science. —K. WEIERSTRASS.

In the solution of mathematical problems, the object of which is to represent the progress of nature, we are led by very rapid methods to results which are often overlooked, and which now and then excite our surprise by the paradoxical form in which they are presented; but when guided by simple reasoning, we return step by step over the course which was so quickly bridged by calculation, we end by perceiving the action of the principles which have given birth to these results.—R. J. HAÜY (1822).

In a paper, *Zur Theorie der spezifischen Wärmen*, P. Debye (1912)[1] argued that the whole heat energy of a solid resides in the energy of the vibrations of the constituent atoms, and that each vibration has exactly the energy allotted to it by the quantum theory, and therefore the heat vibrations are the same as light vibrations of identical frequency. He supposes that it is not likely there is only one value for the vibration frequency of an oscillating atom, and that it is more probable that a whole series of values of ν exists. It is, however, necessary to postulate an upper limit to the range of vibration frequencies, and P. Debye assumes that the number of frequencies for N atoms per unit volume cannot exceed $3N$. At the higher temperatures, where each frequency has the same average energy kT—corresponding with both kinetic and potential energy—the total energy will be $3NkT$ corresponding with Dulong and Petit's law. As the temperature is lowered, the average energy with the higher frequencies is less than with the lower frequencies, so that, when the temperature is low enough, only those atoms having vibrations of very low frequency, with $h\nu$ small, can obtain enough energy to vibrate. These low frequencies must correspond with ordinary sound vibrations, and accordingly, P. Debye identifies the thermal oscillations of the atoms with the elastic vibrations of the solid, and he shows that the maximum frequency ν for monatomic solids can be calculated from the elastic constants of the material. P. Debye utilized the quantum hypothesis and deduced an expression for the average energy of the individual frequencies:

$$\text{Atomic energy}=9R\int_0^{\frac{x}{T}} T\left(\frac{T}{x}\right)\frac{u^3du}{e^u-1}$$

By differentiating this expression for the atomic heat, C_v at constant volume, he obtained the

$$\text{Atomic heat}=3R\left\{12\left(\frac{T}{x}\right)^3\int_0^{\frac{x}{T}}\frac{u^3du}{e^u-1}-\frac{3\frac{x}{T}}{e^{\frac{x}{T}}-1}\right\}\quad . \quad . \quad (17)$$

where u is put in place of $h\nu/kT$, and x in place of $\beta\nu=h\nu/k$, so that $x/T=u$. P. Debye called x the *characteristic temperature* of the particular solid, or it can be called **Debye's constant.** Debye shows how the numerical value of x can be calculated from the elastic constants of the solid. This equation is taken to mean that **the atomic heat of a monatomic solid is a function of the ratio x/T, where x is a characteristic temperature for each substance, and is dependent upon its density and elastic constants.** The above expression cannot be integrated, but P. Debye has shown that it can be reduced to W. Nernst and F. A. Lindemann's formula by a series of approximations. At very high temperatures, when the value of x becomes very small, and the value of T/x is large, the value of the expression in brackets approximates to unity; and the atomic heat reduces to $3R$. P. Debye's equation is more complicated than the empirical relation of W. Nernst and F. A. Lindemann, but the latter is a good approximation to P. Debye's at low temperatures. For low values of T/x, P. Debye's constant x is large, and the atomic heat C_v then approximates to

$$\text{Atomic heat}=3R\times 77{\cdot}94\left(\frac{T}{x}\right)^3 \quad . \quad . \quad . \quad . \quad (18)$$

meaning that **at sufficiently low temperatures, the atomic heat varies as the third power of the absolute temperature**; or by integration, the total energy of monatomic solids near absolute zero is proportional to the fourth power of the absolute temperature. This agrees with the radiation law deduced by J. Stefan in 1879, and somewhat later by L. Boltzmann. These investigators showed that the total energy radiated by a black body is $5{\cdot}7\times10^{-5}(T^4-T_0{}^4)$ ergs per sq. cm. per second, when T represents the absolute temperature of the radiator and T_0 the absolute temperature of the body receiving the radiation.

Working from A. Einstein's (1911) relation between the elastic constants of a solid and the vibration-frequency of its atoms, P. Debye (1913) has shown that the characteristic temperature x can be calculated from the formula

$$x=35{\cdot}74\times10^{-4}w^{-\frac{1}{3}}D^{-\frac{1}{6}}\kappa^{-\frac{1}{2}}F^{-\frac{1}{3}} \quad . \quad . \quad . \quad . \quad (19)$$

where κ is the compressibility coefficient; D, the density; w, the atomic weight; and F is a function of the coefficient of linear expansion a such that

$$F=2\left(\frac{2(1+a)}{3(1-2a)}\right)^{\frac{3}{2}}+\left(\frac{1+a}{3(1-a)}\right)^{\frac{3}{2}} \quad . \quad . \quad . \quad . \quad (20)$$

Some data given by P. Debye are indicated in Table XXV. E. H. and E. Griffiths [2] found P. Debye's formula to be more accurate than any other existing

TABLE XXV.—DEBYE'S CONSTANTS.

	m	D	$\kappa\times10^{12}$	F	x
Aluminium .	27·1	2·71	1·36	10·2	399
Copper . .	63·6	8·96	0·74	10·5	329
Silver . .	107·9	10·53	0·92	15·4	212
Gold . . .	197·2	19·21	0·60	24·7	166
Nickel . .	58·7	8·81	0·57	7·38	435
Iron . .	55·9	7·85	0·62	5·86	467
Cadmium . .	112·4	8·63	2·4	7·89	168
Tin . . .	119·0	7·28	1·9	8·50	185
Lead . .	207·1	11·32	2·0	61·0	172
Bismuth . .	208·0	9·78	3·2	8·98	111
Palladium . .	106·7	11·96	0·57	18·8	204
Platinum . .	195·0	21·39	0·40	17·1	226

expression for reproducing their observations of the specific heats between −165° and atm. temperatures, although here, systematic divergences occur at the higher temperatures. In general, observations of the specific heats of various metals at low temperatures agree remarkably well with the values computed from Debye's formula, even though the elastic constants for evaluating $\beta\nu$ have been determined at room temperatures. According to W. H. Keesom and H. K. Onnes (1914), the specific heat of copper is 0·0396 at —258·49°; 0·1155 at —252·89°; 0·2340 at —246·63°; and 0·8700 at —232·78°, and therefore decreases more rapidly on a falling temperature than it should do according to P. Debye's third-power law.

The curve for aluminium calculated from P. Debye's formula is indicated in the diagram, Fig. 11, where the circles represent the observed specific heats. A. Eucken and F. Schwers (1913) found that Debye's third-power law holds very well for the minerals fluorspar and pyrite from about —260° to about 187°. The application of the quantum theory to the explanation of low temperature specific heats by A. Einstein and by W. Nernst and F. A. Lindemann can be regarded as preparatory to that of P. Debye. H. von Jüptner and E. Rasch[3] have suggested simpler formulæ for the change in the specific heats of solids with temperature which gave very good results, but they have no known theoretical foundation. J. H. Jeans (1914) considers that both from its complete naturalness and from its agreement with experiment, P. Debye's treatment of the specific heats of solids seems destined to be final.

Various attempts have been made to improve Debye's theory. For example, M. Born and T. von Kármán (1912), and H. Thirring (1913),[4] assume that the atoms are arranged in the solid like a space-lattice. There are probably motions of the atoms or molecules other than vibratory and translatory movements which contribute something to the specific heat. For instance, (i) the subatomic electrons may have their energy increased when a gas is raised to a high temperature, but, if so, the increment is too small to have any appreciable effect on the specific heat of a monatomic gas. A. Eucken (1914)[5] found that the value of C_v for helium is virtually constant between temperatures ranging from —256° to 2350°. Again, (ii) the molecules may have rotational movements. The rotation of atoms is illustrated by the movement of the optical axes of a crystal as a whole when the crystal is rotated in the hand. The agreement between theory and observation when the electronic and rotary movements are neglected shows that they are too small to have an appreciable influence on the specific heat—unless perchance the specific heats are determined near the melting points of the solids. J. H. Jeans (1914) considers that this is due to the circumstances that the forces opposing the rotational movements of the atoms inside the solid are so large that the corresponding vibrations are of high frequency, and so normally possess but little energy. A. E. Oxley (1914) observed that the specific heats of sodium and mercury near the melting points are in excess of the theoretical values; and E. Grüneisen (1913) argues that the forces which prevent the atoms rotating are relaxed, and then an additional term—similar to Einstein's (35)—should be added to the theoretical specific heat formula to allow for vibrations which depend upon the rotations of the atoms.

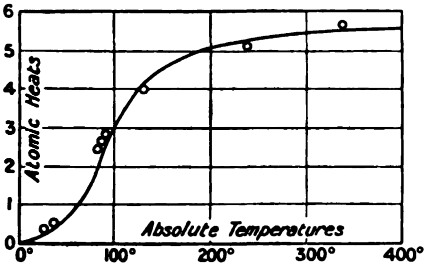

Fig. 11.—The Effect of Temperature on the Atomic Heat of Aluminium.

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§ 17. The Kinetic Theory of Solids

> We must infer that constituent parts of all bodies are in perpetual motion.—R. WATSON (1789).
>
> Nature gives no evidence of absolute rest. All matter, so far as we can ascertain, is ever in motion, not merely in masses, as with planetary spheres, but also molecularly throughout its most intimate structure.—W. R. GROVE.

Many phenomena commonly associated with liquids and gases—vaporization, crystallization, dissolution, diffusion, chemical action, etc.—are also manifested by solids under the right conditions of temperature and pressure. The solid state is not a condition of molecular inactivity and rest. The reason why the phenomena which indicate molecular activity in solids are so often overlooked, is due to the fact that these changes are usually very slow. In solids, the translatory motion of the particles must be very greatly hampered by adjacent molecules; and, except possibly in the case of amorphous solids, it is highly probable that the forces of cohesion cause the molecules in the solid to oscillate about a fixed position of equilibrium so that their movements are restricted; and it is doubtful if the molecules change their locality in the same sense that the molecules of liquid and gases are continually moving from one part of the mass to another.

When a liquid is cooled below its freezing temperature, a certain amount of heat is evolved—latent heat of fusion—as the liquid solidifies. The solidification of a liquid must therefore be attended by a reduction in the mean kinetic energy of the molecules; and the intermolecular attractive forces then probably restrict the migrations of the molecules to oscillatory or vibratory motions about their positions of equilibrium. The low compressibility of solids, and the comparatively slow rate at which one solid diffuses into another, show that the molecules of a solid have a comparatively *low* mobility. One molecule can get away from contact with another molecule only very very slowly, if at all. Solid diffusion, however, seems to be confined to those systems in which solid solutions can be formed; raising the temperature or subjecting the system to a uniform pressure also appears to augment the speed of diffusion.[1]

The fact that many solids evaporate or sublime very slowly, shows that their molecules probably do possess a certain mobility. Thus, zinc at 370°, though still a solid, volatilizes to such an extent that a clean copper plate placed just above appears on the under side to have been coated with brass. The fact that most solids retain their shape for indefinitely long periods, unless prevented by chemical, mechanical, or physical actions, shows that the molecules of solids have a very *limited* mobility—*e.g.* some ancient jewellery appears to be the same now as when first engraved. On the other hand, a mass of pitch may be so brittle as to be readily fractured by a blow, and yet, when placed on an inclined plane, it gradually loses its shape, and, following the solicitations of gravity, begins to flow (not slide) downwards; similarly, a long glass tube or rod supported at both ends, gradually sags in the middle. The substances, glass and pitch, are therefore regarded as extremely viscous liquids. Accordingly, it is not possible to draw a sharp line of demarcation between amorphous solids and liquids.

The term **solid** is therefore ambiguous in that it has at least two meanings. Amorphous solids are frequently harder and more brittle than the same substance in the crystalline condition, and yet the amorphous state is indistinguishable from the liquid state; while a liquid can be readily distinguished from a crystalline solid, it is sometimes said that all true solids are in a crystalline state, and that amorphous solids are super-cooled liquids. This view is discussed in G. Tammann's *Kristallisieren und Schmelzen* (Leipzig, 1903). From his investigation of the structure of the co-called amorphous solids, R. Gross infers that there are probably no true amorphous solids, only crystals and liquids with varying degrees of viscosity up to the high viscosity of glasses.

The stress and strain of solids.—Many properties of solids—*e.g.* tenacity, hardness, etc.—depend on intermolecular forces and also on the grouping of the particles. In general, the particles are in stable molecular equilibrium because, like the so-called conservative system, they tend to restore any work done upon them. For instance, any displacement of the particles within the limits of elasticity produces a counter or restitutional pressure equal and opposite to the distorting stress. The effect of cohesion or the attraction of the particles of a solid for one another must also be attributed to the same molecular forces; and the cohesive forces are measured by the amount of force which must be applied in order to overcome them.

The term *stress* is applied to a force or system of forces which acts upon a body or system of bodies producing an alteration of form. The change or alteration in form which is produced by the application of a stress is called a *strain*, the magnitude of the stress is usually referred to unit area of surface across which it acts. For instance, if a bar of metal of n sq. cm. sectional area and fixed at one of its ends, sustains a load of w kilograms, uniformly distributed, the *longitudinal stress* is w/n kilograms per sq. cm.; and if a portion of the bar increases in length from 100 to 100·01 cm., and the increase be uniformly distributed over the portion lengthened, the *longitudinal strain* will be (100·01–100)/100=0·0001 cm. per sq. cm.

According to R. Hooke,[3] 1676, *ut tensio sic vis*—**strain is proportional to stress**—a relation known as **Hooke's law**. Consequently, the strain will be k times the stress, where k is a constant. The observed relations between the two variables indicate that when the stress is a compression, the curve showing the corresponding change of volume, Fig. 12, does not approach the strain-axis so rapidly as when the stress is a tension. Hence, the intensity of the force resisting compressive strains decreases more rapidly than is the case with the force resisting tensile or dilative strains.

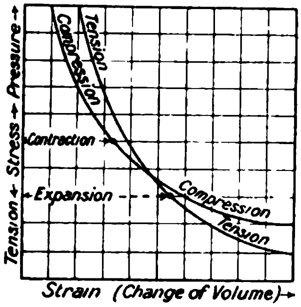

FIG. 12.—Hooke's Law.

If a body subjected to a stress experience no strain, it would, if it existed, be called a *perfectly rigid body*. There are no such bodies.[4] Consequently, every solid can sustain stress or transmit force only by suffering strain. A body is said to be *perfectly elastic* if, when subjected to a given stress at a given temperature, it experiences a definite strain which does not increase when the stress is prolonged, and which disappears completely when the stress is removed. If the form of the body be permanently altered when the stress exceeds a certain value, the body is said to be *soft* or *plastic*, and the state of the body when the (permanent) alteration is just going to take place, is called the *limit of perfect elasticity*. According to the British Standard Specification,

> The **elastic limit** is the point at which the extensions cease to be proportional to the loads. In a stress-strain diagram plotted to a large scale it is the point where the diagram ceases to be a straight line, and becomes curved. The **yield point** is the point where the extension of the bar increases without increase of load. In practice, the yield point is the load per sq. in. at which a distinctly visible increase occurs in the distance between the gauge points on the test-piece, observed by using dividers; or at which when the load is increased at a moderately fast rate there is a distinct drop of the testing machine lever, or in hydraulic machines, of the gauge finder.

If the stress, when it is maintained constant, causes a strain which increases with time, the substance is said to possess *viscosity* or to be *viscous*. According to J. C. Maxwell, a viscous material is fluid when any stress, however small, produces a constantly increasing strain , and he draws a distinction between elasticity of bulk and elasticity of shape. The latter is peculiar to solids. A body possesses elasticity of bulk or **volume elasticity,** when, on removal of the stress, it returns to its original volume, even though the form of the surface be permanently altered. Under a compressive stress, the elasticity of bulk may far exceed the elasticity of shape. According to Lord Kelvin [5]

> If we reckon by the amount of pressure, there is probably no limit to the elasticity of bulk in the direction of the increase of pressure for any solid or fluid , but whether continued augmentation produces continued diminution of bulk towards zero without limit, or whether for any or every solid or fluid, there is a limit towards which it may be reduced in bulk, but smaller than which no degree of pressure, however great, can condense it, is a question which cannot be answered in the present state of science.

The volume elasticity is also called the *cubic elasticity* or *bulk modulus*, or the *resistance to compression*, and it is represented in dynes per sq. cm.

> If other units are employed it is convenient to remember that a *megabar* is equivalent to 10^6 dynes per sq cm , or to 0 987 atm , or to 750 15 mm. of mercury at 0°, sea level, and latitude 45°. One gram per sq. cm. is equivalent to 981 dynes per sq cm

When a uniform pressure of dp dynes per sq. cm reduces the volume v of a body to $v-dv$ the **compressibility** is measured by the fractional change of volume dv/v per dyne of applied pressure per sq cm. The volume elasticity is the reciprocal of the compressibility. Hence

$$\text{Compressibility, } \beta=-\frac{\frac{dv}{v}}{dp};\quad \text{or, } \beta=-\frac{1}{v}\cdot\frac{dv}{dp}.\qquad \text{Volume elasticity } \frac{1}{\beta}=\frac{dp}{\frac{dv}{v}};\ \text{or, } \frac{1}{\beta}=-v\frac{dp}{dv}$$

where the negative sign indicates that the volume decreases as the pressure increases. The volume elasticity is therefore the quotient of a given stress p, by the strain it produces. For example, if a liquid contracts 50 millionths of its volume when subjected to a pressure of 1000 dynes per sq. cm. the modulus of elasticity is 2×10^7 dynes per sq. cm. The compressibility measures the sensitiveness of a body to changes of pressure under the specified conditions. These results apply to gases, liquids, and solids. The temperature is supposed to be constant, and the result is called the **isothermal elasticity** of the gas. If the operation be conducted adiabatically, $pv^\gamma=$a constant, and by differentiation and rearrangement of terms, $vdp/dv=\gamma p$. Hence, the **adiabatic elasticity** of a gas is γ times the pressure, where γ denotes the ratio of the two specific heats of the gas. Similarly, by differentiation of Boyle's law, $pv=$a constant, when the temperature is constant, $vdp/dv=p$. Hence, the ratio of the adiabatic and isothermal elasticities of a gas is equal to the ratio of the two specific heats of the gas.

If a solid bar, supposed perfectly elastic, be exposed to *longitudinal stress*, the ratio of the stress to strain or the *longitudinal elasticity* or the *coefficient of resistance to extension*, is called **Young's Modulus** [6]—symbolized E. The longitudinal elasticity or Young's modulus is represented in dynes per sq. cm. This constant is sometimes referred to as the *modulus of elasticity*, though this term is liable to confusion there are so many kinds of elasticity. If a wire of a sq. cm cross-sectional area be stretched by a force of F dynes, and its length changes from l to $l+dl$, Young's modulus is $lF/a\,dl$. If Young's modulus for a bar of the given material be independent of the direction in which the axis of the bar is taken, the material is said to be *isotropic*, all other materials are said to be *æolotropic*. If a bar be exposed to simple longitudinal traction, the ratio of the lateral contraction to the longitudinal extension of an isotropic elastic solid—each measured per unit of length—is called **Poisson's ratio,**[7] and symbolized σ. Thus, if the diameter of a bar under a uniform longitudinal stress changes from 10 to 9 9997 cm , the lateral contraction is 0 0003 cm , and if the longitudinal strain be 0 0001 cm , Poisson's ratio will be 0·3.

A *shear* is a particular kind of strain in which there is an extension in one direction combined with an equal compression in a perpendicular direction, as when a sphere is converted into an ellipsoid, or a square into a rhombus. The shear is measured by the tangential stress required to produce unit shear, *i e* a shear of one radian, θ, or 57 3°. The *resistance to transverse distortion*, the so-called **rigidity,** n, is therefore $n=F/\theta$ The rigidity, or *shear modulus*, is expressed in dynes per cm , for example, if a tangential stress of 10^8 dynes per sq cm deflects a steel rod through an angle of 0 7°, then $F=10^8$, and $\theta=0\ 7/57\ 3=0\ 0122$ radians ; and $n=F/\theta$, or the rigidity is $8\ 2\times10^{11}$ dynes per sq. cm. This magnitude is sometimes called the *modulus of torsion*, but this term is also applied to another concept, and is best not employed for rigidity.

The relation between the elastic constants are as follows. If β be used to denote the coefficient of compressibility ; E, Young's modulus, or the longitudinal elasticity ; n, the rigidity ; and σ, Poisson's ratio, the relations [8] between these constants for a homogeneous isotropic substance are $E=2n(1+\sigma)$; and $\beta E=3(1-2\sigma)$.

Assuming that the molecules of the different metals show a similarity in behaviour in passing from the rigidity of rest at absolute zero, to the vanishing point of rigidity at the melting point, W. Sutherland [9] found empirically that the relation between rigidity and temperature can be represented by the simple parabolic formula :

$$\frac{n}{N}=1-\left(\frac{\theta}{T}\right)^2$$

where n denotes the rigidity at the absolute temperature θ° ; N is a constant supposed to represent the rigidity at absolute zero ; and T is the absolute melting temperature of the metal. The following values of $10^{-6}N$, that is, 10^{-6} times the rigidity at absolute zero, were calculated from the observed values of n at θ° :

Cu	Ag	Au	Mg	Zn	Al	Sn	Pb	Fe	Ni	Pt
452	295	284	164	426	264	200	118	771	781	661

By plotting n/N as ordinates and θ/T as abscissæ from zero to unity in each case, a parabolic curve is obtained on which the values for the different metals fall. This result establishes the relation between the rigidity of the metals and their melting points, and according to W. Sutherland shows that " rigidity is in its essence a kinetic phenomenon almost as simple in character as the elasticity of perfect gases."

The older writers distinguished between *cohesion*—the mutual attraction of particles of the same substance—and *adhesion*—the mutual attraction of particles of different substances—but there is nothing to show that there is any distinction in kind between the two phenomena.

It is the custom to explain the cohesion of solids as an effect of intermolecular attraction. The laws of gravitational attraction explain the movements of planets at great distances, and a similar law for molecular distances served P. S. de Laplace to explain the surface tension and capillary action of liquids. Many attempts have been made to correlate the elastic constants with molecular attraction. There are difficulties in the application of the gravitational law of inverse squares to solids.

According to R. A. Fessenden's hypothesis cohesion is primarily due to the ionic charges of electricity. The magnitude of the electrical attraction can be calculated from the magnitude of the charges on the atoms, and the number of atoms per c.c. Measurements of the electro-chemical equivalent of silver show that the atoms in one c.c. of silver have a total ionic charge of about 1000 coulombs. The diameter of the silver atom approximates 10^{-4} cm. and there are about 10^{24} atoms per c.c. Consequently, the total quantity of electricity on a single atom is about 10^{-24} coulombs, or, on a single layer of atoms, 10^{-8} coulombs per sq. cm. Two adjacent layers of atoms may be regarded as two plates of a condenser 10^{-8} cm. apart and charged with 10^{-4} coulombs of electricity. Assuming the charges to act as if concentrated at the centres of the atoms, the force required to separate the two layers will be 44×10^5 dynes. According to G. Wertheim, the tensile strength of silver is 37×10^5 dynes per sq. cm., a number in fair agreement with the calculated in view of the approximations made concerning the size of the atoms.

The metals with the smallest atomic volumes usually have the greatest tensile strength. It follows that if the atoms in one rod are twice the diameter of those in another rod, and if the charges behave as if located at the centres of the atoms, then since the charge on each atom is the same, and the smaller atoms are as close again as the larger atoms, twice as much work will be required to shear the rod made of the smaller atoms through a certain angle as with the rod with the larger atoms ; there will also be twice as many atoms in the smaller rod to be sheared ; consequently, the force required to produce a given shear, *i.e.* the rigidity of the rod will vary inversely as the fourth power of the atomic diameter, or as the four-thirds power of the atomic volume.

The rigidity and Young's modulus vary with temperature, and therefore these properties can be compared only when the metals are in corresponding states.

R. A. Fessenden found empirically that Young's modulus and rigidity are approximately two-thirds the atomic volume, so that the rigidity and Young's modulus vary inversely as the square of the atomic volumes. The relation between atomic volume v and rigidity was pointed out by G. Wertheim; R. A. Fessenden plots the two curves: Rigidity, $n=28\times10^{12}v^{-2}$; and Young's modulus, $E=78\times10^{12}v^{-2}$, and found the observed values for a number of metals fall close to the values so calculated. If the attractive force between the atoms with the same charge varies inversely as the square of the distance, the attraction of the smaller atoms in a given rod will be 2^2 times as great per atom as with the larger atoms. There will also be 2^2 times as many atoms. Hence the tenacity will also vary as the four-third power of the atomic volume. Assuming the change of the tensile strength with temperature is proportional to the melting point $T°$ measured from absolute zero, R. A. Fessenden gives: Tensile strength$=0\cdot5208Tv=\frac{4}{3}$ kilograms; and, comparing the calculated results with G. Wertheim's observations, he finds that—

	Fe	Cu	Pt	Ag	Au	Al	Zn	Sn	Pb
Calc. . . .	74	48	48	29	29	18	16	5	4
Obs. . . .	65	41	35	29·6	28·5	18	15·7	3·4	2·36

W. C. Roberts-Austen has shown that the addition of a metal of small atomic volume to one of large atomic volume will increase the tensile strength of the latter provided chemical combination does not supervene.

Several have assumed that the cube root of the molecular or atomic volume v of a metallic element is proportional to the average distance r between adjacent atoms. For example, G. Wertheim[10] showed that the longitudinal elasticity, E, increases as the magnitude r decreases; and H. Tomlinson further showed that for a number of metals, the product E (grams per sq. cm.) into r^7 approximates to a constant, 1711×10^8. Hence, H. Tomlinson assumed that the modulus of longitudinal elasticity varies inversely as the seventh power of the average distance between the atoms; that is, as the seven-thirds power of the atomic volume.

If the intermolecular attraction diminishes rapidly as the molecules move apart, the more a solid is strained by a tensile stress, the less should be the force required to maintain that strain. This is in direct opposition to the observed facts. Similarly with a compressive stress: the greater the strain, the less should be the compressive strength required to maintain that strain. This also does not agree with observation. The molecules of a solid under no stress are presumably in a state of equilibrium but still rotating or oscillating about definite mean positions from which they do not depart except when constrained to do so by the application of an external force which is greater than the force or forces which determine the position of equilibrium of the vibrating molecules. A disturbance of that condition by compression appears to be opposed by *repulsion* as a restoring force. This is shown by the *elastic compressibility* of solids and liquids. By compression, the particles of a solid or liquid can be brought closer together, and the mutual repulsive forces, when developed, result in the storage of energy in the strained body which makes the particles return to their former position when the pressure is relieved. Similarly with *elastic tension*, where the separated molecules are drawn together by attraction as a restoring force when the tension is released.

The fact that a solid resists both compression and dilation, is usually taken to demonstrate the existence of an intermolecular force which changes from a repulsion at small distances to an attraction at greater distances. This means that the intermolecular force either changes instantaneously from attraction to repulsion and *vice versâ*, or else there is a neutral zone in which some or all the molecules of a solid exhibits no cohesion when a solid gradually passes from a state of compression to a state of tension. There is no evidence of such a state of neutrality. The invention of an intermolecular force which changes abruptly from attraction to repulsion is not very satisfactory. The identification of the repulsive forces with the thermal oscillations of the molecules or the resilience which attends molecular impacts,[11] leads to the assumption that the thermal oscillations do not cease at absolute zero since the elasticity at that temperature is not markedly different from what it is at ordinary temperatures.

The assumption that the attractive and repulsive forces are independent of one another is fairly old, and it was developed by G. Mie and E. Grüneisen [12] on the assumption that both forces are inversely proportional to some power of the distances of the molecules apart.

The molecules of a solid may conceivably possess axes along which the attractive forces are particularly active. In gases and liquids the molecules are in constant rotation, and the haphazard translatory motions as well as the distances between the centres is so great that the directional forces are inappreciable; but in crystals directed forces predominate. The orderly configuration of the molecules in a crystalline solid shows that the intermolecular forces are *directed forces.*

There is nothing incompatible with a law of intermolecular attraction which refers the elastic strength of a solid in tension or compression to the increasing resistance which a given configuration of the molecules offers to deformation. Under the influence of a gradually increasing compressive stress, the deformation of the molecular configuration continually increases as the particles are forced closer together, but at a certain point, allotropic or chemical change may occur so that the atoms rearrange themselves to form new molecules. This is shown very well by P. W. Bridgman and G. Tammann's experiments on the effects of pressure on single and mixed solids. When the deformation becomes too great, a form stable under the new conditions replaces the former configuration. J. C. Maxwell,[13] in an essay on the *Constitution of Bodies,* considers that the molecules of a solid oscillate about mean positions so that with certain groups of molecules, the configuration is never very different from the mean stable positions about which the oscillations occur. This will be the case even if the solid be in a state of strain provided the amplitude of the oscillations does not exceed a certain limit; if it exceeds this limit, the oscillating molecules do not return to their former configuration, but begin to oscillate about new positions of stability in which the strain is less than in the original configuration. There are probably many groups of such molecules with oscillations of different amplitude. Thus, the breaking up of any one configuration depends partly upon the magnitude of the strain on the original configuration, and partly on the amplitude of the oscillation.

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§ 18. Reactions between Solids—Spring's Experiments

In W. Spring's experiments,[1] two cylinders of copper were placed end to end with clean surfaces in contact, and heated to 400° for some hours under pressure; the cylinders united together so completely that when the resulting cylinder was broken, the fracture did not pass through the jointed surfaces. The melting point of the copper was far above the temperature of the compressed metals, and thermoscopic observations have shown that the result cannot be explained by the rise of temperature due to the compression. Cylinders of aluminium, bismuth, cadmium, tin, gold, and lead behaved similarly, but the experiment was not successful with antimony and platinum; G. Spezia (1911) failed to obtain any signs of combination with a mixture of finely divided silver and copper after being a month under a uniform pressure of 8000 atm. W. Spring further reported that precipitated alumina dried at 140° appeared to flow like a liquid when subjected to a pressure of 5000 atm., but neither natural nor artificial silica showed any signs of flow. Cylinders of *different* metals were united by compression, *e.g.* with cylinders of copper and zinc, an alloy of brass, about 18 mm. thick, was formed about the plane of contact. Similar remarks apply to cylinders of iron and zinc, copper and cadmium, tin, or bismuth. Powdered metals when subjected to a pressure of about 10,000 atmospheres, gave coherent masses which appeared as if they had been fused. By repeatedly filing and compressing a mixture of bismuth, cadmium, and tin in the correct proportions, Wood's alloy was formed; similarly with Rose's alloy (lead, bismuth, and tin); mixtures of copper and zinc furnished brass; copper and tin gave bronze. The criterion for judging the formation of the alloy were "general appearance and fusibility." W. Hallock [2] showed the futility of the melting-point test because an alloy may be formed by heating the constituents to a temperature above the melting point of the alloy, but below the melting point of any single constituent. W. Rosenhain and P. A. Tucker could obtain only a conglomerate of tin and lead by compression at 35 tons per sq. in., and similar results were obtained with copper and silver by G. Spezia.[3] In agreement with G. Massing, J. Johnston and L. H. Adams say:

> Compression alone does not result in the production of true alloys. In those systems in which the metals crystallize out from the melting as pure components, there is no essential difference between the conglomerate produced by compression and that obtained by fusion. In all other systems, the immediate effect of compression is slight, and consists solely in the fact that compression brings about very intimate contact between the particles, the result of which, in turn, is the formation at the contact of a compound (if such be possible) or the promotion of diffusion (when the metals can form mixed crystals).

J. Johnston and L. H. Adams contend that in Spring's experiments the results must be attributed not to the pressure itself, but rather to the grinding stress to which the material was subjected, for W. Spring frequently speaks of his materials squirting out around the piston which did not fit the cylinder very well. For the effects recorded by W. Spring can be more simply observed by grinding the materials in a mortar; the alloys produced by W. Spring's process are agglomerates. Pressure can favour the formation of alloys by bringing into good contact metals capable of forming solid solution, this process going on very slowly by the diffusion of one metal in another. A uniform pressure can fuse only those metals whose melting points are lowered by pressure, and few metals other than bismuth satisfy this condition. On the other hand, a grinding process may produce results which are not obtained by a uniform pressure—*e.g.* calcium carbonate ground in a mortar loses a little carbon dioxide, but not if this compound is subjected to a uniform high hydrostatic pressure.

This relation between the volume of liquid and solid phases and the lowering of the melting point dT by a pressure dp, is given by Clapeyron's equation:

$$\frac{dT}{dp}=\frac{T_m}{\lambda}(v_2-v_1) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

when v_2 denotes the specific volume of the liquid, v_1 that of the solid, T_m the melting point on absolute scale of temperature, and λ the latent heat of fusion. This means that a pressure acting *uniformly* on the solid and liquid phase of a single substance raises or lowers the melting point according as the process of melting is accompanied by an increase or decrease of volume.

The effect of a non-uniform pressure on solids.—The volumes of most of the silicates increase during fusion.[4] For instance, the specific gravity of a sample of fireclay was 2·627 before fusion, and after fusion 2·470. This corresponds with an expansion of about 6 per cent. Consequently an increase of pressure should raise, not lower, the fusion temperature of the clay.

It has been assumed that the latent heat of fusion λ is constant, and independent of temperature. Experiment shows that this assumption is generally valid, although G. Tammann [5] and others have discussed the possibility of the latent heat of fusion changing from a positive to a negative value. G. Tammann has also shown that since a liquid is usually more compressible than a solid, a positive value of v_2-v_1 will diminish with an increase of pressure, and, after passing through zero, will gradually assume an increasing negative value. It is not probable that the discrepancy between theory and practice is to be attributed to either of these possibilities, rather is the formula not applicable to the case under discussion. Theory assumes that the pressure is uniformly exerted in all directions, whereas the interstices between the grains of a pulverulent material would give the pressure the character of a shearing stress. The solid and liquid phases do not therefore suffer the same increase of pressure.

H. W. B. Roozeboom [6] uses the following illustration: If V_s and V_l, Figs. 13 and 14, represent the vapour pressure curves of the solid and liquid states at a pressure p, and

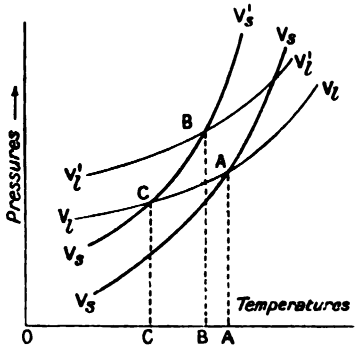

FIG. 13.

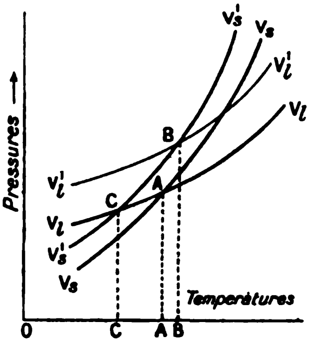

FIG. 14.

V'_s and V'_l represent the vapour pressure curves of the solid and liquid at a higher pressure, when the two phases—liquid and solid—are subjected to the same pressure, the point of intersection A of the V_s and V_l curves will represent the melting point of the substance under a pressure p; similarly, the point of intersection B of the curves V'_s and V'_l will represent the melting point of the substance under a pressure higher than p. When the solid phase alone is subjected to the increased pressure it will melt at the point of intersection C of the V_l and V'_s curves. The temperature OC is always less than OA whether OB be greater or less than OA. Consequently, *the melting point of a solid will always be lowered when the pressure acts on the solid but not on the liquid.* E. Rieke calculates that by the application of a tensile or compressive stress p, the lowering of the melting point $=vT_mp^2/2E$, where E represents the elasticity of the solid in the direction of the applied stress p; λ the latent heat of fusion; T_m the absolute melting point; and v the specific volume of the solid.

J. Johnston and L. H. Adams have shown that pressure decreases the stability of a phase which then exhibits an increased tendency to pass into another phase; otherwise expressed, pressure acting only on a solid phase increases its vapour pressure, and the solubility in a given solvent. Pressure also lowers the melting point in accordance with the relation:

$$\frac{dT_1}{dP} = -\frac{T_m}{\lambda}v_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

when v_1 is the specific volume of the solid and the temperature and pressure in question. Since the quantities on the right are always positive, **the application of an excess of pressure on the solid phase alone always lowers the melting point.** If dT_1 refers to the depression of the melting point when the pressure dp acts on the solid phase alone, and dT the depression when both phases are subjected to the same pressure dp, the combination of equation (1) and (2) furnishes the relation

$$\frac{dT_1}{dT} = \frac{v_1}{v_2 - v_1}$$

meaning that the ratio of the lowering of the freezing point of the solid phase, when this alone is subjected to pressure, to that observed when the same given pressure acts on both phases, is equal to the ratio of the specific volume of the solid phase to the change of specific volume on freezing. This result shows how much the melting point is lowered when the pressure acts on the solid phase alone. For example, with a uniform pressure, the melting point of ice is lowered 0·00752 per atm., but by an unequal pressure the melting point is lowered 0·09° per atm.—*i.e.* twelve times as much. J. Johnston further estimates that if D denotes the specific gravity of the solid, T the normal melting point on the absolute scale, the lowering of the melting point is $0·0242T_m/D\lambda$ per atm. Thus, if potassium melts at 62° (*i.e.* 335° K.), and its heat of fusion is 15·7 cals., and specific gravity 0·87, its melting point will be lowered 0·59° per atmosphere unequal pressure. It is therefore important to distinguish clearly between the effect of uniform and of non-uniform pressure in all discussions on the effects of compression on solid systems; neglect to do so has given rise to some apparently contradictory statements.

Chemical action between compressed solids.—W. Spring claimed to have crystallized amorphous substances like bismuth, zinc (130°), manganese dioxide, zinc and lead sulphides, mercuric iodide, and transformed plastic or monoclinic sulphur into the rhombic varieties. These statements have been contradicted by C. Friedel, E. Jannettaz, and J. Johnston and L. H. Adams. The latter say that compression alone will not in general produce crystallization, or transform one modification of a substance into another. It is true that a uniform or nearly uniform pressure will tend to produce any reversible (enantiotropic) transformation in favour of the system with the smaller volume, but it often does not do so because the reaction velocity is very small. In irreversible (monotropic) changes, no positive statement can be made as to the influence of pressure except by empirical trials. The effects produced by uniform pressure are comparatively slight. If the pressure, uniform or non-uniform, be such as to make the substance melt at the temperature of the investigation, crystallization or recrystallization may ensue; but pressures up to 15,000 atm. do not convert calcite—sp. gr. 2·71—into the denser aragonite—sp. gr. 2·93; nor marcasite—sp. gr. 4·9—into the denser pyrites—sp. gr. 5·0—and this even at 425° under 2000 atm. pressure when the change takes place under ordinary pressures at about 450°.

W. Spring claims to have formed sulphides and arsenides of the metals by the alternate compression and filing of intimate mixtures of the metals with sulphur or arsenic respectively. C. Friedel considered that sulphides were really formed in Spring's experiments because of the change of colour, which he regarded as a more certain indication than the evolution of hydrogen sulphide when treated with hydrochloric acid, and because he found that a mixture of zinc and sulphur gave rise to the evolution of this gas. W. Hallock, however, obtained sulphides at ordinary temperatures with copper and sulphur an inch apart and with a wad of cotton wool in between. He claims that it is the vapour of sulphur which attacks the copper. The same remark applies if the sulphur is replaced by mercuric chloride. There is no reason to doubt that combination did occur even if the reactions did not go to completion, as W. Spring, judging from a microscopic examination, thought really occurred. Hence, although chemical combination no doubt occurred in these experiments—just as the trituration of two solids will sometimes induce combination—yet it does not follow that pressure, *per se*, promotes chemical action. Further examples of the chemical union of solids were reported by W. Spring to occur by compressing mixtures of sodium carbonate and barium sulphate; sodium sulphate and barium carbonate; potassium nitrate and sodium acetate; lead chloride and potassium nitrate; mercuric chloride and potassium iodide; arsenious oxide and cadmium nitrate; etc. Dry sodium nitrate and zinc chloride or sulphate react when shaken together forming zinc nitrate; the heat of the reaction decomposes part of the latter forming zinc oxide and brown vapours. T. von Hagen studied the effect of pressure on powders with the object of preparing tabloids by compression.

While chemical reaction may be favoured by close contact, by the grinding action which attends the application of pressure, and by the slow diffusion which is possible in certain systems, J. Johnston and L. H. Adams have pointed out that W. Spring's tests for chemical combination were defective. For example, the small cylinder obtained by compressing a mixture of powdered and dried anhydrous sodium carbonate and barium sulphate to 3000 atm. was pulverized and "washed completely in cold water; the insoluble residue filtered off, and analysed." W. Spring's results, therefore, show the composition of the compressed mass *after the addition of water*, but not the composition of the dry solid phases, for it is known that the system, $BaSO_4+Na_2CO_3\rightleftharpoons Na_2SO_4+BaCO_3$, when in the presence of water reaches equilibrium after the elapse of a certain time. In the case of potassium nitrate and sodium acetate, the mixture was left four months in a desiccator, and he noticed the mixture was deliquescent. The original salts do not deliquesce; hence, said W. Spring, some deliquescent potassium acetate must have been formed. Here again, the equilibrium was tested after exposure to water vapour, but there is no indication of the state of equilibrium of the dry solids. Mere trituration of the pure and dry salts in the presence of water vapour suffices to start the deliquescence.

In general, only those reversible reactions—physical or chemical—which are accompanied by a diminution in volume are favoured by an increase of pressure. The fact that substances can react in the solid state by trituration or grinding, or by the application of a non-uniform pressure, shows that the molecules of solids can be brought close enough for chemical union. The older chemists did not believe that solid substances could react chemically, and their experience is summarized in the oft-quoted phrase: *corpora non agunt nisi soluta*—substances do not react unless they are in solution. J. L. Gay Lussac combated this dogma as far back as 1846. He said:

> Il est certain, au contraire, que tous les corps solides, liquides, ou aériformes agissent les uns sur les autres, mais que, des trois états des corps, l'état solide est le moins favorable à l'exercice de l'affinité.

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§ 19. The Vibration Frequency of Atoms and Molecules

> The more boldly we advance beyond experience, the broader the survey we obtain. the more surprising the facts we discover, but the greater the likelihood of one going astray.—L. BOLTZMANN (1899).

In recent years, the mathematical treatment of the theory of solids has been largely based upon the quantum theory principally in connection with the specific heats of solids, but also in connection with the co-relation of the physical properties of solids with a property called the periodic time or the vibration frequency—*Schwingungszahl*—of the atoms or molecules. W. Sutherland[1] made an attempt in 1890. He showed that if the molecules of a solid vibrate about a mean position, it can be assumed that at the melting point the vibratory motion will just break down; and the vibration frequency or the period of vibration of the elements at their melting points becomes

$$\text{Vibration frequency} \quad \nu=K\sqrt{\frac{T_m}{Mv^{\frac{2}{3}}}}$$

where K is a constant. W. Sutherland's argument is somewhat as follows:

Let a molecule or atom of mass M and mean specific heat C, be heated from absolute zero to its melting point T_m; it will receive heat MCT_m, and this will be proportional to the kinetic energy $\frac{1}{2}MV^2$ of the molecule, where V is the velocity of vibratory motion at the melting point, provided the body undergoes no expansion when heated. By Dulong and Petit's rule, MC is almost constant for the elements, and therefore V the mean velocity of the vibrations at the melting point is proportional to NT_m/M. If D denotes the density of the element, M/D will represent the molecular volume, v; and if a denotes the mean coefficient of linear expansion of the substance between absolute zero and T_m, the increase in the linear dimensions of the space occupied by the molecule when heated from zero to T_m will be $aT_mv^{\frac{1}{3}}$. This represents the length or amplitude of the vibrations just as the molecule is going to leave the vibratory state characteristic of the solid, on the assumption that the amplitude of the vibrations of the particles is augmented as the temperature rises from absolute zero to the melting point, at which temperature the amplitude becomes comparable with the distances of the molecules apart. At the melting point, the crystalline form of the solid is destroyed. Hence, the vibration frequency of the molecule at the melting point is proportional to $aT_m(M/D)^{\frac{1}{3}}/T_m/M$. Assuming that aT_m is a constant, a relation verified by E. Grüneisen,[2] it follows that if the constants be collected together the vibration frequency is proportional to $(M/D)^{\frac{1}{3}}/(T_m/M)^{\frac{1}{2}}$.

W. Sutherland estimated the relative vibration frequencies of the elements of the alkali family to be in the proportion:

Li	Na	K	Rb	Cs
0·21	0·43	0·66	0·96	1·23

i.e. approximately as 1 : 2 : 3 : 4·5 : 6 ; and for the alkaline earth metals :

Be	Mg	Ca	Sr	Be
0·35	0·70	1·04	1·62	1·88

or approximately as 1, 2, 3, 4·5, 5·3. Similarly, for other groups when data are available. Consequently, the periods of vibration of the molecules at their melting points show simple harmonic relations. Analogous results were obtained with some compounds of the elements. A precisely similar expression was obtained by F. A. Lindemann [3] for the relation between the vibration frequency, ν, and the melting point, T_m. F. A. Lindemann gave the constant the empirical value $2·06 \times 10^{12}$, which W. Nernst afterwards altered to $3·08 \times 10^{12}$. The vibration frequencies of the atoms of the solid have been determined by a number of independent methods and the average values so obtained agree fairly well with one another.

(1) *From the melting point.*—The vibration frequency ν by means of W. Sutherland's formula, with W. Nernst's constant,

$$\nu = 3·08 \times 10^{12} \sqrt{\frac{T_m}{Mv^{\frac{2}{3}}}} \text{; or, } \nu = \frac{3·08 \times 10^{12}}{v^{\frac{1}{3}}} \sqrt{\frac{T_m}{M}} \quad . \quad . \quad (1)$$

where M denotes the molecular or atomic weight ; T_m, the absolute melting temperature; and v, the atomic weight. The agreement between the observed vibration frequencies and those calculated by F. A. Lindemann's formula is very fair :

	Al	Cu	Zn	Ag	Pb	Diamond
$\nu \times 10^{-12}$ (Observed) . .	8·3	6·6	4·8	4·5	2·0	40
$\nu \times 10^{-12}$ (Calculated) . .	8·4	7·5	4·8	4·8	1·9	35

The low atomic weights and the high melting points of these elements, diamond, boron, and silicon, give these elements abnormally high vibration frequencies. Lithium has a low atomic weight, but its low melting point gives its vibration frequency a normal value. The atomic frequencies of the elements calculated from F. A. Lindemann's formula [4] are indicated in Table XXVI.

TABLE XXVI.—ATOMIC VIBRATION FREQUENCIES OF THE ELEMENTS.

Element.	$\nu \times 10^{-12}$	Element.	$\nu \times 10^{-12}$	Element.	$\nu \times 10^{-12}$
Hydrogen . .	4·88	Iron . .	9·11	Antimony .	3·22
Helium-liquid .	0·66	Cobalt . .	8·87	Tellurium . .	2·69
Lithium . .	10·65	Nickel . .	8·86	Iodine . .	1·82
Beryllium . .	23·65	Copper . .	7·40	Xenon-liquid .	0·85
Boron . .	28·10	Zinc . .	4·79	Cæsium . .	1·12
Carbon-graphite .	27·70	Gallium . .	2·82	Barium . .	2·66
Carbon-diamond .	31·70	Germanium .	5·23	Lanthanum .	3·04
Nitrogen . .	2·50	Arsenic . .	4·20	Cerium . .	2·86
Oxygen . .	2·54	Selenium-grey .	2·79	Praseodymium .	3·24
Fluorine-liquid .	1·80	Bromine-liquid .	1·70	Neodymium .	3·11
Neon-liquid . .	0·34	Krypton-liquid .	1·90	Samarium . .	3·76
Sodium . .	4·31	Rubidium .	1·54	Tantalum . .	5·72
Magnesium . .	7·88	Strontium .	3·44	Tungsten . .	6·06
Aluminium . .	8·33	Yttrium . .	4·07	Osmium . .	5·96
Silicon . .	10·50	Zirconium .	4·63	Iridium . .	5·47
Phosphorus, red .	6·72	Columbium .	6·73	Platinum . .	4·75
Phosphorus, white	3·83	Molybdenum .	5·57	Gold . .	3·69
Sulphur-rhombic .	4·30	Ruthenium .	6·99	Mercury . .	1·38
Sulphur-monoclinic	4·24	Rhodium . .	7·01	Thallium . .	2·00
Chlorine-liquid .	2·24	Palladium .	6·16	Lead . .	1·99
Argon-liquid .	1·32	Silver . .	4·80	Bismuth . .	1·80
Potassium . .	2·53	Cadmium . .	3·01	Thorium . .	3·06
Calcium . .	4·28	Indium . .	2·37	Uranium . .	4·67
Scandium . .	6·84	Tin . . .	2·50	Chromium .	9·23
Titanium . .	9·17	Vanadium .	9·26	Manganese .	8·35

The numbers are based on the assumption that the molecules of the solid are monatomic. It is also assumed that the molecular structure remains unchanged—without polymerization or dissociation—in cooling from the melting point to absolute zero. If the molecular weight changes from M to nM, the molecular volume will be increased n times. Consequently, in virtue of the terms $m^{\frac{1}{2}}$ and $v^{\frac{1}{3}}$, the frequency calculated by F. A. Lindemann's equation must be divided by $n^{\frac{1}{2}+\frac{1}{3}}$, or $n^{\frac{5}{6}}$. The molecular volume is usually computed from density determinations at ordinary temperatures; and it is assumed that the molecular volume is a constant, whereas it is not likely that the molecular volumes of a substance at absolute zero and at the melting point are the same; hence the formula probably needs a correction term for the change in the molecular volume of temperature.[5] It must also be emphasized that the constant has been evaluated empirically, and that a series of approximations have been made in the deduction of the formula. The different allotropic forms of an element may have different frequency numbers. The atomic frequencies of the elements also exhibit periodic properties, as W. Sutherland (1890) and later W. Biltz (1911) have shown. The curve, Fig. 15, recalls L. Meyer's atomic volume curve, Fig. 14, Cap. VI Thorium, manganese, tin, and tellurium do not sit on the curve. Argon and potassium occupy their anomalous position; hydrogen seems to fall with the halogens. The unique chemical character of carbon in its great capacity for forming compounds seems to correspond with its exceptionally large vibration frequency. H. S. Allen[6] has shown that if N be the atomic or Moseley's number for an element, a large proportion of the elements furnish values of the product $N\nu = na$, where n is a whole number, and a is a constant, approximately $21{\cdot}3 \times 10^{12}$; and for a few others—lithium, beryllium, sodium, magnesium, phosphorus, sulphur, potassium, arsenic, rubidium, indium, iodine, mercury—n involves fractions. E. Grüneisen

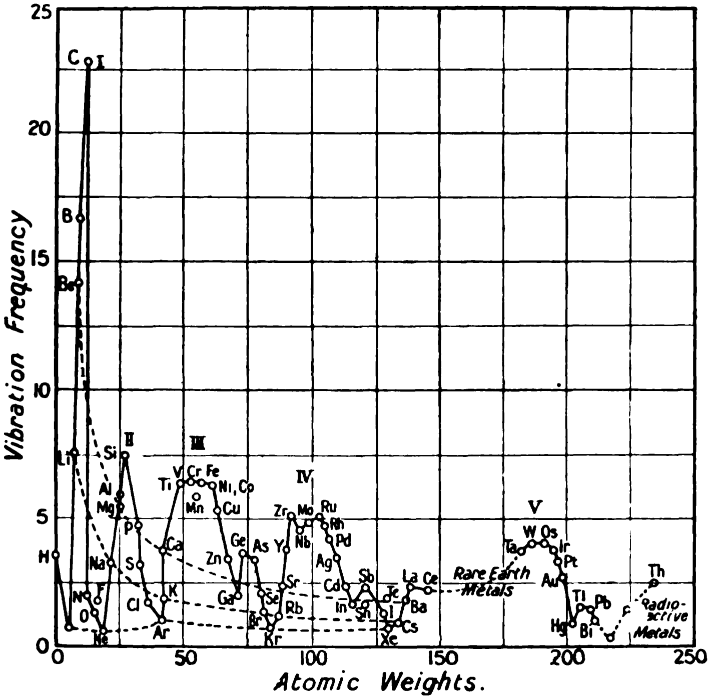

FIG. 15.—Vibration Frequencies and Atomic Weights.

found the product of the linear expansion coefficient, α, and the absolute temperature of the melting point to be a constant; H. Alterthum substituted the reciprocal of α for T_m in Sutherland and Lindemann's formula, and obtained

$$\nu=4\cdot2\times10^{11}\sqrt{\frac{1}{M\alpha v^{\frac{2}{3}}}} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The deviations of the results with this formula from others are probably due to the use of values of α determined at ordinary temperatures.

(2) *From the elastic constants of the solid.*—The relation between the natural vibration frequency ν of the atoms, the atomic weight M, the compressibility β, and the density D of a solid was computed by A. Einstein (1911) to be

$$\nu=3\cdot3\times10^{7}\sqrt{\frac{v^{\frac{1}{3}}}{M\beta}} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

showing that the forces which produce the thermal oscillations of the solid are the same in kind as those which produce elastic oscillations—*e.g.* sound waves. A. Einstein's constant was $2\cdot77\times10^7$, but the empirical value $3\cdot3\times10^7$ was found to give more satisfactory agreement with the values obtained by the preceding formula. F. A. Lindemann modified A. Einstein's formula to

$$\nu=3\cdot58\times10^{7}M^{-\frac{1}{3}}D^{-\frac{1}{6}}\beta^{-\frac{1}{2}}$$

E. Grüneisen (1912)[7] obtained a relation (4) between the coefficient of linear expansion, α; the compressibility, β; and the specific heat at constant volume, C_v, in gram calories per degree. When this relation was combined with A. Einstein's specific heat formula, an expression for the vibration frequency is obtained:

$$\nu=2\cdot92\times10^{11}\sqrt{\frac{C_v}{3\alpha v^{\frac{2}{3}}}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This shows a good agreement with values obtained by other methods.

(3) *From the frequencies of the longest heat waves in the dispersion spectrum.*—The natural vibration frequency ν of the atoms of the elements for any temperature can be calculated from the abnormally low specific heats. In order that the specific heat may be less than normal at ordinary temperatures—say, 27°, when $T=300$—the vibration frequency ν must lie between $6\cdot5\times10^{13}$ and $6\cdot5\times10^{12}$. Vibration frequencies of this range lie in the infra-red spectrum, and therefore all elements with abnormally low specific heats must have a value of ν in this part of the spectrum. Adapting a table from N. R. Campbell's *Modern Electrical Theory* (Cambridge, 242, 1913), it has been found

	S and P	Fl	O	Si	B	H	C
C_v . .	5·41	5·0	3·99	3·81	2·68	2·32	1·79
$\nu\times10^{-12}$.	7·1	9·1	14·3	15·0	20·0	23·1	25·0

These values of ν are in fair agreement with such observations as have been made on the absorption frequencies of the atoms in compounds of these elements. The agreement is surprising, because, as N. R. Campbell says, it might have been anticipated that the forces under which the atoms would vibrate in the compounds would be entirely different from the vibrations of these same atoms when they form part of a solid element. While the absorption bands in the infra-red probably represent the free vibrations of the atoms and not of the electrons inside the atoms, the vibrations of transparent bodies in the ultra-violet are probably contributed by the *electrons*. The spectrum shows that the vibrating atoms have many degrees of freedom, which are very important optically, but they possess such high values of ν that they do not absorb appreciable amounts (quanta) of energy when the body is heated.

According to S. Pagliani,[8] the vibration frequency ν of a molecule can be calculated from the vibration frequencies ν_1 and ν_2 of its component atoms by the formula $\nu=\frac{4}{3}(\nu_1+\nu_2)$; and it is connected with the entropy ϕ of the compound by the expression $\nu=9·6\times10^{12}\phi$.

The specific heats of compounds.—At ordinary temperatures the additive nature of the specific heat laws of F. E. Neumann, J. P. Joule, and H. Kopp show that the heat energy of the molecules is mainly derived from the vibrations of the individual atoms. At high enough temperatures, the vibrational energy of the atoms approaches the value $3RT$; but at low temperatures, W. Nernst [9] assumes that the vibrations of the molecules play a more important part than the vibrations of the atoms in the molecule. W. Nernst further assumes that the heat energy of a compound in the solid state is made up of the energy due (i) to the motions of the molecules relative to one another, and (ii) to the internal energy of the molecules owing to the vibrations of the atoms in the molecule. The first contribution is calculated by P. Debye's formula ; the second by A. Einstein's. Each calculation involves a knowledge of the characteristic vibration frequencies—the first, symbolized by ν_1, is given approximately by F. A. Lindemann's formula ; the second, symbolized by ν_2, obtained by the optical measurements of H. Rubens' residual rays—*Reststrahlen* [10]—by repeated reflexions from the surfaces of solids. It is assumed that the frequency of such infra-red radiations corresponds with the frequency of vibration of an electrically charged ion which may be identified with an atom, and that the forces which control the heat vibrations of the atoms of a solid are the same, whether specific heats or the reflexion of infra-red radiations are involved. Consequently, the specific heat of the compound will be :

$$2C_v=\frac{d(\text{Debye's function})}{dT}+\frac{d(\text{Einstein's function})}{dT}$$

According to W. Nernst, for KCl, $\beta\nu_1=166$ and $\beta\nu_2=213·5$, where $\beta=4·78\times10^{11}$. The calculated mean values of C_v at different temperatures are compared with the observed values of C_p in Table XXVI. The agreement between hypothesis and observation is good. The analogy between the results with the atoms of the elements and the molecules of compounds has led H. S. Allen to infer that

> The forces binding the atoms in the molecule are similar in character to those which bind the molecules of the solid, that is, the forces of chemical affinity are of the same nature as the forces of molecular cohesion.

TABLE XXVII.—SPECIFIC HEAT OF POTASSIUM CHLORIDE.

Temperature °K.	Internal vibrations.		Calculated $2C_v$.	Observed $2C_p$.	Difference between C_p and C_v.
	C_v from Debye's formula.	C_v from Einstein's formula.			
22·8	1·04	0·046	1·086	1·16	0·04
30·1	1·87	0·25	2·12	1·96	−0·08
48·3	3·52	1·43	4·95	5·70	0·37
70·0	4·57	2·89	7·50	7·58	0·04
235·0	5·81	5·55	11·68	11·78	0·05
550·0	5·93	5·87	12·70	13·08	0·19

It is found that if the single ions are situated at the points of the space lattice of a crystalline solid, the mean atomic weights can be substituted in the formula for calculating the frequencies. The agreement is then not nearly so good as when the residual rays of H. Rubens are assumed to be reflected from the molecules as a whole. The calculated results with mercurous chloride and with water agree with observations only when more complex molecules than HgCl and H_2O are respectively assumed.

If the values of the vibration frequencies are known, it is possible to calculate the molecular weight of elements and compounds from Lindemann's formula by substituting molecular weight and molecular volume in (33). The observed values for crystals of lead, silver, zinc, copper, aluminium, and carbon in the diamond agree with those calculated on the assumption that these elements are monatomic; with sulphur and graphitic carbon, the molecules are more complex—with sulphur probably S_8. Similarly with crystals of sodium chloride, NaCl; potassium chloride, KCl; potassium bromide, KBr; silver chloride, AgCl; lead chloride, $PbCl_2$; and benzene, C_6H_6. The molecular weights so determined agree with the formulæ usually assigned to these compounds, whereas with crystals of water, silica, and mercurous chloride, the ordinary formulæ are doubled so as to furnish H_4O_2, Si_2O_4, and Hg_2Cl_2 respectively.

The relation between the vibration frequency and the atomic heat of fusion.—If λ denotes the latent heat of fusion of a crystalline solid, and M the atomic weight, the number of calories required to melt a gram-atom of the solid will be $M\lambda$. The energy required to melt the solid may be regarded as equivalent to the work required to rupture the bonds which hold the crystal units in position, and enable the molecules to move freely amongst themselves. According to the quantum theory, the energy of a solid is the energy of the oscillators which it contains, and H. S. Allen[11] assumes that the latent heat of fusion is equivalent to the energy required to counterbalance the energy of a certain number of oscillators. The average amount of energy associated with a vibration frequency ν, at a temperature T, is $RTu/(e^u-1)$, where u is put in place of $h\nu/RT$, and h is Planck's constant, R the gas constant per gram-molecule. If c denotes the ratio of the number of oscillators to the number of atoms, there will be cN oscillators in a gram-molecule, where N denotes Avogadro's constant. The total energy of the atoms in a monatomic solid is accordingly

$$M\lambda=\frac{cNRTu}{e^u-1}\,;\ \text{or,}\ \frac{M\lambda}{NRT}=c\frac{u}{e^u-1}$$

NR is the value of the gas constant per gram-molecule, *i.e.* 1·989 calories per degree. The vibration frequencies of a number of elements are known, and consequently the values of c can be computed. H. S. Allen finds the value of c for nickel, cobalt, rubidium, sodium, potassium, iron, silver, lead, copper, and palladium to be nearly unity; for aluminium, mercury, cadmium, and platinum, 1⅓; for zinc, 1½; for tin, 1¾; and for gallium and bismuth, 2½. H. S. Allen's expression for the latent heat of fusion λ resembles H. Crompton's formula indicated in the next section. The relation of H. Crompton's formula to H. S. Allen's is seen by writing the latter

$$\frac{M\lambda}{Tc}=NR\frac{u}{e^u-1}$$

when, as H. S. Allen shows, the expression $u/(e^u-1)$ is not far from unity, the right side of the equation is approximately constant and equivalent to H. Crompton's relation. A great deal of the work which has been done with the classical doctrine of energy can now be translated into the language of the quantum theory.

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§ 20. Empirical Relations between the Properties of Solids

> We cannot attain to a real theory of chemistry until we are able to connect the science by some hypothesis with a general theory of dynamics.—A. C. Brown (1874).

The kinetic theory of solids is in the earlier stages of its development in that it is based upon very imperfect knowledge and arbitrary assumptions. There have been quite a number of attempts to develop the subject.[1] The greatest success has been obtained by considering the properties of solids at low temperatures as a limiting case in the same sense that gases have been more amenable to mathematical treatment when in a rarefied condition. The amplitude of the oscillating molecules at low temperatures is probably small, and but a relatively small number are vibrating. This assumption is in conformity with the fact that many properties of solid bodies at very low temperatures are small, and vary almost proportionally with the temperature—this applies, for example, with the specific heats, coefficients of thermal expansion, the temperature coefficients of compressibility, etc., at low temperatures.

C. M. Guldberg (1868) sought to establish the relation

$$pv=RT-\beta\log\frac{v}{v_0}$$

as the **equation of state of ideal solids** in the same sense that $pv=RT$ is the equation of state of ideal gases. In C. M. Guldberg's equation, R, β, and v_0 are constants which have specific values for different substances—v_0 is considered to be the specific volume of the substance at absolute zero. It is further shown that if w denote the weight of a cubic metre of the solid; E, the modulus of elasticity; a, the coefficient of thermal expansion; and λ, the latent heat of fusion, these constants are related so that $E=wK$; $aw\beta=4240$; $\beta=4\times10^4\lambda$. The agreement between the observed values and those calculated by these relations is remarkably good, and it shows that some intimate relation probably subsists between the latent heat of fusion, the coefficient of thermal expansion, and the elasticity or compressibility of solids.

E. Grüneisen has also found empirically that the quotient of the coefficient of linear expansion, a, and the specific heat at constant pressure, C_p, of a number of metals is nearly a constant—that is, $a/C_p=$a constant; he also found empirically that the product of the atomic volume, v, and the coefficient of linear expansion, a, divided by the product of the coefficient of compressibility, β, and the atomic heat, C_v, is a constant—that is, $av/\beta C_v$ $=$a constant; and that the product of the coefficient of linear expansion, a, and the absolute melting temperature, T_m, is nearly constant—that is, $aT_m=$a constant.

R. Pictet [2] assumed that the mean values of the amplitudes of the vibrating molecules in a melting solid are always the same; that the product of the mean distances of the molecules and the coefficient of linear expansion, a, is proportional to the absolute temperature of the melting point, T_m; and that the product of all three variables is constant.

In ignorance of the absolute distances between the vibrating particles, and since the volume of a solid is proportional to the cube of the linear dimensions, the cube root of the atomic volume v may be substituted for the distances between the particles, and Pictet's rule assumes the form $aT_m v^{\frac{1}{3}}=$a constant. This rule applies very well for the heavier metals where the mean value of the constant lies between 4 and 5. The constant for aluminium is 6·6; for magnesium, 5·7; tin, 2·8; antimony, 2·2; and bismuth, 2·05, although there is some uncertainty as to the exact values of the melting points and the coefficients of expansion of some of the metals. It has been proposed to use Pictet's rule for the calculation of melting points of elements. W. Sutherland, however, found the empirical rule $aT_m M^{\frac{1}{3}}=0{\cdot}04$ to 0·05—say, 0·045—gives better results for all the metals tried, with the exception of antimony, bismuth, and tin. The rule applies to sodium, magnesium, and aluminium—iridium gives a constant 0·037.

J. W. Richards[3] found empirically that the latent heats of fusion of about 15 elements is one-third the amount of heat required to raise the metal from absolute zero to its melting point within an error of from 5 to 10 per cent. If the average atomic heat of an element between −273° and its melting point is approximately 6·4, Dulong and Petit's rule, then, the amount of heat in a gram-atom of the metal at its melting point is $6{\cdot}4T_m$. Assuming that the latent heat of fusion is one-third the total heat in the metal at its melting point, the latent heat of fusion will be one-third of $6{\cdot}4T_m$; and, from Pictet's rule, the latent heat of fusion $=9{\cdot}5/av^{\frac{1}{3}}$ cals. per gram-atom. Richards found that this agreed well with all the metals for which the necessary data were available with the exception of aluminium, *e.g.* for copper $9{\cdot}5/a\sqrt[3]{v}=3006$, and dividing by the atomic weight to get the amount per kilogram, the latent heat of fusion is 46·2—the observed value is 43·0.

H. Crompton's formula[4] is $M\lambda=1{\cdot}38T_m\Sigma v$ nearly; here M denotes the molecular weight of the solid; Σv, the sum of the valency bonds; λ, the latent heat of fusion of unit weight of the substance; and T_m is the absolute temperature of fusion. H. Crompton's formula also gives a constant ranging between 1·8 and 2·56 for a number of organic compounds, but for normal or non-associated liquids he obtained satisfactory results with $\lambda D=0{\cdot}099T_m$—the variations from the mean value of the constant 0·099 ranged from 0·080 to 0·142. He has also shown that for a series of metals the atomic heat of fusion divided by the absolute temperature of the melting point, T_m, is almost independent of the nature of the metal, for the quotient lies between 1·84 and 4·82. P. Walden obtained similar results by using the molecular heat of fusion of 33 compounds; here the quotient fell between 12·5 and 14·8 with a mean value of 13·5. If the compounds are associated in the liquid state, the constant assumes a lower value. G. Tammann, however, examined a far larger number of compounds than P. Walden, and only about a quarter fell between the limits indicated by P. Walden. P. W. Robertson,[5] also starting from Pictet's rule, obtained the expression $w\lambda/T_m\sqrt[3]{v}=$a constant, which gave better results than H. Crompton's equation for all the elements with atomic weights over 40 for which data are available. The constant ranges from 0·87 to 1·28—gallium, bismuth, and bromine gives values respectively 2·05, 1·75, 1·63. The formula also applies to compounds when w denotes the molecular weight.

E. Obach[6] found a relation between the specific inductive capacity, K, and the latent heat of evaporation λ of a number of related organic liquids, such that $\lambda/K=$a constant. From Trouton's rule, $M\lambda/T_b=$a constant, where T_b denotes the absolute boiling point, it follows that MK/T_b is also a constant, and accordingly, *the absolute boiling point of a series of related bodies is proportional to the molecular inductive capacity.* P. de Heen found the absolute boiling point at 760 mm., and the coefficient of expansion α at 0° are inversely proportional, or the product αT_b is a constant. Hence also αKM must be constant, or the coefficient of expansion at 0° is inversely proportional to the molecular inductive capacity. Accordingly, the product αKM represents P. de Heen's intermolecular work, or that part of the heat spent in physical dissociation as contrasted with heat required for chemical dissociation. The approximate proportionality between the latent heat of vaporization and the dielectric constant of a liquid observed by E. Obach,[6] was extended by P. Walden to a relation between the internal pressure and the dielectric constant. W. C. McC. Lewis, however, found that there is no direct proportionality between the cohesion or intrinsic pressure and the dielectric capacity. Although substances with a large dielectric capacity have generally a large intrinsic pressure, the relationship is rather more complex than is implied in E. Obach's or in P. Walden's rule. W. C. McC. Lewis has also shown that the approximate relation indicated by E. Obach and P. Walden follows from the assumption that the cohesion or intermolecular attraction is an electromagnetic and not an electrostatic effect. A. P. Mathews also postulated that, while the intramolecular affinity uniting the atoms in a molecule is an electrostatic effect produced by valency electrons, intermolecular cohesion is a magnetic effect produced by the valency and other electrons.

According to H. Tomlinson, if w denotes the atomic weight of an element of density D, and C_m, the thermal capacity per unit mass, then the thermal capacity

C per unit volume is $C=DC_m$; and by Dulong and Petit's rule, wC_m=constant. Since, as shown above, Er^7=constant, and r is proportional to $(w/D)^{\frac{1}{3}}$, it follows that $EC^{-\frac{7}{3}}$=a constant; this means that the cube of Young's modulus varies as the seventh power of the thermal capacity of the atoms per unit volume. It follows also that the same constant is equal to Er^7.

According to A. H. Stuart,[7] the relation between the coefficient of longitudinal elasticity E; the density D; the specific heat C_p; and the coefficient of thermal expansion α, is $C_p=4{\cdot}44\alpha E/D$; and if Dulong and Petit's rule be $C_pw=6{\cdot}25$, the atomic weight of an element is equal to $1{\cdot}41D/\alpha E$. The application to the few metals for which reliable data are available is indicated in Table XXVIII.

TABLE XXVIII.

Metal.	D	E kilograms per sq. mm.	$\alpha\times10^5$	Atomic weight.	
				Calculated.	Observed.
Aluminium	2·6	6,710	2·313	23·7	27·1
Copper	8·9	12,140	1·666	63·4	63·57
Gold	19·3	9,650	1·443	196·0	197·2
Iron	7·9	18,500	1·210	50·0	55·84
Platinum	21·5	17,044	0·902	197·0	195·2
Silver	10·5	7,141	1·921	108·0	107·88
Tin	7·3	4,170	2·234	111·0	119·0

J. D. van der Waals' equation of state for solids.—R. H. McCrea (1907)[8] tried to adapt J. D. van der Waals' equation to the solid state, but with no definite result. K. Eisenmann deduced

$$\left(p+\frac{a}{v^2}\right)\frac{v(v-b)}{b}-\frac{1}{v}\cdot\frac{h\nu}{e^{-\frac{h\nu}{kT}}-1}=kT$$

as the equation of state of solids with spherical atoms—here k is Boltzmann's constant. E. Kohl (1913) deduced a formula for the two specific heats: $C_p-C_v=3\alpha M\lambda D/(D_s-D_l)$, where α denotes the coefficient of linear expansion; M, the molecular weight; λ, the latent heat of fusion; D, the specific gravity; and D_s and D_l, the respective specific gravities of solid and liquid at the melting point. It is assumed that J. D. van der Waals' equation is applicable to the solid, and that the variation of the energy with temperature is independent of the state of aggregation. The results are not good.

I. Traube also applied J. D. van der Waals' equation to highly compressed gases and liquids by assuming that the observed volume is made up of two components: (i) the volume of the molecules; and (ii) the *co-volumes* or intermolecular spaces. I. Traube calculated the J. D. van der Waals' constants a and b of the metals by introducing two values for the volume v at two temperatures near 0°. The one value of v was obtained by making $v=w/D$, where w denotes the atomic weight, and D the density, and the other value of v was calculated from the coefficient of cubical expansion 3α. The values of a and b can be computed by substituting these values of v and T in J. D. van der Waals' equation $a(v-b)/v^2=RT$, when the external pressure is negligibly small in comparison with a/v^2. I. Traube's results are shown in Table XXIX.

TABLE XXIX.—VALUES OF J. D. VAN DER WAALS' a AND b FOR SOLID ELEMENTS.

Elements.	$v=\frac{w}{D}$	b	a litre atm.	$K=\frac{a}{v^2}$ atm.	$3a$	$3a\frac{v}{v-b}$
Potassium	45·00	42·230	17·3	8,080	0·0002490	0·0040
Sodium	23·58	22·360	10·2	18,300	0·0002160	0·0042
Lead	18·20	17·760	18·1	50,800	0·0000882	0·0036
Thallium	17·22	16·810	16·2	54,600	0·0000924	0·0039
Magnesium	14·00	13·690	14·2	72,200	0·0000819	0·0037
Cadmium	13·02	12·710	12·3	72,200	0·0000930	0·0039
Tin	16·23	15·900	17·9	67,800	0·0000675	0·0033
Aluminium	10·50	10·310	13·1	117,800	0·0000696	0·0038
Mercury (liquid)	14·66	14·010	7·4	34,400	0·0001810	0·0041
Copper	7·13	7·034	11·9	233,100	0·0000504	0·0037
Silver	10·25	10·072	13·2	125,700	0·0000576	0·0033
Gold	10·21	10·083	19·7	176,200	0·0000435	0·0035
Platinum	9·30	9·200	19·4	320,000	0·0000270	0·0035
Palladium	8·51	8·464	35·2	22,380	0·0000354	0·0033
Osmium	7·12	7·050	16·2	486,600	0·0000197	0·0036
Iron	6·60	6·520	12·2	319,700	0·0000366	0·0037
Nickel	21·27	21·040	44·1	97,300	0·0000384	0·0032
Bismuth	17·88	17·690	37·7	117,700	0·0000396	0·0037
Antimony	23·09	13·020	54·9	319,700	0·0000345	0·0033
Arsenic	19·84	19·310	16·65	42,200	0·0000174	0·0039
Tellurium (cryst.)	16·83	19·310	19·1	35,500	0·0001032	0·0039
Selenium (cryst.)	16·83	16·200	10·0	41,400	0·0001480	0·0039
Sulphur	15·50	14·960	4·6	41,400	0·0001370	0·0046
Phosphorus	16·89	15·500	41·5	16,200	0·0003750	0·0046
Silicon	12·91	12·820	41·5	248,700	0·0000231	0·0033
Diamond	3·41	3·406	63·6	545,800	0·0000375	0·0031

The numbers in the last column are remarkably concordant when the heterogeneous character of the data is taken into consideration; the average of these numbers approximates to $\frac{1}{273}$. The value for carbon is exceptional. The values of $K=a/v^2$ are about one-third those obtained by T. W. Richards[9] on the assumption that the stress, P, under which a substance rests can be measured by the heat C absorbed per gram-molecule when the volume changes dv/dt. Whence $P=CdT/dv$. Accordingly, $K=\frac{1}{3}CdT/dv$; but if $K=a/v^2$, it follows from van der Waals' equation $a(v-b)/v^2=RT$, or $K(v-b)=RT$, and that

$$\frac{1}{v-b}\cdot\frac{dv}{dT}=\frac{c}{3RT}; \text{ or, } \frac{1}{v-b}\cdot\frac{dv}{dT}=\frac{1}{273}; \text{ or, } \frac{C}{3RT}=\frac{1}{273}$$

which says in words: *at a given temperature T, the coefficient of expansion of the co-volume of a solid element, or the change per unit volume of the co-volume, is in general constant, viz.* $\frac{1}{273}$. This rule applies to the metals (monatomic) and the metalloids (polyatomic), but not to the halogens. It also follows that the atomic volume is nearly $3R$ cals. at 0°, when $T=273°$.

The relation between the latent heat of fusion and the coefficient of expansion.—Again, the greater the coefficient of expansion of a metal the lower the melting point,[10] although the results may be disturbed by changes in the complexity of the molecules near the melting point. The rule is illustrated by data in Table XXIX. It has been shown that for the solid metals J. D. van der Waals' equation assumes the forms $a(v-b)/v^2=RT$, and $dv/(v-b)dT=\frac{1}{273}$; substituting the latter value of $v-b$ in the former, it follows that at 0°, when $T=273$,

$$\frac{a}{v}\left(\frac{1}{v}\cdot\frac{dv}{dT}\right)=R$$

where the term in brackets represents the change in volume which occurs per unit volume when the temperature alters 1°—*i.e.* the coefficient of cubical expansion $3a$; and the term a/v represents the internal heat of vaporization, *i.e.* the observed latent heat of vaporization less the work done in expansion against atmospheric pressure during the change of state, and

$$\text{Internal latent heat, } \lambda = \frac{a}{v} + RT \text{ ; or, } \frac{a}{v} = \lambda - RT$$

Consequently, from the preceding expression, $3(\gamma - RT)a = R$, or *the product of the internal molecular heat of vaporization, and the coefficient of cubical expansion is equal to the constant* R—this is illustrated in Table XXIX., where the product $3a(\lambda - RT)$ is approximately constant for the elements which follow Dulong and Petit's rule. H. F. Wiebe[11] assumed that the coefficient of cubical expansion $3a$ is proportional to the amount of heat required to raise an element of atomic weight w from its melting point T_m to its boiling point T_b. If C denotes the specific heat of the element, the product $Cw(T_b - T_m)$=constant, which is nearly 2·03. Again, assuming that the amount of heat required to raise the temperature from absolute zero to the melting point T_m—or the thermal energy of the atoms of an element just before it melts—is almost inversely proportional to its coefficient of expansion, a, so that the product of these two constants are approximately constant; and $wCT_m a$=a constant. Both rules apply to some families of elements, but there are many exceptions.

TABLE XXX.—RELATION BETWEEN COEFFICIENT OF EXPANSION AND INTERNAL HEAT OF VAPORIZATION.

Element.	Coeff. cubical expansion $3a$.	Melting point.	Boiling point.	$\lambda - RT$	$3a(\lambda - RT)$
Phosphorus	0·000375	317	—	6,600	2·5
Potassium	0·000249	328	960	9,200	2·3
Sodium	0·000216	363	1090	10,500	2·3
Selenium	0·000148	490	—	14,550	2·1
Sulphur	0·000137	388	—	15,650	2·1
Tellurium	0·000103	760	—	20,350	2·1
Cadmium	0·0000930	594	1110	22,900	2·1
Thallium	0·0000924	563	1110	22,800	2·1
Lead	0·0000882	601	1170	24,100	2·1
Magnesium	0·0000819	905	1190	24,600	2·0
Aluminium	0·0000696	929	1470	30,300	2·1
Tin	0·0000675	505	1300	26,800	1·8
Silver	0·0000576	1234	1510	31,200	1·8
Copper	0·0000504	1355	1970	40,500	2·0
Gold	0·0000403	1337	2270	46,800	2·0
Bismuth	0·0000396	540	—	50,300	2·0
Nickel	0·0000384	—	2170	44,800	1·7
Iron	0·0000366	—	2680	55,200	2·0
Palladium	0·0000354	—	2460	50,600	1·8
Antimony	0·0000345	710	—	51,100	1·8
Platinum	0·0000270	—	3670	75,500	2·0
Graphite	0·0000237	—	—	76,700	1·8
Silicon	0·0000231	—	—	78,000	1·8
Osmium	0·0000197	—	4900	100,600	2·0
Arsenic	0·0000174	—	—	101,700	1·8
Diamond	0·00000375	—	—	45,200	1·7

W. Spring[12] found that for a number of related isomorphous elements—iron and aluminium; cobalt and nickel; sulphur, selenium, and tellurium—the product of the increase in volume which occurs on heating the element from 0° to 100° into the atomic weight is a constant—*e.g.* for sulphur, 0·035408 × 32 = 1·2330; selenium, 0·017610 × 78 = 1·3657; tellurium, 0·010634 × 127 = 1·3505. P. de Heen also has shown that the product of the coefficient of expansion and the absolute temperature of fusion is a constant or a multiple of this constant for compounds which are chemically related, and crystallize in the same system.

The above relations are either wholly empirical, or else they are based upon quite arbitrary or empirical assumptions as to the constitution of matter. Some of them may at times be useful in making approximations when observational data are wanting. They are also instructive in revealing the probability of the near discovery of a great law which will co-relate all the so-called physical constants of the metals, and include these empiricisms as special cases of restricted application. There is another side to this. By the substitution of one or more of these various formulæ in others, it is possible to obtain an indefinitely large number of equations correlating various physical properties. The changes can also be rung with the different forms of the gas equation. Consequently, a game of permutations and combinations can be played in physical chemistry just as in organic chemistry a similar game is possible with the methyl, ethyl, propyl, . . . radicles. C. F. Schönbein[13] said:

> I regard the discovery of thousands and thousands of new organic compounds in the same light as I do the infinite number of figures which may be produced by the kaleidoscope. What would the world say of a man who should take the trouble to shake for whole years that plaything, and describe minutely all the shapes (pretty as they might be) he had obtained from his operation ?

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§ 21. The Kinetic Theory of Liquids

> It must be remembered that in every dynamical investigation, what the mathematician really investigates is not the problem presented by nature, but some simplification of it. . . . For any purpose which is of use to man, the approximation arrived at by the simpler problem is sufficient, wherever the errors are of such a nature that they are not cumulative. Nevertheless, it should be clearly recognized that it is a mechanism illustrating nature, and not nature itself, that has been mathematically investigated.—G. J. STONEY (1895).

The molecules of a liquid seem to have less freedom for movement than gases, although the molecules are sufficiently mobile to allow the liquid to take up, more or less quickly, the shape of the containing vessel. The mobility of liquids is indeed their most obvious quality. It is very probable that the kinetic energy of the translatory motions of the molecules of a liquid and its vapour, at the same temperature, are equal.[1] A molecule can, in time, travel to any part of the liquid mass. The rate of diffusion of one liquid in another shows that the movements are rather slow, probably because a molecule in its travels must be continually abutting against other molecules. The number of molecules in a gram-molecule of a compound is approximately 6×10^{23}; and for a non-associated liquid, say fluobenzene with a gram-molecular volume of 91·7 c.c., the volume of the molecular domain is $1·5 \times 10^{-22}$ c.c. Consequently, the average distance between the centres of adjacent molecules is of the order 7×10^{-8} cm., which is the same order of magnitude as the diameter of the molecules. Further, while the intermolecular attraction with gases is relatively small, the attraction between the molecules of a liquid must be greater because of the closer packing. Again, approximately 1700 c.c. of steam at 100° condenses to one cubic centimetre of liquid water at the same temperature, so that the average distance between the molecules of the liquid must approximate at least to the cube root of 1700, that is, about one-twelfth of the average distance between the molecules of the gas. The slow evaporation of liquids also shows that the molecules possess a certain mobility, and that the velocities of the moving molecules are not all the same.

The resistance offered by liquids to compression is very great; a fluid can support a stress only when the stress is uniform in all directions. For example, one c.c. of water at about 10° is reduced 0·000048 c.c. per atmosphere, or each additional atmosphere pressure brings the particles $\sqrt[3]{0·000048}=0·036$, *i.e.* about one-thirtieth nearer to one another, provided the volume of the molecules remains constant. The fact that a liquid readily changes its shape but strongly resists any force tending to diminish its volume, is taken to indicate that the potential energy depends only on the mean distance between the molecules, and not on their configuration. The small variation in the volume of liquid with increasing pressure has led to the idea that the molecules are very close together. On the other hand, this result, at first sight, is not parallel with the effect of temperature on the volume of a liquid, for water at 10° will contract nearly six times as much in cooling to 4°.

P. S. de Laplace (1806)[2] assumed that the molecules of a liquid attract one another with a force which extends over a very short distance which he called the *radius or sphere of molecular attraction*. The range of this action has been shown to be nearly 5×10^{-7} cm., for many experimenters have found that cohesion is inappreciable at greater distances. It is assumed that if it were not for the relatively great intermolecular attractive forces, the molecules of a liquid would travel in approximately straight lines; as it is, they are supposed to describe curved paths.

In any given liquid, the attractive forces tending to draw the molecules closer together are balanced against the centrifugal forces or the tendency of the molecules, so to speak, to move tangentially outwards away from the curved path. This tendency to move outwards is proportional to the square of the mean velocity V of the molecules, and inversely as the radius of curvature r of the path; for, with a molecule of mass M moving on a circular path, the centrifugal force is equivalent to MV^2/r; and, if the attractive force for unit distance be F, then, for equilibrium,

$MV^2/r=Fr$. The radius of curvature is probably very small and of molecular dimensions; accordingly, the intermolecular attraction R must be proportionally great. If the speed of the molecules be reduced by cooling, the centrifugal tendency is lessened, the attractive forces predominate, and the molecules move closer together into a new position of equilibrium. Accordingly, the liquid contracts in volume; and it also becomes more viscous owing to the greater difficulty experienced by the molecules in moving away from the sphere of one another's influence against intermolecular attraction. Isothermal compression also brings the molecules closer together—this favours the inward attractive forces; but the kinetic energy of the molecule is at the same time augmented—this increases the speed of the molecules, and strengthens the centrifugal forces which make the liquid resist further compression.

The cohesive attraction of the molecules of liquids.—The resultant of the mutual attraction of molecules simulates an inward pressure which opposes a resistance to the forces tending to enlarge its volume. Consider two layers of molecules in proximity to one another; the resultant attraction of molecule for molecule will be proportional to the number of attracted and attracting molecules, that is, to the square of the number of molecules. The number of molecules in unit volume of a liquid or solid will be proportional to the density, D, so that if a be the constant of proportion, the **intermolecular attraction,** the **internal pressure,** the **cohesive pressure,** or the **intrinsic pressure,** P—as Lord Rayleigh[3] called it—will be $P=aD^2$; and if v denotes the volume occupied by one gram of the substance, $P=a/v^2$, which is the term employed for intermolecular attraction in J. D. van der Waals' equation. The relation av^{-2} also follows directly from the assumption that the molecular attraction varies inversely as the fourth power of the distance of the molecules apart. The magnitude of the intrinsic pressure for water, determined by two independent methods, is very great—approximately 11,000 atm.; carbon disulphide, 2900 atm.; ethyl alcohol, 2400 atm.; and for ethyl ether, 1300 atm. P. S. de Laplace[4] was surprised at the magnitude of his own estimate of this pressure, for he obtained what he called *une aussi prodigueuse value qui ne peut pas être admise avec vraisemblance*—approximately 10^{12} tons per sq. in. The intrinsic pressure is a measure of the cohesion of a liquid or solid, that is, it measures the force—tensile strength—required to separate one portion of a liquid from another. **Laplace's constant** K is equivalent in meaning to J. D. van der Waals' av^{-2}; and T. Young estimated that the surface tension σ of a liquid is equal to one-third the total cohesive force, P, into the radius r of the molecule, or $\sigma=\frac{1}{3}rP$.

The intrinsic pressure of liquids.—The intrinsic pressures of a liquid calculated from J. D. van der Waals' equation and from A. Dupré's relation between the internal latent heat of vaporization are somewhat discrepant. The former gives 10,500 to 11,000 atm., the latter 23,900 atm. The discrepancy has been attributed (i) to the invalidity of the assumption that the density of the liquid in the surface layer is the same as in the bulk of the liquid, and G. Bakker therefore assumes that there is a gradual decrease in density in passing from the liquid to the vapour phase; and (ii) to the assumption that the molecular forces have no temperature effect, whereas it is certain that the intrinsic pressure P decreases as the temperature rises, and W. C. McC. Lewis[5] shows that the relation between the intrinsic P pressure and temperature T probably has the form $P=a+b\log T+cT$, where a, b, and c are constants. The different expressions which have been suggested for evaluating the intrinsic pressure have been compiled by W. C. McC. Lewis.

In 1869, A. Dupré suggested that the intrinsic pressure is equal to the internal work done per unit volume of liquid against the molecular attracting forces when the molecules are drawn apart until they are outside the range of their mutual attractions. Hence, A. Dupré assumed that the work done against intrinsic pressure, P, is equal to the internal latent heat per unit volume λ, or $P=\lambda$; but W. C. McC. Lewis emphasized that this can be true only when P is independent of temperature, and that the true relation probably has the form of H. von

Helmholtz's free energy equation $P=\lambda+T(dp/dT)_v$; and H. Davies has shown that dP/dT is equal to $-4R/v_c$; to $-R/b$; or to $-14{\cdot}8p_c/T_c$, which enables P to be calculated from observed values of λ and the critical constants.

A. Dupré showed that if β denotes the coefficient of compressibility, and a the coefficient of cubical expansion, J. D. van der Waals' equation furnishes the relation $P=-Ta/\beta$, on the assumption that P is independent of the temperature. The original edition of J. D. van der Waals' thesis also showed that if v be the volume of a given mass of vapour, v_1 the volume of the same mass of liquid, a the coefficient of gaseous expansion, and β the compressibility of the liquid, then, at $\theta°$, $P^2=v(1+a\theta)/v_1\beta$, and I. Traube has applied this result to liquid and solid elements.

T. W. Richards assumed that the heat C required to raise the temperature of unit volume by the amount dT, is equivalent to the intrinsic pressure P such that $P=CdT/dv$, on the assumption that P is independent of temperature and volume. C is here the atomic heat—approximately 6. The numerical values obtained with the elements are very large. I. Traube showed that T. W. Richards' expression gives very nearly three times the values obtained by J. D. van der Waals' expression, and he therefore writes $P=\frac{1}{3}CdT/dv$. C. Benedicks also deduced the expression $P=av^{-2}$ of J. D. van der Waals' equation, and assuming that a is independent of temperature and a denotes the coefficient of cubical expansion, he found $P=R(a^{-1}+2T)v^{-1}$, or approximately $P=R/va$, which is virtually equivalent to T. W. Richards' expression only if C were put equal to R. R. H. Davies obtained the expression $P=4R/av_c$, where v_c denotes the critical volume, and a the coefficient of cubical expansion, which H. Davies found to be equal to $(2T_c-T)-1$. At absolute zero, this reduces to $P=8RT_c/v_c$.

J. D. van der Waals' equation may be written $(p+P)(v-b)=RT$, where p denotes the external and P the internal pressures, and b the limiting molecular volume at the absolute zero. Accordingly, if the small pressure p be neglected in comparison with the large pressure P, it follows that the intrinsic pressure, $P=RT/(v-b)$. C. M. Guldberg extrapolated Cailletet and Mathias' linear diameter to absolute zero, and found the densities of a number of substances at absolute zero and at the critical temperature, the ratio being practically a constant 3·75 or $b=0{\cdot}27v_c$, for substances. D. Berthelot also found for oxygen, chlorine, carbon dioxide and sulphur dioxide, carbon tetrachloride, and benzene, $b=0{\cdot}26v_c$. The results furnished by calculating the numerical value of $P=RT/(v-b)$ at 0° on these assumptions represent minimum values of P, because the values of b are not likely to be independent of temperature, since b probably increases as the temperature rises. Taking P. Walden's or S. Young's values of v_c, the molecular critical volume, $b=0{\cdot}27v_c$; and v the molecular volume at 0°, the intrinsic pressures P at 0° of 36 liquids were calculated by W. C. McC. Lewis in atm. per sq. cm.

TABLE XXXI.—INTRINSIC PRESSURES OF LIQUIDS.

	v_c	b	v	$v-b$	P
Water	50·3	13·58	18·00	4·42	5084
Methyl alcohol	117·6	31·75	39·5	7·75	2898
Ethyl alcohol	166·9	45·06	56·1	11·04	2035
Carbon disulphide	166·0	44·82	58·78	13·98	1610
Benzene	256·1	67·15	86·7	20·55	1093
Carbon tetrachloride	276·2	74·57	94·3	19·73	1138
Ethyl ether	281·9	76·11	100·5	34·39	1653
Stannic chloride	351·8	94·99	114·5	19·51	1135

The relation between intrinsic pressure and surface tension.—The conception of an internal, intrinsic, molecular, or cohesive pressure presupposes the existence of attractive forces between the molecules diminishing rapidly with distance.

G. N. Antonoff has deduced a relation between the surface tension and the internal pressure on the assumption that the attractive force between the molecules is electro-magnetic in nature, and that the molecules can be treated as if they were electro-magnetic doublets. If P denotes the molecular or internal pressure; σ, the surface tension; n, the number of doublets or molecules in unit volume of liquid; D, the specific gravity of the liquid; M, its molecular weight, and $1{\cdot}64\times10^{-24}$, the weight of an atom of hydrogen, then $n=1{\cdot}64\times10^{24}D/M$, and therefore $P=2\sigma n^{\frac{1}{3}}$. Hence, if the surface tension of benzene be 32 dynes per cm.; the molecular weight, 78; and the specific gravity, 0·890; then $n=6{\cdot}8\times10^{21}$, and $P=12\times10^{6}$ dynes per sq. cm., a magnitude very nearly equal to 1200 atm.

Since the surface tensions and intrinsic pressures of liquids are closely related, it follows that when the exact connection between the various physical properties of the one is known, their relations with the other follow as a matter of course. S. W. Smith [6] assumed that the surface tension σ of some liquid metals is related with the intrinsic pressure P by the empirical formula: $\sigma=200+0{\cdot}00437P$, when σ is expressed in dynes per cm., and the intrinsic pressure P in megabars—10^6 dynes—per sq. cm. P. Walden found for a number of organic liquids $P=1{\cdot}82\sigma$, when the surface tension is determined at the boiling point. Otherwise expressed, the intrinsic pressure of a liquid at its boiling point is proportional to the surface tension at the boiling point. The relation between the surface tensions or intrinsic pressure and some other physical properties of liquids is shown in S. W. Smith's Table XXXII. The elastic moduli and the other properties run parallel with the surface tensions.

TABLE XXXII.—RELATIONS BETWEEN THE PHYSICAL PROPERTIES OF SOLIDS AND SURFACE TENSION.

	Surface tension (fluid) dynes per cm. σ	Internal pressure (solid) megabars, P	Compressibility per atomic vol. per megabar, $\times10^6$	Elastic modulus.	Atomic concentration, sp. gr. ÷ atomic wt.	Hardness.
Lead . .	424	51,500	40·04	1,800	0·0550	1·0
Tin . . .	480	68,700	25·92	5,000	0·0619	2·5
Aluminium .	520	119,300	13·13	7,200	0·0821	—
Zinc . . .	707	108,900	13·70	—	0·1077	6·0
Silver . .	858	161,900	8·65	7,300	0·0963	—
Gold . .	1018	178,500	4·79	8,100	0·0979	—
Copper . .	1178	236,100	3·83	12,400	0·1364	8·0
Iron . . .	(1244)	239,000	2·84	20,900	0·1375	15·0
Nickel . .	(1538)	306,300	1·76	—	0·1408	—

The relation between intrinsic pressure and latent heat.—J. E. Mills (1902) [7] assumes that the resultant attraction between two molecules varies as the square of the distance of the molecules apart, and is a mutual property of each pair of molecules, so that the resultant attractive force $F=km^2/r^2$, where r denotes the distance apart of the two molecules—each of mass m; and k is the attraction constant whose numerical value is dependent on the nature of each of the attracting molecules. Consequently, the assumed law of molecular attraction differs from the attraction of gravitation in being dependent on the nature of the molecules and not solely dependent on their mass. If L denotes the observed heat of vaporization; E, the work of expansion against external pressure; D_1, the density of the liquid; and D that of the vapour, J. E. Mills finds that

$$\frac{L-E}{\sqrt[3]{D_1}-\sqrt[3]{D}}=\text{Constant}$$

If a mass of liquid of volume v has n particles at a distance r apart; and if V denotes the volume of the same mass in the gaseous state when the molecules are a distance R apart, the work W expanded in tearing the molecules asunder, against the assumed intermolecular attraction, during vaporization will be

$$\int_R^r F.dr = km^2\int_R^r \frac{dr}{r^2};\text{ or, } W = km^2\left(\frac{1}{r}-\frac{1}{R}\right)$$

Again, if L denotes the observed heat of vaporization, and E represents the work spent in overcoming the external pressure of the atmosphere during vaporization, the work W required to pull apart the n molecules of mass m will be $W=nm(L-E)$. Note that v and V respectively denote the volumes of the liquid and vapour, each containing n molecules of mass m, $r=\sqrt[3]{v/n}$, and $R=\sqrt[3]{V/n}$; and that the density D_1 of the liquid is $D_1=nm/v$, and of the vapour, $D=nm/V$; substituting for D_1 and D, in the two preceding values of W; and remembering that k, m, and n are constants. Mills' expression follows at once.

The work E spent in overcoming the external pressure by altering the distance apart of the molecules is calculated from the equation $E=0{\cdot}0000318p(V-v)$ cals., where p denotes the pressure of the air in millimetres of mercury, and V and v the respective volumes before and after expansion. The values of the constant for carbon disulphide at different temperatures selected from Mills' tables are indicated in Table XXXIII.

TABLE XXXIII.—MILLS' CONSTANT FOR CARBON DISULPHIDE.

Temperature.	Density of liquid, D_1	Density of vapour, D	Latent heat, L	External work, E	Mills' constant.
0°	1·2921	0·000966	90·00	7·24	82·22
20°	1·2775	0·000350	89·06	7·48	82·38
40°	1·2321	0·0024	85·64	8·10	82·71
60°	1·2003	0·0044	82·87	8·42	82·85
80°	1·1684	0·0075	79·70	8·67	82·82
100°	1·1684	0·0120	76·14	8·85	82·61
120°	1·0997	0·0182	72·18	8·94	82·23

J. E. Mills also found that out of 435 observations on 26 different non-associated liquids over ranges of temperature, only 30 differed from the mean value of the constant for the specific substance in question by more than 2 per cent. and only four of the 30 by more than 5 per cent. The data thus support the assumption that the molecular attraction (i) is independent of the temperature; (ii) varies inversely as the square of the distance apart of the molecules; and (iii) is a constant for any particular substance.

G. N. Antonoff showed that the relation between the internal pressure and the surface tension is the same whatever be the law of attraction between the molecules. For many purposes, therefore, it is not necessary to specify the attractive forces other than that they diminish rapidly with the distance. R. D. Kleeman[8] has also shown that it is possible to obtain an infinite number of formulæ for the surface tension of a liquid, and each of these formulæ corresponds to a law of molecular attraction, so that any number of laws of attraction will give latent heat formulæ agreeing with facts. All these laws of attraction are but fragments of a general law which must contain an arbitrary function of the distance between the attracting molecules and their temperature. J. E. Mills argues that a change of temperature does not change the nature or magnitude of molecular attraction, but rather determines the orbit the molecules will follow in obedience to the attractive force. In reply to R. D. Kleeman's proof that the molecular attraction must decrease at a much greater rate with the distance of the molecules than is given by the law of inverse squares, J. E. Mills postulates a mutual absorption or cancellation of the whole or part of the attractive force when this attraction is exerted upon other particles.

W. Sutherland (1893)[9] used the hypothesis that the intermolecular attraction varies inversely as the fourth power of the distance apart of the molecules; R. D. Kleeman (1910) examined a fifth power law; A. Albertosi (1915) a sixth power law; and P. de Heen a seventh power law. The fifth power law proposed by J. C. Maxwell in 1866 was abandoned by him in 1879. Newton's gravitational law thus includes but one term in a possible series:

$$F=ar^{-2}+br^{-3}+cr^{-4}+dr^{-5}+\ldots$$

where the coefficients b, c, d, . . . are so small that they can be neglected except where r is itself small.

P. S. de Laplace's formula for the pressure P within a sphere of liquid of unit radius is $P=K+H$, where Laplace's constant K involves the intrinsic pressure, and the term H involves the surface tension. A high intrinsic pressure is accompanied by a large surface tension. The intrinsic pressure has been related with the surface tension, the coefficient of thermal expansion, molecular volume, compressibility, vapour pressure, viscosity, etc. If the attractive forces between the molecules, or the intrinsic pressure, be very great, the coefficient of thermal expansion as well as the compressibility and viscosity will be smaller than when the attractive forces are small. Similarly also the latent heat of vaporization of a liquid will be larger when the molecular attraction is great than when the molecular attraction is small. Consequently, a large latent heat, a small compressibility, a small coefficient of thermal expansion, and low viscosity should run together. This is illustrated qualitatively in Table XXXIV. An enormous number of changes have been rung with formulæ connecting the various physical properties of liquids. In a general way, it may be said that when a relation has been found to obtain between certain physical properties of a liquid over a certain range of temperature, it is almost sure to be applicable to other liquids over a similar range of temperature.[10] This probably also applies to the so-called associated liquids; for the apparent failure with these is mainly due to the use of incorrect molecular weights; with corrected molecular weights the associated liquids would also fall in line with other liquids. If the physical properties are markedly constitutive, that is, are dependent upon the inner structure of the molecule—the formulæ are not general—*e.g.* viscosity, latent heat, specific heat, surface tension. Of course every physical property is to some extent constitutive, and small deviations are found, but in view of the sparsity of accurate and comparable observational data, the general agreement just indicated is rather striking.

TABLE XXXIV.—SOME EFFECTS OF MOLECULAR ATTRACTION IN LIQUIDS.

Liquid.	Molecular latent heat, Cals.	Coefficient thermal expansion.	Compressibility.	Viscosity at 0°.
Mercury	12·4	0·00018	0·000004	0·0168
Water	11·1	0·00006	0·000053	0·0178
Alcohol	9·6	0·00103	0·000112	0·0177
Carbon tetrachloride	7·9	0·00124	0·000125	0·0133
Chloroform	7·9	0·00127	0·000128	0·0071
Carbon disulphide	6·8	0·00146	0·000174	0·0044
Ether	6·5	0·00166	0·000176	0·0029
Sulphur dioxide	6·2	0·00215	0·000303	—

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§ 22. The Surface Tension and Surface Energy of Liquids and Solids

Capillary force may be considered as the first degree of chemical affinity.—M. L'HERMITE (1855).

The molecular forces at the surface of a liquid do not produce the same effects as in the interior. In the interior of a liquid, the molecules are attracted equally in all directions, those at the surface are attracted inwards, in a direction perpendicular to the free surface. The surface tension, of course, is not the cause but rather a consequence of the internal pressure. The effect of this inward pressure is in many respects analogous with what would obtain if the surface was enveloped by an elastic membrane in a state of tension. The tension is called the **surface tension** or **surface pressure** of the liquid. For equilibrium, the surface tension of a given liquid is the same in all directions and at all points on the surface. There is a difference between the tension of the imaginary membrane and the actual tension, or inward pressure of the free surface of the liquid, in that when the surface of the liquid increases, it does so by exposing fresh particles, and not by stretching the old surface of the liquid in the sense that indiarubber would be stretched. The elastic membrane is merely an analogy to assist the mind in forming a concept of a number of different phenomena ; but it does not enable us to form a satisfactory mental picture of the distribution of the molecules in the surface film of a liquid. It is therefore convenient to regard liquids as if they were enclosed in a contractile membrane in a state of uniform tension which makes the free surface the smallest that circumstances will allow. The sphere has the smallest surface of any given mass of liquid, consequently, drops of liquid assume the form of a sphere, unless they are so large that gravitation can exert an appreciable influence, and flatten the drop to a thickened disc. The smaller the drops the more nearly do they approach perfect spheres.

EXAMPLES.—(i) Mercury globules on a flat board show the phenomena well. (ii) By suspending a drop of, say, ortho-toluidine in a 3 per cent. solution of sodium chloride large spherical drops 5 to 6 cm. diameter are easily obtained since the effect of gravity on the drop is cancelled, so to speak, because the drops are suspended in a liquid of the same density they are themselves. Similarly, (iii) soap-bubbles in air are spherical, and they would remain suspended therein and not sink if it were not for the actual weight of the film of soap solution.[1]

In the case of liquid crystals, the surface tension of the crystals tends to make them assume the form of spherical globules, but this is opposed by the special molecular force—the *Gestaltungskraft* of O. Lehmann—which makes normal crystals assume their characteristic forms. Hence, photographs show that the liquid crystals of some substances are spherical, while others have pyramidal forms with more or less rounded edges.

The pressure in the space enclosed by a spherical liquid surface.—Imagine the liquid sphere to be divided into two hemispheres by an imaginary plane. Let r be the radius of the sphere; p, the pressure at any point inside; and σ, the surface tension. The only forces acting on the hemisphere $ABCD$, Fig. 16, are (i) a thrust on the plane face ABC, due to the pressure of the liquid in the half sphere not shown in the diagram, and which is equal to the pressure $p \times$ the area of ABC, *viz.* πr^2; and (ii) the tension of the surface acting round the edge of the circle ABC, and which is equal to σ times the perimeter ABC, that is, to $\sigma.2\pi r$. These two forces are in equilibrium, and therefore balanced so that $p\pi r^2 = \sigma 2\pi r$. Hence, the pressure $p = 2\sigma/r$, that is, the pressure is inversely proportional to the radius of the sphere; it is produced by surface tension only; and is the excess of the internal over the external pressure. If a soap-bubble be in question, there are two surfaces, each of which exerts a pressure $2\sigma/r$, so that the pressure within a soap-bubble is $4\sigma/r$. The same reasoning coupled with hydrostatic pressure can be applied to gas-bubbles rising in a liquid.

FIG. 16.

A liquid boils when the bubbles of vapour formed in the interior can rise and escape at the surface. The pressure of the vapour within a bubble at a depth h below the liquid is equal to the pressure of the atmosphere plus the pressure equal to the weight of a corresponding column of liquid of height h, and $2\sigma/r$. If the pressure of the vapour within the bubble be less than this, the bubble must collapse. The smaller the bubble, the smaller the value of r, and the greater the pressure of the vapour. Hence the temperature of a liquid must be much higher to maintain small than to maintain large bubbles in equilibrium. If there are no facilities for producing bubbles which are fairly large to start with, the temperature may rise above the boiling point until a large bubble is formed—this may give rise to **bumping,** or portions of the liquid may be projected from the vessel, with explosive violence. The presence of a small piece of capillary, closed at one end, and filled with air, enables the vapour of the liquid to be formed in the interior, and fairly large bubbles to be formed at the open ends. This explains how the presence of these capillary tubes, porous earthenware, charcoal, etc., enables liquids to boil steadily without bumping.

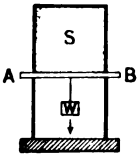

FIG. 17.—Surface Tension of Liquids.

Surface tension is evidence of the presence of cohesive forces between the molecules of a liquid. J. C. Maxwell[2] illustrated surface tension by supposing a film of liquid S, Fig. 17, to be stretched on a wire framework, and attached to a light wire AB, and a weight W. Assume the part of the wire wetted by the film is of unit length. The force exerted per unit length of the stretched film is termed the **surface tension.** It is usually more convenient to consider not the actual surface tension or force acting on the surface of the liquid, but rather the energy associated with that surface, the so-called **surface energy.** If W just supports the stretched film, the surface tension σ of the film is equal to $\frac{1}{2}W$, because there are two surfaces to the film. If the weight suffices to stretch the film a distance s, the work performed against surface tension will be the product $2\sigma s$. The potential energy of the surface of the film has therefore increased by an amount $2\sigma s$; and each side of the film has increased by an area s; hence, the increase of energy per unit area is $2\sigma s/2s = \sigma$. Hence if W denotes the surface energy per unit area, $W = \sigma$. Consequently, the surface tension of a liquid is equal to the work done in enlarging the surface of the liquid by one sq. cm., under isothermal conditions, although it is not permissible to define surface tension as the energy per unit area of the surface of a liquid. The surface tension in dynes per cm. is numerically equal to the surface energy expressed in ergs per sq. cm.; the surface tension may be expressed in dynes per cm.; in grams per cm.; or in mgrm. per mm. In converting from one system of units to another, the number of grams multiplied by 980 furnished the equivalent in dynes; and mgrm. per mm. multiplied by 9·8 changes the result into dynes per cm.

There are several more convenient methods of measuring surface tension. When a capillary tube is plunged vertically in a liquid, the surface tension inside the tube ranges over the liquid within the circumference of the *capillus* or internal bore, and the liquid rises, *A*, Fig. 18, or falls, *B*, Fig. 18, below the level of the liquid outside the tube, according as the liquid wets, *A*, Fig. 18, or does not wet, *B*, Fig. 18, the walls of the tube. The vertical component of the surface tension between the liquid and the walls of the tube at the level of the liquid within the tube acts along a ***length*** equivalent to the circumference of the internal bore, *i.e.* $2\pi r$; and at an *angle* α—called the *angle of contact*, or edge angle—between the normal to the free surface, and the tangent to the liquid surface, where it meets the solid walls. Consequently, the vertical component of the surface tension at the point of contact between liquid and solid is equivalent to $2\pi r \times \sigma \times \cos \alpha$. This is balanced by the weight of the column of liquid within the tube which is above the level of the liquid outside the tube; or, if the liquid does not wet the tube, by the column of liquid which is held back by the surface tension. If h denotes the height of this column, the volume of this liquid is $h\pi r^2$, and if D be the density of the liquid, and g the acceleration of gravity, the weight of this column of liquid is $h \times \pi r^2 \times D \times g$ dynes. When these two forces are balanced, or in equilibrium, $\sigma \times 2\pi r \times \cos \alpha = h \times \pi r^2 \times D \times g$ or $\sigma = \frac{1}{2}ghrD/\cos \alpha$ dynes, which represents the surface tension in terms of the height h of the capillary effect; the radius r of the tube; the density D of the liquid; and the constant angle α. When the contact angle is nearly 180°, cos α approaches unity, and the surface tension can be experimentally measured from the formula $\sigma = \frac{1}{2}ghrD$. Sometimes, the relation rh or $2\sigma/D$ is called the **specific cohesion** of a liquid, and it is symbolized by a^2, such that $a^2 = 2\sigma/D = rh$. For example, if the density of water is unity, and the surface tension 7·25, the value of a^2, the specific cohesion is 14·50. The surface tension can also be measured from the wave-lengths of ripples on clean surfaces;[3] from the number of drops which fall from a given orifice in a given time; etc.

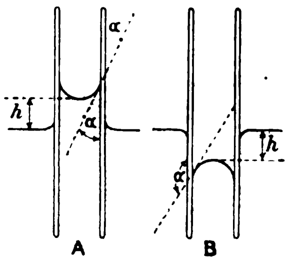

FIG. 18.—Contact Angle.

Numbers ranging from 7·13 to 7·945 mgrm. per mm. have been published for the surface tension of water at 18°; and from 39·23 to 55·78 for mercury at 20°. The surface tensions of a few liquids in dynes per cm. are:

Mercury (18°).	Water (20°).	Carbon disulphide (20°).	Chloroform (20°).	Carbon tetrachloride (20°).	Alcohol (20°).	Ether (20°).
440	75	32·7	25·68	21·6	26·3	15·9

The kinetic theory of vaporization would lead to the assumption that the properties of a liquid surface must be radically different if it is in contact with another liquid instead of its own vapour. At the boundary surface of the gas-liquid system the mean free paths of the molecules are of a very different order of magnitude, while at the surface of the liquid-liquid system, the mean free paths will be of the same order of magnitude and characteristic of each liquid. M. Planck and M. Cantor[4] believe that the surface of a liquid when in contact with another liquid retains the same properties as it had when in contact with its own vapour. Two liquids of limited solubility are in equilibrium when each liquid is saturated with the other, and D. Konovaloff showed that the saturated vapours emitted by each of the two layers of liquid have the same vapour pressure, and the same vapour composition although their own composition is very different. G. N. Antonoff believes that the surface tensions of the layers of the two liquids of limited miscibility are identical in the two contact planes. Lord Rayleigh's hypothesis led to the conclusion that the surface tension σ_{12} at the limiting surface of the two liquids with the respective surface tensions σ_1 and σ_2 when in contact with their own vapour is given by $\sqrt{\sigma_{12}}=\sqrt{\sigma_1}-\sqrt{\sigma_2}$; but G. N. Antonoff did not find this formula to agree with experiment, and he has shown that the interfacial surface tension σ_{12} is equal to the difference of the surface tensions against air of the two superposed liquids in equilibrium such that $\sigma_{12}=\sigma_1-\sigma_2$, so that two superposed liquids, of limited solubility and in equilibrium, must be regarded as solutions in the same solvent; and he also believes that they contain an equal number n of molecules per unit volume so that $n_1=n_2$, by A. Avogardo's hypothesis, for, says G. N. Antonoff, "if two solutions in the same solvent have the same freezing and boiling points, as is the case with two superposed liquids of limited solubility and in equilibrium, they must contain an equal number of molecules in unit volume." This is possible only when the molecules of the one component B form a compound with some of the molecules in the solution, and any further addition of B would not increase the number of molecules present in the solution. Hence, all properties depending on the number of molecules and not on their dimensions remain invariable.

The relation between surface tension and temperature.—According to D. I. Mendeléeff,[5] one characteristic of a perfect liquid is that its surface tension should be a linear function of its temperature, and this view was confirmed by A. L. Selby. The decrease of the surface tension with a rise of temperature is usually represented by a simple linear equation, for in most cases the surface tension σ at $\theta°$ is equal to $\sigma_0(1-a\theta)$, where σ_0 denotes the surface tension at 0°, and a is a constant characteristic of particular liquids.[6] Thus,

	Water from 0° to 70°.	Ether from 2° to 25°.	Alcohol from 5° to 72°.	Cadmium from 365° to 431°.	Lead from 389° to 498°.
a	0·0021	0·0060	0·0034	0·00042	0·00029

The ordinary linear equation $\sigma=\sigma_0(1+a\theta)$ and the parabolic equation $\sigma=\sigma_0(1+a\theta+b\theta^2)$ hold only over a very restricted range of temperatures, but they probably become very inaccurate when extrapolated far beyond the range of observation.

According to J. D. van der Waals,[7] the surface tension σ of a liquid at a temperature T, not far removed from the critical temperature T_c, is

$$\sigma=A\left(\frac{T_c-T}{T_c}\right)^{\frac{3}{2}}$$

where A is a constant independent of the temperature. At the critical temperature, both σ and $d\sigma/dT$ are zero.

Just as the kinetic energy of an ideal gas remains constant during an isothermal expansion, because the external work performed during the expansion is derived from the heat which enters the gas, so, when the surface of a liquid is stretched isothermally, the energy of the new surface is not equal merely to the mechanical work performed during the stretching, for an allowance must be made for the energy which enters or leaves the surface in the form of heat. The mechanical work performed when the surface of a liquid is increased is spent against molecular forces in bringing additional molecules within the surface-layer. If energy be expended in work against the cohesive forces during the stretching, the surface of the liquid will be cooled; and if the process be conducted isothermally, the inflow of heat will increase the surface energy; and the total surface energy will therefore be the sum of two factors; (i) The mechanical work σ performed against the intermolecular forces—with water at 0°, for example, this is equivalent to 75 ergs; and (ii) the inflow of heat—bound energy—required to maintain the temperature of the film constant during the stretching—with water at 0°, for example, this is equivalent to about 40 ergs. Lord Kelvin (1858),[8] by reasoning analogous to that employed in deducing H. von Helmholtz's equation, showed that the free energy, W, or the energy which is available for doing work, is then equal to the surface energy σ less the heat energy absorbed from the surrounding bodies, which is represented by the product of the absolute temperature and the temperature coefficient, $d\sigma/dT$, or the variation of surface tension with temperature is given by

$$W=\sigma-T\frac{d\sigma}{dT}\text{; or, }\sigma=W+T\frac{d\sigma}{dT}$$

The change of surface tension with temperature is a linear function over a considerable range of temperature, such that the surface tension σ at a temperature θ is, $\sigma=\sigma_0-b\theta$, where σ_0 and b are constants; accordingly, under these conditions, the temperature coefficient by the surface energy is a constant, or $d\sigma/dT=-b$, where the negative sign means that the surface tension decreases with increasing temperature.

P. S. de Laplace inferred that the ratio of the temperature coefficient of the surface tension and the coefficient of thermal expansion should be a constant, and this has been verified in a number of cases. For example, if σ_0 be the surface tension at 0°, and the surface tension σ at $\theta°$ is $\sigma=\sigma_0(1-a\theta)$; and if 3α be the coefficient of cubical expansion, the ratio $a/3\alpha$ is nearly constant:

	Benzene.	Alcohol.	Phenol.	Acetic acid.	Nitrobenzene.	Carbon disulphide.
σ_0	29·4	34·3	40·6	28·9	48·2	54·6
a	0.0035	0·0027	0·0029	0·0038	0·0028	0·0029
3α	0·00139	0·00124	0·00089	0·00116	0·00089	0·00121
$a/3\alpha$	2·5	2·2	3·3	3·3	3·1	2·0

Hence, the effect of temperature on the surface tension is largely an effect of the change of density. R. D. Kleeman [9] obtained the relation $\sigma=K(D_1-D)$ between the density of a liquid D_1 and of its saturated vapour D, when K is a constant dependent on the nature of the liquid. According to W. A. Kistiakowsky, at the absolute boiling point, T_b, the capillary rise a^2 in a tube of 1 mm. radium, is $a^2M=KT_b$, where M represents the molecular weight, and K is a universal constant with the same value, 0·00116 ± 0·004, for all non-associating liquids. By definition, their boiling points are proportional, and the constant $K=KT_b/MD_b{}^3$, where D_b denotes the density of the liquid at its boiling point. C. Schall found that the surface tension of liquids varies approximately as the 2⅔'s power of the density: $\sigma/D^{\frac{8}{3}}$=a constant. P. S. de Laplace's assumption that the surface density is the same as the density of the main body of the liquid failed to explain why the surface tension diminished with temperature more rapidly than the body density. By assuming that the densities of the surface film and the body of the liquid are markedly different, and that there is a corresponding difference of stress in the two regions, it will be understood how the rate of variation of surface density with temperature, as hinted at by C. Schall's rule, can be more rapid than that of the body density. This is evidenced by the heating of the upper film of liquid in a capillary tube producing a more marked effect than heating the liquid lower down. E. H. Amagat [10] also found that a stress of 3000 atm. diminishes the coefficient of thermal expansion of ether, between 0° and 50°, from 0·0017 at one atm. pressure to about one-third this value at 3000 atm. pressure. J. W. Gibbs (1876) also showed that the surface layer may be regarded as a special phase with its own characteristic density and entropy.

The relation between surface tension and compressibility.—As a rule the surface tension of highly compressible liquids is low,[11] provided there are no changes in the character of the molecules of the liquids under investigation. For example, representing the compressibility per atmosphere by β, and the surface tension by σ,

	Ether.	Acetone.	Alcohol.	Chloroform.	Benzene.	Water.	Mercury.
$\beta\times10^4$	190	121	105	103	92	48	3·83
	15·9	23·3	21·6	26·8	28·3	75	440

The product $\beta\times\sigma$ is not a constant, but, according to T. W. Richards and J. H. Mathews (1908),[12] the product of the surface tension σ of about thirty-seven organic liquids with the cube root of the fourth power of the compressibility κ, is constant. There are difficulties in comparing the compressibilities of different liquids, because the results are in part determined by the shapes of the molecules. I. Traube found that the product of the intrinsic pressure into the square root of the atomic (or molecular) compressibility is approximately constant for 14 elements in the solid state. Impurities in the metals may disturb the relation, for small traces of foreign matter may have exerted marked effect on the internal pressure.

The relation between surface tension and latent heat of vaporization.—J. J. Waterston [13] made one of the first attempts to connect the surface tension, σ, with the molecular latent heats of evaporation, $M\lambda$, and the molecular volumes, v. His expression $M\lambda=k\sigma v^{\frac{2}{3}}$—where k is a constant—is but a rough approximation, which, according to R. Eötvös, gives better results if the data for different substances are determined for corresponding states, *i.e.* at their critical temperatures, or the same temperatures reckoned downwards from the critical temperatures as zero. J. Stefan [14] has shown that the observed heat of vaporization, L, expressed in suitable units, is equal to the internal work performed in transforming the liquid into vapour; and that this, in turn, is equal to the product of the volume v of the liquid, and the difference in the internal pressure P and the vapour pressure of the liquid p. Otherwise expressed, $L=(P-p)v$. G. Bakker (1888) regards P as the internal or cohesive pressure per unit area across any section in the interior of the liquid. In that case, Pdv represents the internal work done when a liquid expands by dv; and, if the liquid changes its state so that v_0 volumes of liquid become v_1 volumes of vapour, at the same temperature, the observed latent heat will be $L=Pdv+p(v_1-v_2)$; and the internal latent heat will be $\lambda=\int Pdv$. G. Bakker further assumed that K is a function of v such that $P=Av^{-2}$, so that the internal latent heat

$$\lambda=A\int_{v_0}^{v_1}\frac{dv}{v^2};\ \lambda=A\left(\frac{1}{v_0}-\frac{1}{v_1}\right);\ \text{or, }\lambda=\frac{A}{v_0}$$

when the volume v_1 is very large compared with v_0. If A is independent of temperature the internal latent heat will be identical with av^{-2} in J. D. van der Waals' equation, and accordingly will correspond with the assumption that the molecules attract one another inversely as the fourth power of their distance apart. The values of P calculated from this relation and also from the assumption that P is equivalent to the av^{-2} of J. D. van der Waals' equation, agree in a number of cases; but G. Bakker believes that A is a function of the temperature such that $A=a-Tda/dT$. Assuming that G. Bakker's A is equal to J. D. van der Waals' a at the temperature of vaporization, the

$$\text{Latent heat of vaporization, } L=\frac{a}{v_0}+\frac{RT}{M}$$

where v_0, being small in comparison with v_1, has been neglected and $p(v_1-v_0)$ becomes pv_1; and hence if M be the molecular weight of the vapour, and Boyle-Charles' law obtains, $pv=RT/M$. Calculations [15] based on this relation do not agree very well with the observed latent heats.

P. Walden [16] has indicated a number of relations between the surface tension and the latent heat of vaporization L in calories. If L_b and L_m respectively denote the latent heats of weight; and σ_b and σ_m, the surface tensions at the boiling and melting points respectively: vaporization and fusion; v, the molecular volume; D_b and D_m, the density; M, the molecular $D_bL_b=34{\cdot}8\sigma^b$; $ML_b=3{\cdot}64v\sigma_b$; $D_mL_m=7{\cdot}2\sigma_m$, provided the liquids do not form more normal complex molecules than is indicated in the normal formula weights. D. L. Hammick gives the relation $6\sigma V/d=L$, where d denotes the molecular diameter; L the internal latent heat; and V the gram-molecular volume.

E. T. Whittaker found empirically that for about half a dozen liquids, the surface energy σ of a liquid in contact with its own vapour is proportional to the product of the internal latent heat λ and the absolute temperature T. Accordingly. $\sigma=kT\lambda$, where k is a constant which R. D. Kleeman computed to be equal to $0{\cdot}557M^{\frac{1}{3}}D_c/T_c$, when D_c and T_c respectively denote the critical density and critical temperature. E. T. Whittaker's rule is but an empirical density approximation. Several other relations between the molecular internal latent heat, $M\lambda$, and the densities of the liquid, D_1, and saturated vapour, D, have been proposed.[17] C. Dieterici (1908), for instance, suggested $M\lambda=kT \log (D_1/D)$; R. D. Kleeman and A. J. Batschinsky, $M\lambda=k_1(D_1^2-D^2)$, where k and k_1 are constants dependent on the nature of the liquid. The changes have been rung on these relations by substitutions with the various vapour pressure formulæ. R. Clausius and E. Clapeyron's equation, Trouton's relation, R. Eötvös' rule, and many other subsidiary relations have been obtained. W. C. McC. Lewis deduced a relation between the latent heat of vaporization, L, of a liquid and the product of absolute temperature, T, and the coefficient of thermal expansion a divided by the product of the density D and the coefficient of compressibility κ at constant volume, such that $L=-Ta/D\kappa$. L. Henry found this relation agrees very well with a number of observations but for the exceptional behaviour of water,[18] the alcohols, and the fatty acids, for which there is a large amount of evidence pointing to irregularities in the molecular structure.

J. D. van der Waals [19] deduced a form of Trouton's rule from his equation of state $M\lambda/T_c$ is a constant, where T_c denotes the critical temperature; and further that the latent heat of vaporization of all substances is independent of the temperature reckoned from the critical temperature. This does not agree with experiment. Several other more or less empirical relations have been obtained. Thus, P. de Heen [20] obtained from his theory of fluids $C_l-C_g=1{\cdot}333a\lambda$, when C_l and C_g respectively denote the specific heats of liquids and gas; a, the coefficient of expansion; and λ, the latent heat of vaporization; A. Nadejedine, $\lambda=kCp$, when k is a constant; C, the specific heat of the liquid; and p, the pressure under which evaporation proceeds; O. Tumlirz, $\lambda=0{\cdot}67537\gamma T/D$, which can easily be reduced to Trouton's rule.

The relation between intrinsic pressure and solubility.—P. Walden [21] has compared the intrinsic pressures of a number of liquids with their solubilities in water, and found that they run parallel with one another, for the mutual solubility of two liquids was found to be greater, the smaller the difference in their intrinsic pressures; and if this difference is very great, the two liquids are immiscible. S. W. Smith (1917) illustrates this rule by the cases of silver and gold, and of zinc and lead. The ratio of the intrinsic pressures with the former pair of metals is as 1 : 1·08, and of the latter, 1 : 2·13. The former are completely miscible, the latter only partially so.

It can be shown thermodynamically that the **specific heat** of a liquid is independent of the magnitude of the surface and that the amount of energy necessary for the production of a new surface is dependent on the temperature. This, says H. Freundlich, is because the surface energy is of a potential not a kinetic nature. P. N. Pavloff [22] found that the effect of surface tension on the **melting point** shows that very small particles have a greater surface tension and a smaller melting point than coarser-grained particles. According to P. Walden, if M denotes the molecular (or formula) weight of a substance which has a specific cohesion a_m^2 at the melting point T_m° K., then $Ma_m^2=3{\cdot}65T_m$.

The solvent powers of liquids for the indifferent gases have been found by G. Geffcken,[23] A. Ritzel, etc., to run parallel with the compressibility of the solvents. There is also a parallelism between the lowering of the compressibility and the lowering of the solubility when salts are added to water. The greater the compressibility of the solvent, the greater the amount dissolved. A. Ritzel postulates that every gas possesses what he calls a solubility pressure—*Löslichkeitsdruck*—π, for a given fluid. The solubility pressure, which favours solution, is opposed by a counter pressure which hinders solution. When the solution is saturated, the opposing pressures are balanced. If β denotes the compressibility coefficient of the liquid, S, the solubility of a given gas in the liquid, and δ the change in volume which occurs when unit volume of the liquid is saturated with gas, A. Ritzel assumes that

$$\pi=\frac{\delta S}{\kappa}\text{; or, } S=\frac{\pi\beta}{\delta}$$

meaning that the solubility is greater, the greater the solubility pressure, the greater the compressibility of the solvent, and the smaller the change in volume which occurs on solution. Without testing this equation quantitatively owing to lack of measurements of the solubility pressure, π, A. Ritzel calculates values of π, and shows qualitatively that the preceding assumptions are valid. The results for the solutions of carbon monoxide in some liquids are shown in Table XXXV.

TABLE XXXV—SOLUBILITY PRESSURE OF CARBON MONOXIDE.

Solvent.	β	δ	S	π
Acetone . . .	0·0001210	0·00211	0·238	4·15
Chloroform . . .	0·0001030	0·00224	0·206	4·48
Benzene . . .	0·0000915	0·00231	0·174	4·39
Alcohol . . .	0·0000875	0·00209	0·172	4·11

The surface tension decreases as the compressibility increases, and the solvent powers of liquids decrease as the surface tension increases. The surface tension curve for the solubility of gases in binary mixtures exhibits a maximum where the solubility curve shows a minimum; but not always conversely owing possibly to secondary disturbing effects.

Several attempts have been made to represent the surface tension of a mixture by the mixture law: $\sigma=a_1\sigma_1+a_2\sigma_2+\ldots$, where a_1, a_2, . . . denote the fractional proportions of the two liquids, so that $a_1+a_2=1$, and σ_1, σ_2, . . . their respective surface tensions. H. Rodenbeck found this rule to apply with mixtures of alcohol with water or chloroform; and chloroform with ether or petroleum. W. Sutherland[24] deduced, from the inverse fourth law of molecular attraction, the expression:

$$\frac{\sigma}{D^2}=\left(\frac{w_1\sqrt{\sigma_1}}{D_1}+\frac{w_2\sqrt{\sigma_2}}{D_2}\right)$$

where D_1 and D_2 denote the respective specific gravities of the components of the mixture; σ_1 and σ_2, the respective surface tensions: w_1 and w_2, the proportions by weight; and σ and D, the respective surface tension and specific gravity of the mixture. This is regarded as a special case of S. D. Poisson's formula $\sigma=a_1^2\sigma_1+2a_1a_2\sigma_{12}+a_2^2\sigma_2$, where σ_{12} is a characteristic constant for the interface of the superposed liquids. P. Volkmann, C. E. Linebarger, and W. H. Whatmough found the formula to be applicable in some cases, not in others.

Very little advance has been made in deducing relations between the **chemical constitution** and the surface tension of chemical compounds. D. I. Mendeléeff[25] has shown that the product of the molecular weight and the surface tension—unfortunately called the *molecular cohesion*—with certain homologous series of compounds varies proportionally with the number of CH_2 groups introduced; and that the constant $2\sigma/D$ generally varies in the same direction as the latent heat of vaporization. The substitution of hydrogen by an equivalent of oxygen or the halogens raises the coefficient. Dilute solutions have also been investigated. The surface tension of a liquid is altered when a substance is dissolved therein. In general, the inorganic salts slightly raise the surface tension of water; hydrogen chloride or bromide and ammonia lower the surface tension of water; sulphuric acid and alkali hydroxides raise the surface tension of water.

The surface tension of solutions.—In 1875, G. Quincke showed that the surface tension of aqueous solutions, σ, is a linear function of the concentration C expressed in gram-equivalents per litre, then $\sigma=\sigma_s+bC$, where b is a constant—0·1566 for sodium chloride, and 0·1666 for potassium chloride. Otherwise expressed, the so-called *molecular rise of the surface tension of solutions* defined by $(\sigma-\sigma_s)/C$, is perceptibly constant for dilute solutions.[26] G. Pann found that this proportionality does not obtain with more concentrated solutions, and E. H. Archibald connected the raising of the surface tension with the degree of ionization a of the salt in solution by the expression $\sigma-\sigma_w=a(1-a)C+baC$, where a and b are constants.

The relation between the concentration of the surface film and the body of a solution.—The distribution of the solute between the surface film and the body of the liquid is not necessarily the same. J. W. Gibbs,[27] in his classical memoir *On the equilibrium of heterogeneous substances* (1876), first showed the relation between the concentration of the surface film and the surface tension :

$$u\frac{dp}{dC}=-C\frac{d\sigma}{dC}$$

where u denotes the excess concentration in grams per sq. cm. surface over the concentration C in the body of the solution ; dp/dC denotes the coefficient of the change dp in the osmotic pressure which is attended by a change dC in the concentration. This magnitude is positive for all solutions. The coefficient $d\sigma/dC$ represents the coefficient of the change in the surface tension for a small change dC in the concentration of the solution. Since u and $d\sigma/dC$ are always opposite in sign, the surface tension will increase with concentration if the concentration of the surface film is less than in the interior of the liquid ; and conversely, for dilute solutions obeying J. H. van't Hoff's osmotic pressure formula $p=RCT$, or $dp/dC=RT$, and therefore J. W. Gibbs' relation between the amount u of solute adsorbed by a surface film and the change in the surface tension per unit change of concentration, assumes the form :

$$u=-\frac{C}{RT}\cdot\frac{d\sigma}{dC}$$

This same expression follows directly from the principle of virtual work. A surface s contains a gram-molecule of salt and the surface tension is σ, so that the surface tension is diminished $d\sigma$, when a little solute enters the surface, and the change of surface energy is $sd\sigma$. To remove this amount of solute from a volume v of the solution against the osmotic pressure p, requires the expenditure of energy vdp so that $sd\sigma+vdp=0$. If the gas law is applicable, $v=RT/p$, and therefore $d\sigma/dp=-RT/sp$; but the osmotic pressure is directly proportional to the concentration C, so that $d\sigma/dC=-RT/Cs$. Again, since s is the surface which contains a gram-molecule excess of solute, and if u denotes the excess in unit area, $u=1/s$. Hence, rearranging terms, $u=-(C/RT)(d\sigma/dC)$.

It will be observed that if $d\sigma/dC$ be positive, *i.e.* when the increase of the surface tension with increasing concentration of the solute in the film is negative, the surface will contain less solute than the body of the liquid—this is called ***negative adsorption***—and the effect of the salt in raising the surface tension of the solvent will in consequence be partially counteracted. Again, if $d\sigma/dC$ be negative, the surface tension will decrease with concentration, as is the case with many organic compounds—*e.g.* the oleates, amyl alcohol, etc.—and u will be positive, meaning that the solute will be absorbed by the surface so that the concentration of the solute in the surface film will be greater than in the body of the liquid. This is called ***positive adsorption.*** The term adsorption is usually applied to this surface layer. Consequently, ***a solute is positively adsorbed by a surface film when it lowers the surface tension of a solvent towards its own vapour, and negatively adsorbed when it raises the surface tension of the solvent.*** A small quantity of the dissolved substance can lower the surface tension of a solution to a marked degree, but a solute cannot raise the surface tension very much because in the latter case, the concentration of the solvent in the surface film will be less than in the body of the liquid, and the extreme limit is attained when the surface film is purely solvent. Here then u and $d\sigma/dC$ can possess only a small value. On the other hand, if the adsorption be positive, the whole of the dissolved substance, under suitable conditions, will be concentrated in the surface layer, and this can reduce the surface tension very much. There is a limiting case with a solution containing 0·000022 gram-molecule of salicylic acid per litre, for all the solute collects in the surface film. The concentration of the solute in the surface film has been investigated by J. von Zawidsky,[28] C. C. Benson, and S. R. Milner by producing a copious froth which has a very large surface, and comparing the concentration of the solute in the froth and in the body of the liquid. Thus, with an aqueous solution of amyl alcohol, it was found that when C for the original solution was 0·0375 gram-molecule, C for the foam was 0·0394 gram-molecule, hence $u=0·0019$ gram-molecule. Near the critical point, where $d\sigma/dC=0$, $u=0$, so that with an increase of concentration, the solute distributes itself in the interior of the liquid, and does not enrich the surface layer. W. C. McC. Lewis' results[29] did not agree with theory, and hence S. Arrhenius inferred that the phenomena of adsorption does not depend on surface tension, and that all attempts to correlate these phenomena are doomed to failure.

According to I. Traube,[30] the more a solute diminishes or increases the surface tension of a solvent, the smaller or greater is its intrinsic pressure, and the difference between the surface tensions of a solvent and a solution is a measure of the intrinsic pressure of the solution. P. Walden (1909) also showed that the greater the internal pressure, the greater the surface tension, and the greater the tendency of the molecules of a liquid to form complex aggregates; and further, that the intrinsic pressure in atmospheres is 75·3 times the surface tension of the liquid at the boiling point.

The surface energy of liquids.—The volume energy of gases is a linear function of the temperature for $d(pv)/dT=R$, where R is a constant; and in 1886, R. Eötvös, in a paper *Ueber den Zusammenhang der Oberflächenspannung der Flüssigkeiten mit ihrem Molekularvolumen,*[31] called attention to the fact that the surface energy of liquids, $d(\sigma s)/d\tau$, is likewise a function of the temperature τ measured downwards from the critical temperature, since $\sigma s=k\tau$, where k is a constant. This is **Eötvös' rule.** In illustration:

	k
Ether (6° to 120°)	0·227
Chloroform (20° to 60°)	0·230
Carbonyl sulphide (3° to 63°)	0·231
Carbon disulphide (22° to 78°)	0·237
Sulphur dioxide (2° to 60°)	0·230

W. Ramsay and J. Shields, however, have shown that a slight correction is necessary, since the line representing the product of the surface tension σ and molecular surface s has its origin about 6° below the critical temperature, Fig. 19. Consequently, $\sigma s=k(\tau-6)$. In order to make his formula apply to all liquids, R. Eötvös made the surface s such that the same number of molecules are distributed over the same surface area, and obtained what has been called the *molecular surface;* he also assumed that the molecular surface of a liquid was equal to $(Mv)^{\frac{2}{3}}$, where Mv denotes the molecular volume of the liquid, that is, that volume of the liquid which contains the same number of molecules, for if this volume were a cube, the edge would be $(Mv)^{\frac{1}{3}}$, and any face $(Mv)^{\frac{2}{3}}$. Substituting this value of s in Eötvös' formula, what W. Ostwald[1] calls the *molekulare Oberflächenenergie*—the molecular surface energy —is obtained, namely

$$\sigma(Mv)^{\frac{2}{3}}=k\tau \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where τ denotes the temperature, T, reckoned downwards from the critical temperature, T_c, that is, the difference between the critical temperature and the temperature of the experiment, $\tau=T_c-T$. The molecular surface energy, $\sigma(Mv)^{\frac{2}{3}}$, represents the work necessary to enlarge the surface of a liquid by an amount proportional to the molecular weight—the molecules being treated as spheres. The formula assumes that the distribution of the simpler and more complex molecules over the surface is the same as in the body of the liquid; this assumption is justified from the circumstance that the molecular surface energy of a mixture is the mean of those of its constituents determined at the same temperature.

W. Ramsay and J. Shields tested Eötvös' formula for about fifty liquids at temperatures ranging from −89·8° up to the critical temperature. It was found that the liquids arranged themselves into two groups when the observed data were substituted in the formula :

$$\sigma(Mv)^{\frac{2}{3}}=k(\tau-d)\ ;\ \text{or}\ \sigma(Mv)^{\frac{2}{3}}=k(T_c-T-d) \qquad . \quad . \quad (2)$$

The theory of the equations of R. Eötvös and W. Ramsay and J. Shields is somewhat as follows : Assuming that the internal attraction of the molecules varies inversely as the fourth power of their distance apart, or, what is the same thing, inversely as the volume of unit mass—specific volume—the work of expansion W from a specific volume v of liquid to a specific volume V of vapour against internal molecular forces, will be

$$\text{Internal work}=\int_V^v \frac{a}{v^2}dv\ ;\ \text{or,}\ W=a\left(\frac{1}{V}-\frac{1}{v}\right)$$

where the constant a can be calculated from the internal latent heat of vaporization of the liquid. If the internal heat of vaporization be denoted by λ, it follows that $W=\lambda$; and, since the specific volume is inversely as the density, if D_1 and D respectively denote the densities of liquid and vapour. The internal latent heat of vaporization, $\lambda=a(D_1-D)$. If the density of the vapour be negligibly small in comparison with that of the liquid, $\lambda=aD_1$, but by L. Cailletet and E. Mathias' rule, if the density of the vapour be likewise negligibly small, $D_1=a-bT$. By differentiating these two expressions with respect to T, $d\lambda/dT=adD_1/dT$; and dD_1/dT=constant, meaning that the decrease in the latent heat or the density of a liquid with temperature has a constant value for substances not too near their critical temperatures, and which do not change their chemical character with the change of temperature. Consequently, $d\lambda/dT$=a constant. Again, according to J. Stefan,[32] neglecting the influence of the vapour, a molecule passing from the interior of a liquid to the surface will escape from one-half the molecular attraction, and if it evaporates clear away from the surface, it will escape from the other half of this attraction. Consequently, the work required to bring a molecule from the interior to the surface is one-half the work required to transport a molecule from the interior of the liquid to a point outside where the attraction of the liquid is no longer sensible. The molecular surface energy $\sigma(Mv)^{\frac{2}{3}}$, or the work necessary to bring a number of molecules proportional to the molecular weight to the surface of a liquid, is therefore equal to $\frac{1}{2}\lambda$; and by differentiation of this expression with respect to T, it follows that the variation of the molecular surface energy with respect to temperature is equal to a constant, say k ; by integration, W. Ramsay and J. Shields' expression follows at once.

Returning to the results of W. Ramsay and J. Shields' experiments, in the one group—called *normal liquids*—the value of k was virtually constant, averaging 2·2—with a positive or negative deviation of 5 per cent. when the constant $d=6$. It is assumed that in normal liquids the gaseous and liquid molecules are of the same degree of complexity. If the liquid molecules were formed by the association of a number of gaseous molecules so that (i) all the molecules were associated to an equal extent ; and (ii) the degrees of the association were not altered by changes of temperature, the liquid would give constant values for the constant k ; but it is extremely unlikely that mere liquefaction would produce an equal or uniform association of the molecules, and that the degree of association would not be altered by a rise of temperature. Hence it is inferred that the so-called normal liquids are not associated. Among the normal or non-associated liquids are : Carbon disulphide, nitrogen peroxide (not the gas), silicon tetrachloride, phosphorus trichloride, phosphoryl chloride, sulphur dichloride, thionyl chloride, sulphuryl chloride, nickel tetracarbonyl, carbon tetrachloride, ethyl ether, benzene, hydrocarbons, etc.

In another group—called *associated liquids*—the value of k was not constant, but ranged between comparatively wide limits. Accordingly for these liquids $\sigma(Mv)^{\frac{2}{3}}$ varies with the temperature. Since σ and v are determined experimentally in each case, it follows that M varies with the temperature, and that the molecules must be more complex at low than at high temperatures. Assuming that the molecular weights of non-associated liquids are the same as the molecular weights of the compounds in the gaseous state, the product of the molecular weight, M, in the gaseous state, multiplied by a factor i, will give the relative molecular weight of the liquid molecules ; i of course varies with the temperature, and, for these liquids, $\sigma(iMv)^{\frac{2}{3}}=k(\tau-d)$. If k' denotes the observed value of the constant for any temperature, and $k=2{\cdot}12$, the division of the last equation by (2), gives $i^{2/3}=2{\cdot}12/k'$. Such liquids are undoubtedly associated, and have a greater molecular weight than when in the gaseous state. Among the associated liquids are water, formic, nitric, and sulphuric acids, bromine, the alcohols, organic acids, etc. The values of the constant i for acetic acid, methyl alcohol, and ethyl alcohol are respectively 3·73, 3·43, and 2·79. These numbers are probably a little high. Thus, i for water between 0° and 140° changes from 1·707 to 1·289 ; for acetic acid between 20° to 280° from 2·13 to 1·30 ; for methyl alcohol between —89·8° and 220°, from 2·65 to 1·75 ; and for ethyl alcohol, between —89·8° to 230°, from 2·03 to 1·00. The variation of $i^{2/3}$ with temperature was not allowed for, and a new formula making provision for this variation has been obtained, and the results are better.

$$\sigma(Mv)^{2/3}=\frac{k(\tau-d)}{1+e\tau} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The revised formula includes the constants d and e, whose numerical values are dependent upon the nature of the liquid. The constants are :

	k	d	e	Critical temperature.
Methyl alcohol	1·489	4·22	0·00104	240·0
Ethyl alcohol	2·170	4·8	0·00193	243·1
Water	2·631	19·5	0·00218	358·1
Acetic acid	1·910	11·9	0·00163	321·5

The formula for computing the degree of complexity i of the molecules of the liquid now assumes the form :

$$i=\left\{\frac{2{\cdot}121}{k}(1-e\tau)\right\}^{3/2} . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The degree of association for water thus becomes :

i	0°	20°	60°	100°	140° C.
Water . . .	1·7	1·6	1·5	1·4	1·3
Ethyl alcohol . .	2·0	1·7	1·4	1·2	1·0
Methyl alcohol . .	2·7	2·3	2·1	1·9	1·8
Acetic acid . . .	2·1	1·9	1·7	1·5	1·3

The general conclusion is that W. Ramsay and J. Shields' equation $\sigma(Mv)^{2/3}=k(\tau-d)$, where $k=2{\cdot}12$ (nearly), applies generally for substances whose chemical nature does not alter with temperature. If the expression $\sigma(Mv)^{2/3}=k\tau$ be plotted, the slope of the curve represents the value of k, and the introduction of the constant d means that the straight line starts not from the critical point, but from a point at a distance d from the critical point. The distance between the dotted and the curved line OA, Fig. 19, represents the deviation of the observations from Ramsay and Shields' rule in the vicinity of the critical temperature.

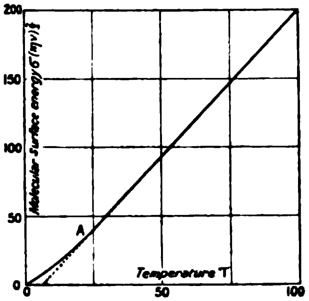

FIG. 19.—R. Eötvös' Curve for Benzene.

F. M. Jäger has measured the surface tension and molecular surface energy of about 200 organic liquids between —80° and 250°, and of about 50 inorganic substances in the molten condition between 300° and 1650°. The surface tension, σ, and the molecular surface energy, μ, of the halides of phosphorus, arsenic, antimony, and bismuth increase with the molecular weight, while the variation of μ with temperature, $d\mu/dT$, is more or less normal. With the halides of the five alkali metals the surface tension of the molten salt decreases (i) with increasing atomic weight of the halogen from fluorine to iodine, and also (ii) with increasing atomic weight of the metal. The molecular surface energy varies in an irregular manner, while $d\mu/dT$ is in all cases small. The alkali sulphates, nitrates, borates, molybdates, and tungstates were also investigated.

The association of the molecules of liquids.—The abnormal vapour densities of certain liquids at temperatures near their boiling points, led chemists—*e.g.* A. Neumann[33]—to the view that the molecules of such liquids may be formed by the coalescence or association of two or more molecules of the substance as they occur in the gaseous state, and in 1888, P. de Heen[34] developed a theory of liquids based upon the assumption that the constituent molecules of certain liquids are aggregates of the molecules as they occur in the gaseous state, so that he postulated what he called liquidogenic and gasogenic molecules. A liquid under ordinary conditions is a solution of gasogenic in the liquidogenic molecules. If a very small volume of liquid is in equilibrium with a large volume of vapour, the liquid will be saturated with gasogenic molecules and cannot furnish liquidogenic molecules to the vapour; conversely, if the volume of the liquid is large, and the vapour small, the vapour will consist largely of liquidogenic molecules. The density of a saturated vapour of a pure substance, like that of a mixture, is therefore supposed to be dependent on the relative masses of liquid and vapour phases. This is contrary to experience. Modifications of P. de Heen's theory in which the two forms of molecules are in a definite state of equilibrium have been employed to explain supposed phenomena which occur at the critical temperature of a liquid or gas, namely, that (i) the greater the proportion of liquid confined in the tube, heated to the critical temperature, the higher the critical temperature; and (ii) that the critical temperature at which a meniscus appears on cooling is lower than that obtained on heating. There is, however, considerable doubt about the accuracy of both conclusions, since the experimental errors are large, and care has not always been taken to use pure materials free from absorbed air.[35] It is generally held that the difference between the liquid and gaseous states is solely due to the greater propinquity of the molecules in the liquid state, and not to polymerization of the molecules. Nothing very definite, however, was known about this until about 1887, when W. Ramsay and S. Young[36] showed that the density of acetic acid vapour increases as the boiling point is approached; and about 1888, E. Beckmann[37] showed, by freezing-point determinations, that acetic acid and ethyl alcohol possess more complex molecules in concentrated solution than in the vaporous state; while naphthalene does not form complex molecules under the same conditions. J. T. Cundall (1891) also showed that solutions of nitrogen peroxide behave as if the molecules are more complex in solution than in the vaporous state.

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§ 23. The Association or Polymerization of Liquids

> The custom of comparing all liquids in an indiscriminate fashion, in the hope of establishing general relationships has been attended with a certain degree of success, but exceptions of a very puzzling order frequently arise. One great cause of such exceptions is to be found in the fact that monomolecular and associated liquids have been indiscriminately compared one with another, when strictly speaking they are not truly comparable.—H. CROMPTON (1898).

There is much evidence indicating that the normal molecules of certain liquids, vapours, and even solids may coalesce or associate into more complex aggregates when the vapour condenses to a liquid, or even when the temperature is changed without a change in the state of aggregation, as when n molecules of a substance, A, coalesce to form one molecule, and *vice versa* : $nA\rightleftharpoons A_n$. So long as our knowledge of molecular weights was deduced from the study of vapour densities, the conclusions were strictly applicable to matter in the gaseous state only. A large number of attempts have been made to get an insight into the molecular condition of liquids and solids, and in the case of liquids, the problem now approaches within a measurable distance of a successful solution ; indeed, liquids are now classed as associated or non-associated according as the molecular weight can be represented by iM or M, where M denotes the formula-weight deduced from the vapour density, and i the factor of association.

The evidence for polymerization is based upon some irregularity in the variation of many of the physical properties of the liquids with temperature—*e.g.* heat of vaporization ; external work of evaporation ; vapour pressure curves ; molecular volumes ; molecular refraction ; densities ; viscosities ; etc. Several methods are based on the behaviour of liquids either at or near their critical points, for it will be evident that when matter is undergoing a change of state, if the molecules simultaneously alter their degree of association, the variation should be rendered apparent in a marked degree. D. Tyrer lays down the condition that any exact equation which might be employed to calculate the association factors of liquids should conform with the law of mixtures, for with partially associated liquids we are dealing with a mixture and not with an individual in the chemical sense. In the case of water, for example, we are possibly dealing with a mixture containing not one molecule but several, H_2O, $(H_2O)_2$, $(H_2O)_3$, . . . If the first three molecules have the respective molecular weights, M_1, M_2, M_3, . . . and n_1, n_2, n_3, . . . of the respective molecules be present, the mean molecular weight M of the associated liquid, $(H_2O)_i$, will be

$$iM=\frac{n_1M_1+n_2M_2+n_3M_3+\ .\ .\ .}{n_1+n_2+n_3+\ .\ .\ .}$$

and the various physical properties X_1, X_2, X_3, $+$ . . . should be functions of the right member of this equation. This applies for all mixtures whether of associated or normal liquids which have no chemical action on one another.

In 1894, P. A. Guye made a collection of evidence which furnished a number of criteria indicating the association of liquids, but much more has accumulated since then. D. Tyrer has tried a number and found them to fail when tested by the above criterion. Ten of these methods are here indicated :

(1) W. Ramsay and J. Shields' work on surface energy. Various attempts have been made to modify W. Ramsay and J. Shields' equation, thus, A. Batschinsky [1] proposed to substitute $T_c=16{\cdot}31(\eta T^3)^{2/7}/D_c^{1/7}$, where η denotes the viscosity at the absolute temperature T ; and D_c, the critical density—the density at 0° may be substituted for D_c if the constant be altered. P. Walden also says that $\sigma(Mv)=K(T_c-T-d)$ gives as good results as the equation of W. Ramsay and J. Shields.

(2) About 1890, P. A. Guye [2] found it necessary to double the ordinary molecular weights of methyl alcohol, acetic acid, and water in order to make these liquids conform with his rule that the quotient obtained by dividing the absolute critical temperature T_c, by the critical pressure p_c, is equal to the molecular refraction r multiplied by a constant which is 1·85 for most liquids, but 1·1 for associated liquids.

(3) According to S. Young and G. L. Thomas,[3] the ratio of the actual density of a liquid to the density at the critical point is 3·85 ; and with liquids assumed to be associated, the ratio appears to have a greater value—thus with some alcohols and acetic acid, the ratio ranges from 4·0 to 5·0.

(4) If the arithmetical mean of the density of a liquid and gas is not a linear function of the temperature, as indicated in L. Cailletet and E. Mathias' rule,[4] it is assumed that the liquid is associated—*e.g.* water.

(5) If the heat of vaporization rises to a maximum with rise of temperature, and then diminishes, it is assumed that complex molecules are being converted into simpler ones during the descent of the curve. W. Ramsay and S. Young [5] found this to be the case with ethyl alcohol and acetic acid. Normally, the curve shows that the heat of vaporization decreases regularly up to the critical temperature when it becomes zero.

(6) The greater value for the heat of vaporization for unit increase in volume in the case of alcohols and water corresponds with the consumption of a greater amount of internal work for the expansion against external pressure, owing to the dissociation of the complex molecules. For example, F. Trouton's rule, and G. G. Longinescu's rule.[6] G. G. Longinescu found that for non-associated liquids, $n=(T_b/100D)^2$, where T_b denotes the absolute boiling point; D, the specific gravity at 0° ; and n, the number of atoms in the molecule. In W. A. Kistiakowsky's modification of F. Trouton's rule, $a^2M/T_b=1{\cdot}14$, where a^2 denotes the capillary rise in a tube of one mm. radius, at the absolute boiling temperature T_b. For associated liquids, the constant is smaller—*e.g.* for methyl alcohol it is 0·482, and for acetic acid, 0·576.

(7) The vapour pressure curves of normal liquids do not cut one another at any point in their course, but the vapour pressure curves of associated liquids often cut across those of normal liquids.[7]

(8) The ratio of the volume of a saturated vapour at some chosen pressure to that at the critical pressure points to the association of organic acids and alcohols.[8]

(9) J. D. van der Waals' vapour pressure equation,[9] $\log p_c - \log p = f(T_c - T)/T$, where p_c and T_c denote the critical pressure and temperature respectively, and p denotes another pressure at the temperature T, gives a constant approximately 3 to 4 with most liquids, but the numerical value of f rises to 3·2–3·4 for water; 3·36–3·49 for acetic acid; 3·58–4·02 for methyl alcohol; and 3·49–3·77 for ethyl alcohol.

(10) A. E. Dunstan and F. B. Thole[10] have shown that the quotient of the viscosity by the molecular volume is nearly 60×10^{-6} for normal liquids, but for water, the fatty alcohols, and acetic acid, the fraction has more than twice its normal value.

Several other methods have been described—*e.g.* I. Traube's method of molecular volumes, the empirical formulæ of D. Tyrer, M. M. Garver, E. T. Whittaker,[11] and R. D. Kleeman, etc. Indeed, nearly every physical property which has been accurately measured—specific heats, osmotic pressures, etc.—has been related with the molecular weights.

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§ 24. Thermal Effects attending the Expansion and Compression of Gases

> I use the word attraction in a general way for any endeavour of what kind so ever, made by bodies to approach to each other—whether that endeavour arise from the action of the bodies themselves, or whether it may arise from the action of the æther or of any medium whatsoever, whether corporeal or incorporeal, anyhow impelling bodies placed therein towards one another.—Isaac Newton.

In an essay *Of the cold produced by evaporating fluids, and of some other means of producing cold*, W. Cullen (1755)[1] seems to have been the first to notice that the temperature of air is decreased by rarefaction, and increased by compression; and J. Dalton (1802) made an attempt to measure the change of temperature which occurs when air is compressed or rarefied. In a general way, it has been proved that if a gas, whose molecules exert no attraction on one another, be confined in a suitable vessel, and compressed, the mechanical work employed in compressing the gas is equivalent to the product of the pressure into the change in volume. This energy is transformed into an equivalent amount of heat which raises the temperature of the gas. On the other hand, if the gas of itself expands against atmospheric pressure from a volume v to a volume v_1, the gas will be cooled because the gas itself has done a certain amount of work against atmospheric pressure p, equivalent to the product of the atmospheric pressure into the change in volume—*viz.* $p(v_1-v)$, or more accurately, $p \log (v_2/v_1)$. The phenomenon is illustrated by the time-honoured experiment in which a piece of tinder in a glass cylinder containing a little ether is ignited by suddenly compressing the piston in the cylinder.

The adiabatic expansion or compression of gases.—If the expansion of a gas against atmospheric pressure be performed slowly enough, the gas will remain at a constant temperature, and the expansion is said to be **isothermal**; the energy required to overcome the external pressure is absorbed as heat from its surroundings. On the other hand, if the walls of the containing vessel be made of some insulating material which prevents the passage of heat inwards or outwards, the energy required for the expansion is absorbed from the kinetic energy of the gas molecules themselves, and the temperature of the gas decreases. Such an operation is said to be **adiabatic,** from *a*, not; *διαβαίνειν*, to pass through, or transmit. An approximation to an adiabatic change is obtained when gases are *suddenly* expanded or *compressed,* because there is not then time for the heat to dissipate. Boyle's law describes the relation between the pressure and volume of a gas when the operation is performed isothermally; this law will not be valid for adiabatic changes. No perfectly adiabatic substance is available for measuring the relations between the adiabatic changes of volume and the pressure of a gas, but the law has been derived from several lines of reasoning, and the observed results approximate to the theoretical values. Obviously, the actual change of temperature which occurs during the adiabatic process must depend in some way on the specific heat of the gas concerned. If the thermal capacity of the gas be small, the change of temperature will be greater than if the thermal capacity be large. If γ denotes the ratio of the two specific heats of a gas, C_p/C_v, then, if k be a constant,

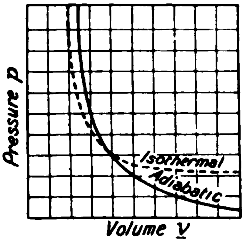

FIG. 20.—Isothermal and Adiabatic *pv*-Curves.

$$pv^{\gamma}=k\,;\ p_1v_1{}^{\gamma}=p_2v_2{}^{\gamma}$$

The dotted curve, Fig. 19, represents Boyle's law (isothermal) curve pv=constant, the other the adiabatic curve pv^{γ}=constant. If the isothermal curve passes through the point O when the volume of the gas is unity and the pressure p, it passes above the adiabatic for values of v greater than unity, and under it for values of v less than unity. By substituting the gas law, $pv=RT$, in these equations, two other equations can be obtained:

$$\left(\frac{v_1}{v_2}\right)^{\gamma-1}=\frac{T_2}{T_1}\,;\ \left(\frac{p_2}{p_1}\right)^{\frac{\gamma-1}{\gamma}}=\frac{T_2}{T_1}$$

which express the relation between the volume, pressure, and temperature of gases undergoing adiabatic changes.

These expressions—pv^{γ}=constant, etc.—can be deduced from the laws of thermodynamics, somewhat as follows: Let the temperature of unit mass of gas at a constant pressure be raised a small amount dT owing to the absorption of an amount of heat dQ, which in turn is equivalent to C_pdT when C_p is the specific heat of the gas at constant pressure; let the volume of the gas at the same time be augmented dv. The final condition of the gas can be regarded as the joint effect of two operations: (i) The temperature may be supposed to increase by an amount dT while the volume remains constant, so that heat equivalent to C_vdT is absorbed; (ii) The temperature remains constant while the volume increases by an amount dv. Let H denote what has been called the latent heat of expansion; that is, the amount of heat absorbed per unit change of volume without change of temperature; accordingly, the quantity of heat absorbed when the volume changes by a small amount dv, at a constant temperature, will be $H.dv$. Consequently, $dQ=Hdv+C_vdT$; or C_pdT

$=Hdv+C_vdT$. From Charles' law, it follows that $(v+dv)/(T+dT)=v/T$; or, $dv=(v/T)dT$; and, after substituting this value of dv in $C_pdT=H.dv+C_vdT$, dividing through by dT, it follows that $C_p-C_v=Hv/T$; or $H=(C_p-C_v)T/v$. Again, if a gas changes its volume dv under adiabatic conditions without any exchange of heat between it and its surroundings, the temperature would change by an amount dT, and dQ must be zero. Hence, $H.dv+C_vdT=0$. Substitute the above value of H in this equation; put γ for C_p/C_v; and it follows that $(\gamma-1)dv/v+dT/T=0$. This on integration gives the relation $pv^\gamma=$constant, and the other expressions follow.

The cooling (or heating) effect obtained by expanding (or compressing) gases adiabatically can be computed from these equations. Thus, air expanded adiabatically from 20° and 50 atm. to 1 atm. pressure will be cooled to −177°; and air at −60° and 50° atm. pressure will be cooled to 204° on expanding adiabatically to one atmosphere pressure. With air initially at 0°, and a final pressure of one atmosphere ($\gamma=1{\cdot}41$),

Initial pressure	50	100	200	300	400	500 atm.
Final temperature	−187·0°	−201·5°	−214·5°	−221·0°	−225·1°	−229·2°

Hence, it is possible to cool gases considerably by adiabatic expansion. By utilizing this principle, L. P. Cailletet (1877)[2] liquefied small quantities of air, oxygen, nitrogen, methane, and carbon monoxide. G. Claude (1909) has employed the principle in the continuous production of liquid air.

EXAMPLES.—(1) A litre of air at 0° expands adiabatically to two litres. Find the fall of temperature when γ for air is 1·4. Here $T_2\times2^{0\cdot4}=273$; $2^{0\cdot4}=1{\cdot}32$; hence, $T_2=207°\ K$ or −66°.

(2) If the ignition temperature of electrolytic gas be 585°, what adiabatic compression would cause the mixture to ignite if the gas were originally at 15° and atmospheric pressure? Assume that the ignition temperature is not altered by variations of pressure. Ansr. 43 atm.

The Joule-Thomson or the Joule-Kelvin effect.—No heat is developed when an ideal gas expands into a vacuum. This was established by some experiments by J. L. Gay Lussac, described in his *Essai pour déterminer les variations de température qu'eprouvet les gaz en changeant de densité* (1807); and by J. P. Joule, in his memoir, *On the changes of temperature produced by the rarefaction and condensation of air* (1845). Compressed air was allowed to expand into an evacuated vessel, and the result, as J. P. Joule expressed it, was as follows: "No change of temperature occurs when air is allowed to expand in such a way as not to develop mechanical power"; and generally, **when a gas expands without doing external work, and without taking in or giving out heat, its temperature does not change**—a statement sometimes called **Joule's law.** The first increment of gas into a vacuum will of course produce a pressure, and each successive increment supplements the pressure produced by the earlier portions. Since a gas expands indefinitely, each increment may be regarded as filling the whole space or volume v, and consequently the work done is simply $v\int dp=pv$. This is also equal to the kinetic energy of the gas. Consequently, the work done in forcing the later portions of gas into the evacuated space against the existing pressure is wholly transformed into kinetic energy. No change of temperature occurs, because the work done *by* the gas is equal to the work done *on* the gas. The case is analogous with the transmission of energy by a rod or belt whose state of strain is steady—the rod or belt transmits the impressed energy without loss; so also if gas be forced into a cylinder when the temperature and pressure are constant, the stress introduced by the entering gas is relieved by the escape of an equal amount of gas. If the gas is in a steady state, the work done by the escaping gas will be equal to the work done *on* the gas. Otherwise expressed, the work required to transform unit mass of any fluid from a place where there is a uniform pressure p_1 to another place where there is a uniform pressure p_2, is equal to $p_2v_2-p_1v_1$, where the subscripts refer to the respective states of the gas if the density of the gas is strictly proportional to the pressure in the two states, p_2v_2

$-p_1v_1=0$, and no work is done. If, however, the external pressure be diminished by internal attractions depending on the distance apart of the molecules, so that p_1v_1 is less than p_2v_2, the external work done *on* the gas is no longer equal to the external work done *by* the gas—because during expansion part of the energy is spent in doing internal work separating the molecules. The assumption made in Joule's law is that no work is performed against intermolecular attractions. However, intermolecular attractions are evidenced with most gases. The experiments of Gay Lussac and Joule[3] were not sufficiently sensitive to detect the small change of temperature which occurs when such gases expand in vacuo, so that although no external work is done by the gas, internal work is done against intermolecular attraction. The molecules are torn apart, so to speak, against the (feeble) attractive force drawing them together. This involves an expenditure of energy—work must be done—and the gas is cooled.

The work W done against intermolecular attractive forces will depend on the distance of the molecules apart. Suppose the attractive forces be such that they vary inversely as the fourth power of the distance apart of the molecules, then, when a gas expands from a volume v_1 to a volume v_2, $W=a(p_1-p_2)$, where a is a constant.

If the molecular attraction f varies inversely as the fourth power of the mean distance r_1 of the molecules apart, $f=c/r_1^4$, where c is a constant; and if the gas expands until the mean distance of the molecules apart becomes r_2, the work done against molecular attraction will be:

$$\int_{r_1}^{r_2} f.dr=c\int_{r_1}^{r_2}\frac{dr}{r^4};\quad \text{Internal work}=\frac{c}{3}\left(\frac{1}{r_1^3}-\frac{1}{r_2^3}\right)=\frac{c}{3b}\left(\frac{1}{v_1}-\frac{1}{v_2}\right)$$

since r is linear, and the volume v of the gas will therefore vary as the cube of r, so that $v_1=br_1^3$ and $v_2=br_2^3$, where b is a constant. Again, since the temperature is nearly constant, $p_1v_1=p_2v_2=$constant. Collecting the various constant terms under the symbol a, it follows that the work done against molecular attraction when the gas expands from a volume v_1 to a volume v_2 is $a(p_1-p_2)$.

Consequently, **the work done in overcoming the intermolecular attractive forces will be proportional to the difference between the initial and final pressures of the gas** (temperature constant). This result is in harmony with observations. The cooling effect actually produced when a gas expands by simple outflow in vacuo is due to the absorption of heat equivalent to this work.

In later and more delicate experiments, Lord Kelvin (W. Thomson) and J. P. Joule—1852-62—forced a steady stream of gas under a pressure slowly along a tube A, Fig. 21, in the direction of the arrows, through small orifice, O, where it expanded against the pressure p_1. To avoid eddies in the gas, a porous plug was actually used. For the sake of simplicity, suppose the tube AB has unit sectional area, and that it is made of some material which does not conduct heat away from the gas. Two phenomena occur: (1) the gas is slightly heated by friction as it passes through the orifice O; and (2) the gas is cooled as it passes through O by doing work against a pressure p_1. Suppose a piston A, Fig. 21, moves from left to right so as to drive a volume of air, v_2, at a pressure p_2, into the compartment BC. The work done *on* the gas is obviously p_2v_2. Similarly, the work done *by* the gas as it pushes the piston from, say, B to C through a distance v_1, will be p_1v_1. Hence, if the gas obeys Boyle's law, we shall have $p_1v_1=p_2v_2$, and there will be no loss in the internal kinetic energy of the gas through overcoming internal attractions, and no variation of temperature of the gas on the sides AB and BC. If, however, work be done against molecular attraction during the expansion of the gas, the work of expansion on the side BC will exceed the work of compression on the side AB. The work

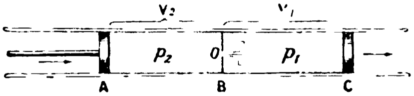

FIG. 21.—J. P. Joule and W. Thomson's Experiment.

performed when the gas expands against intermolecular attractive forces diminishes the kinetic energy of the gas, and this ceases to be sensible as heat; accordingly, the temperature of the gas is lowered owing to the loss of the kinetic energy of the molecules of the gas itself. Hence, the gas on the side *BC* will be cooled below the temperature of the gas on the side *AB*. **The change of temperature which occurs when a compressed gas expands adiabatically through a small orifice is called the Joule-Thomson effect.** In J. P. Joule and W. Thomson's experiments, the temperature of carbon dioxide, nitrogen, oxygen, and air fell about 1°; or, more exactly, the observed fall of temperature per atmosphere difference of pressure was

Air.	Carbon dioxide.	Oxygen.	Nitrogen.	Hydrogen.
0·208°	1·005°	0·253°	0·249°	—0·039°

so that the phenomenon with hydrogen is reversed, there is a rise of temperature of the gas on the side *BC*. This corresponds with Regnault's observation that the product pv increases with hydrogen above a certain temperature; if, however, the experiment be conducted at a lower temperature, hydrogen gas behaves like other gases and is cooled; and at higher temperatures, other gases behave like hydrogen.

According to J. Rose Innes,[4] the measurements of Joule and Thomson can be represented by a formula of the type: Fall of temperature$=aT^{-1}+b$, where a and b are constants such that for air, $a=141·5$, $b=0·697$; for carbon dioxide, $a=2165·0$, $b=4·98$; and for hydrogen, $a=64·1$, $b=-0·331$. In the case of hydrogen, the change of temperature will be zero when $T=194°$ K., or —79° C. This means that the Joule-Thomson effect with hydrogen will change sign from heating to cooling in the neighbourhood of —80°, and this is called the **inversion temperature.** The inversion temperature of helium is —240°.

The porous plug experiment shows that the fall of temperature which occurs when the pressure falls from p to p_1 varies very nearly in the inverse proportion to the square of the absolute temperature, and is approximately 0·25° per atmosphere; or, more exactly.

$$\text{Fall of temperature} = A\left(\frac{273}{T}\right)^2(p-p_1)$$

where T is the temperature of the gas at the initial pressure p, and p_1 the final pressure of the gas. The constant A is $+0·276°$, say $\frac{1}{4}°$ per atm. for air; $+1·388°$ for carbon dioxide; and $-0·049°$ for hydrogen. The magnitude of this constant, and accordingly also the cooling effect, is greater the more the gas deviates from the ideal gas laws—presumably because more work is done against intermolecular attractive forces.

Examples.—(1) If carbon dioxide, at 4 atm. pressure and 0°, on passing through a porous plug falls to a pressure of one atmosphere, show that the temperature falls about 4·2.

(2) If air at 0° is driven through an orifice and at the same time falls 3·6 atm. in pressure, show that the fall in temperature is 0·994°, and if the fall in pressure is 10 atm., the fall in temperature is 2·76°.

The greater the pressure, the smaller the corresponding cooling effect per atmosphere difference of pressure. Thus, E. Vogel[5] found for oxygen at 0°, and an initial pressure p, calculated for a pressure difference $p-p_1$ of one atmosphere:

p . . .	20	60	100	120	140	160 atm.
Cooling effect .	0·260°	0·225°	0·191°	0·174°	0·157°	0·139°

At about 300 atm. pressure and ordinary temperatures the cooling effect is nil.

The observed results are represented by the following modifications of Thomson's equation :

$$\text{Cooling effect} = (0{\cdot}268 - 0{\cdot}00086p)(p - p_1)\left(\frac{273}{T}\right)^2$$

The lower the temperature, the greater the cooling effect. Thus, W. P. Bradley and C. F. Hale found that when $p=204$ atm. and $p_1=1$ atm.,

Temperature .	0°	−20°	−40°	−60°	−80°	−90°
Cooling effect .	44·6°	52·1°	61·1°	72·5°	88·2°	99·2°

If external work W be performed on unit mass of gas compressing it isothermally, the intermolecular attractions will do a quantity of internal work w which will appear as heat. Hence, during an isothermal compression the total heat Q, taken from the gas, will be $Q=W+w$; and the total energy of the gas has been diminished by an amount w. Consequently, if the compressed gas be allowed to expand back to its original volume, without receiving energy from some outside source, internal work equivalent to w will have to be performed at the expense of the kinetic energy of the gas, and the temperature of the gas will accordingly fall. If w is equivalent to the heat abstracted from a gram of gas and which produces a fall of temperature $\theta°$, then if the heat be taken from half the gas, the fall of temperature will be $2\theta°$, and if from an nth part of the gas, there will be a fall of $n\theta°$.

If the specific heat of air at constant volume be 0·177, and if, for convenience, it be assumed that the specific heat is constant, it will require $210\times0{\cdot}177=37$ cals. to lower the temperature of a gram of air from 20° to −190° ; further, if the latent heat of vaporization be 50 cals. per gram, and a gram of the air at −190° be liquefied, it will require $37+50=87$ cals. to cool a gram of air from 20°, and liquefy it at −190°. According to Joule and Thomson's experiment, the expansion of a gram of compressed air will cool it $\frac{1}{4}$° per atmosphere ; if the gram of air expands from a pressure of 160 atm., it will therefore be cooled 40°. This corresponds with 7 Cals. of internal work per gram ; and accordingly, since 87 cals. of heat are required in order to cool a gram of air from 20° and to liquefy it, it follows that under ideal conditions only $\frac{1}{12}$th to $\frac{1}{13}$th of the gram of air can be liquefied by expansion from a pressure of 160 atm. when the rejected air has the same temperature as the compressed air. If m_1 and m_2 denote respectively the masses of the initial and the rejected air, then m_1-m_2 will denote the mass of air which has been liquefied during the expansion. Let W denote the external work done during isothermal compression, and w the work due to intermolecular attractions ; then, if Q_1 and Q_2 respectively denote the heat equivalents of W and w,

$$\frac{m_1}{m_2} = \frac{Q_1+Q_2}{Q_1} = \frac{W+w}{W}; \quad \therefore \quad \frac{m_1-m_2}{m_2} = \frac{w}{W}$$

This means that the ratio of the mass of liquefied air to the mass of rejected air is equal to the ratio of the work due to intermolecular attraction to the external work of isothermal compression. Since the cooling due to expansion of air from a pressure of 160 atm. is equivalent to $w=7$ cals. of internal work per gram, and the work W required for the isothermal compression of a gram of air to 160 atm. is equivalent to $W=98$ cals., it follows that $w/W=\frac{1}{14}$. This means that under ideal conditions, one-fourteenth of the work performed by the isothermal compression of air at 20° to a pressure of 160 atm., and its subsequent adiabatic expansion to the original pressure, is due to intermolecular attractions. In any system of liquefying gases by utilizing the slight cooling effect produced when internal work is done against intermolecular attractions, the test of the efficiency of the process is how near

$$\text{Maximum efficiency} = \frac{\text{Liquid obtained}}{\text{Work done}}$$

approaches the theoretical; for the air costs virtually nothing. Special refrigerants may enable a large percentage of compressed air to be liquefied; reducing the pressure for the expanded air below one atmosphere will give a bigger cooling effect, etc.; but all this requires the application of more work, and it is for the chemical engineer to find if the different factors increase or diminish the efficiency fraction.

As previously indicated, it is sometimes convenient to use an idealized gas as a limiting case or standard of comparison in the theoretical study of molecular forces, etc. Such a gas—called a perfect or ideal gas—(i) obeys Boyle's and Charles' laws for all pressures and temperatures; and (ii) it suffers no change of temperature when it is allowed to expand into an evacuated vessel. In this sense, perfection is not an objective quality of any particular gas, but it rather denotes a favourite and familiar fiction whose sole justification is that it facilitates the general investigation of the properties of gases.

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§ 25. The Liquefaction of Gases

> If the earth should all of a sudden find itself placed in very cold regions, the water which now forms our rivers and seas, and probably the greater number of liquids which we know would be transformed into solid mountains and into very hard rocks. The air, according to this hypothesis, or at least a portion of the aëriform substances which compose it, would doubtless cease to exist in the condition of invisible fluids, and through the absence of a sufficient degree of heat, it would revert to the liquid state, and this change would produce new liquids of which we have no idea.—A. L. LAVOISIER (1789).

The conversion of liquids into vapours, and the reverse condensation of vapours into liquids during distillation must have attracted attention before the Christian era, and have suggested the possibility of the condensation of aëriform fluids in general. M. A. Lucanus, in his satirical *Vera historia*, written in the second century, said that the inhabitants of the moon drink air squeezed or compressed into goblets, for this operation produces a liquid like dew. There are also some poetic references to liquid air in Virgil (*c.* 50 B.C.). This, of course, does not mean that the liquid in question was known to the Greek and Roman poets.[1] Some time before the composition of air was known, H. Boerhaave, in his *Elementa chemiæ* (Lugduni Batavorum, 1732), described an attempt to condense air to the liquid state by artificial cold, although he succeeded in producing no other result than the condensation of the moisture in the air. He therefore concluded:

> We may fairly assert that the fluidity of air, in all the large compass from the most rarefied to the most compressed, remains without alteration; and that therefore it is neither capable of being solidified by the intensest cold, nor the greatest degree of compression.

John Dalton saw as clearly as A. L. Lavoisier the probable result of subjecting gases to a great enough cold and pressure. He said:

> There can scarcely be a doubt entertained respecting the reducibility of all elastic fluids of whatever kinds into liquids; and we ought not to despair of effecting it in low temperatures, and by strong pressures exerted upon the unmixed gases.

Among the early experiments there is M. van Marum's[2] liquefaction of ammonia under a pressure of about 3 atm.; L. B. G. de Morveau, and A. F. de Fourcroy and L. N. Vauquelin's liquefaction of the same gas by cooling with a freezing mixture to about —40°, and their nugatory attempt to liquefy hydrogen chloride, hydrogen sulphide, and sulphur dioxide by similar means. G. Monge and L. Clouet reported the liquefaction of sulphur dioxide by simple cooling. In some cases, the drying of the gases must have been so imperfect that the condensation of moisture or of a solution of the gas in water was mistaken for the liquefaction of gas itself.

T. Northmore's work[3] on the liquefaction of gases by compression is perhaps the most important of the earlier experiments. He succeeded in liquefying chlorine, hydrogen chloride, and sulphur dioxide. When the attempt was made with carbon dioxide, the receiver unexpectedly burst with violence. In 1823, M. Faraday[4] liquefied a number of gases by the joint effect of pressure and cold. The gases were generated in one leg of a hermetically sealed glass V-tube, and condensed by cooling with the other leg of the V-tube in a freezing mixture. The increasing pressure developed by the gas enabled sulphur dioxide, hydrogen sulphide, carbon dioxide, nitrogen monoxide, cyanogen, and ammonia to be condensed; and H. Davy likewise succeeded in condensing hydrogen chloride in this manner.

D. Colladon[5] attempted to liquefy air by confining it in a stout glass tube sealed with mercury so arranged that more mercury could be forced into the tube by hydraulic pressure. He worked at —30° and produced a pressure of 400 atm., but he did not succeed in condensing the air. M. Thilorier, in 1834, generated carbon dioxide in a wrought-iron vessel and used the increasing pressure as the gas accumulated in the vessel for its condensation in an adjacent iron vessel cooled by a freezing mixture. M. Thilorier's apparatus was therefore a kind of Faraday's tube of large capacity, and made of cast iron. One of the cylinders burst before a class, and its fragments were scattered about with tremendous force; it cut off both legs of the unfortunate operator, M. Hervy, and the injury was followed by death. This showed that cast iron was not a safe metal for the chambers of an apparatus for condensing gases under pressures. M. Thilorier succeeded in liquefying and solidifying carbon dioxide, and he also prepared a freezing mixture of solid carbon dioxide and ether which enabled a temperature of —110° to be attained. Modifications of M. Thilorier's apparatus were employed by R. Addams, J. K. Mitchell, M. Faraday, J. O. Natterer, etc.[6] In all these systems the gases were liquefied by cold and pressure acting jointly or alone. A few gases—like hydrogen, oxygen, nitrogen, air, etc.—resisted all attempts to liquefaction in this way, and the refractory gases were called **permanent gases** to distinguish them from those more condensable. The term lost its main significance when L. P. Cailletet and R. Pictet succeeded in liquefying oxygen and hydrogen about 1877, and C. von Linde succeeded in manufacturing liquid air on an industrial scale.

The success of the attempts to liquefy gases has been largely dependent upon the methods for producing great cold. About two centuries ago, 1724, G. D. Fahrenheit congratulated himself that no one could produce a lower temperature than he had done by mixing together snow and salt; and he accordingly made this temperature the zero of his thermometer—Fahrenheit's thermometer. In his wildest dreams, Fahrenheit is not likely to have imagined that temperatures 400° F. below the point he evidently thought a very creditable achievement, would, in later years, be comparatively easily attained. When, a few years afterwards, Fahrenheit succeeded in reducing the temperature a few degrees below his own zero, H. Boerhaave said that the result was incredible, and asked: " What mortal man could ever have thought of it ? " The different methods which have been used for producing low temperatures include:

(1) *Methods involving the use of freezing mixtures.*– If ice or snow be mixed

with salt and water above the eutectic temperature, the water will tend to dissolve salt, and the ice will melt and make the solution capable of dissolving more salt. If the liquid be thermally insulated, the latent heat required for the fusion of the ice is abstracted from the liquid, and the temperature falls until the solution has the eutectic composition. The temperatures obtainable by the use of mixtures of ice and salts—the so-called freezing mixtures—range as low as —55°—the eutectic temperature of calcium chloride and water. The following represent some results actually obtained with mixtures of one part of snow with

	Fall of temperature from 0° to
Sodium carbonate (cryst.)—¼th part	−2°
Potassium chloride—⅓rd part	−12°
Sodium chloride—⅓rd part	−18°
Calcium chloride (cryst.)—2 parts	−42°

(2) *Cooling by the adiabatic expansion of cold compressed gases.*—C. W. Siemens (1857), E. Solvay (1885), and F. Windhausen (1892) [7] obtained patents for producing very low temperatures by the expansion of air in a suitable cylinder, and using the cooled expanded air to cool the incoming air by a kind of recuperation of the cold.

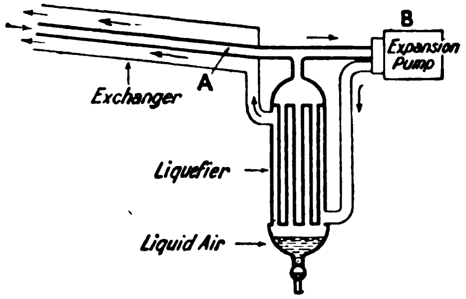

FIG. 22.—Claude's Process for the Liquefaction of Air (Diagrammatic).

In L. P. Cailletet's apparatus, gas is confined in a stout glass tube by mercury and the mercury is pumped by a hydraulic press into a suitable reservoir so as to compress the gas. L. P. Cailletet designed his apparatus so that the pressure confining the gas could be quickly relieved, in order that successive experiments could be made with the same mass of gas. By chance, on relieving the pressure under which some gaseous acetylene was confined, L. P. Cailletet noticed a thick mist—*un brouillard épais*—developed in the tube, and he at first supposed it was produced by the condensation of moisture or impurities in the gas. On testing this assumption with purified acetylene and also nitrous oxide, the sudden expansion of the compressed gas still gave the mist, and he then attributed the phenomenon to liquefaction produced by the intense cooling of the expanding gas. L. P. Cailletet then employed greater pressures with the so-called permanent gases. On Dec. 2nd, 1877, he wrote to H. St. C. Deville :

> I hasten to inform you, and you first without losing a moment, that I have liquefied this day both carbon monoxide and oxygen. I am perhaps wrong in saying liquefied, because at the temperature I obtained by evaporating sulphur dioxide, that is at —29° under 200 atm. pressure, I did not see any liquid, but a dust so dense that I was able to infer the presence of a vapour very close to its point of liquefaction.

He added that no sign of the liquid dust was detected with hydrogen treated in a similar manner, but in a later experiment the mist was obtained working from 300 atm. pressure at —28°. Cailletet's apparatus was used by J. Ogier [8] for liquefying silicomethane ; by L. Ilosvay de N. Ilosva, for liquefying carbonyl sulphide ; by J. Ansdell in studying liquid acetylene, and hydrogen chloride ; by C. Vincent and J. Chappius for methyl and ethyl chlorides, the methylamines, etc. ; by P. Hautefeuille and J. Chappius, L. Troost, and A. Ladenburg for liquid ozone. G. Claude has employed the principle for the continuous liquefaction of air.

The purified air at about 40 atm. pressure is driven through an inner tube *A*, Fig. 22, to an expansion apparatus, *B* ; and the cooled and expanded air circulates upwards about the tube A. The cooled air passes from the liquefier, about the inlet tube A, and is thence returned *viâ* A to the expansion apparatus. The compressed air in the liquefier is thus progressively cooled by the expanded gas from the pump A, until liquefaction is attained. If the temperature of the gas passing to the pump B is too low, there is but a very slight cooling of the gas, and this is aggravated by the increased specific heat of the gas at a low temperature. Consequently, the temperature of the gas entering the pump B is not allowed to fall too low. The liquefied gas is run off at the cock C. Whenever necessary, petroleum ether is used as a lubricant for low temperatures. The advantages claimed for this process are the rapid liquefaction of the air at comparatively low pressures.

(3) *Methods involving the rapid evaporation of volatile liquids.*—In 1755, W. Cullen froze water by its own rapid evaporation, and in 1862, Carré exhibited at the International Exhibition, a machine for manufacturing ice in which the cold was produced by the rapid evaporation of liquid ammonia. Ice is made by this process to-day. In 1835, M. Thilorier showed that the rapid evaporation of liquid or solid carbon dioxide mixed with ether gave a temperature of —100°, and by this means, M. Faraday obtained temperatures as low as —110°. In 1878, J. O. Natterer obtained a temperature of —140° by the rapid evaporation of a mixture of liquid carbon dioxide and nitrous oxide.

A. A. B. Bussy [9] also liquefied sulphur dioxide by cooling, and, on allowing the liquid to evaporate rapidly, produced temperatures which enabled him to liquefy chlorine and ammonia, and to solidify cyanogen. These operations introduce the work of R. Pictet.[10] In order to lessen the risk of compressing gases at enormous pressures, Pictet cooled a gas, B, below its critical temperature by the rapid evaporation of another liquefied gas, A, and used the liquefied gas B to cool a third gas, C, and so on. This is called the **cascade method of liquefying gases.** In one series of experiments, liquid sulphur dioxide was allowed to evaporate around a system of tubes containing carbon dioxide, which then liquefied under a feeble pressure; the liquid carbon dioxide was allowed to evaporate in a similar way about a tube containing oxygen. When the valve closing the tube containing the oxygen was opened, Pictet said that he noticed.oxygen escaped in the form of a transparent jet surrounded by a white cloud which he took to be solid oxygen. As a result, R. Pictet telegraphed to the French Academy of Sciences on Dec. 22nd, 1877:

> Oxygéne liquéfié aujourd'hui sous 320 atmospheres et 140° de froid par acides sulphureux et carbonique accouplés.

This telegram and L. P. Cailletet's letter to J. B. A. Dumas were read at the meeting of the French Academy on Dec. 24th, 1877. Some of R. Pictet's descriptions of liquid oxygen and also of liquid hydrogen, which he claimed to have prepared, have not been confirmed by later work. At the same meeting, J. C. Jamin pointed out that it was still necessary to assemble into a real liquid the impalpable mist which had been momentarily obtained by Pictet and Cailletet; and some time afterwards, S. von Wroblewsky pointed out that the subject required developing so that liquid oxygen could be poured as readily as liquid ethylene. He said:

> It is my conviction that the thing will be successfully carried out only when we return to R. Pictet's method, and by cycles of various liquefied gases make a cascade of temperatures whose last step will produce the stream of liquid oxygen.

S. von Wroblewsky and K. Olschewsky [11] cooled the condensing tube of an apparatus like that of L. P. Cailletet by means of ethylene evaporating under reduced pressure and cooled by solid carbon dioxide. As a result, they were able to telegraph to the French Academy on April 7th, 1883:

> Oxygéne liquéfié, completement liquide, incolore comme l'acide carbonique. Vous recevrez une note dans quelques jours.

Even here comparatively small amounts of liquid were obtained, and it was not until 1895 that C. von Linde was able to liquefy the so-called permanent gases—air and oxygen on a commercial scale. Linde's apparatus was based on quite a different principle. H. K. Onnes [12] at Leyden used the cascade process with methyl chloride, down to —90°; ethylene down to —160°; and oxygen down to —217°. This critical temperature of hydrogen and helium are so much below the lowest temperatures obtained by the evaporation of gases of higher boiling point that the cascade method is inapplicable for their condensation.

(4) *Cooling by the Joule-Thomson effect.*—When a gas, cooled by passing through a small orifice, is made to circulate around the tube leading the compressed gas to the orifice, the gas passing to the orifice is cooled, and on passing through the orifice is cooled still more. By continuing the cycle, it follows that the temperature can be reduced indefinitely low, or the gas liquefies. For example, air at —20° is cooled to —36° by expanding in the orifice from a pressure of 50 atm. to one atmosphere; if this cooled air is compressed and again expanded from —36°, the temperature drops to —54°, then to —101°, —136°, and finally —190°, when the expanding air condenses. The theory was known for almost half a century before it was realized in industrial practice. The so-called self-intensive or cumulative systems for cooling gases were elaborated by C. von Linde,[13] J. Dewar, W. Hampson, and C. E. Tripler between 1894–5.

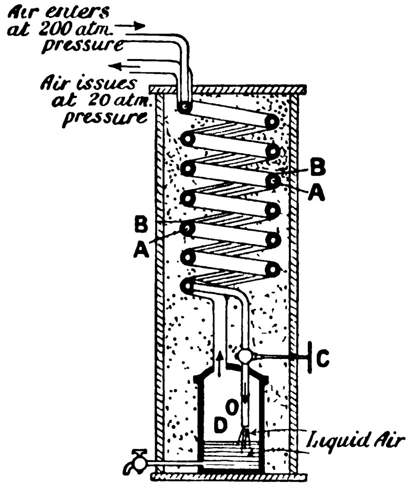

FIG. 23.—Linde's Apparatus for the Liquefaction of Air (Diagrammatic).

The idea will be understood after an examination of Fig. 23. The air to be liquefied —freed from carbon dioxide, moisture, organic matter, etc.—enters the inner tube of concentric or annular pipes, *A*, under a pressure of about 200 atm. This tube is hundreds of yards long and coiled spirally to economize space. By regulating the valve *C*, the compressed air is allowed to suddenly expand in the chamber *D* to a pressure of about 50 atm. The air thus chilled passes back through the tube *B* which surrounds the tube *A* conveying the incoming air. The latter is thus cooled still more. The gas, at 50 atm. pressure, passes along to the pumps, where it is returned with more air to the inner tube. In this manner, the incoming air at 200 atm. pressure is cooled more and more as it issues from the jet *O*. Finally, when the temperature is reduced low enough, drops of liquid air issue from the jet, and collects in the receiver. The tubes must all be packed in a non-conducting medium—wool, feathers, etc.—to protect them from the external heat. From a preceding discussion, the work required to compress a gas from atmospheric pressure to 200 atm. pressure is proportional to log 200, while the work required to compress the gas from 50 to 200 atm. is proportional to log 2. It is therefore found to be more economical and efficient to allow the gas to expand from 200 to 50 atm. pressure rather than from 200 to one atm. pressure, when the expanded gas is returned to the compressor. Several improvements on Linde's form of liquefier have been devised, but the main principles are well illustrated by the original apparatus.

In 1898, J. Dewar liquefied hydrogen by a similar method, but the gas was first cooled below its inversion temperature, —80°, in liquid air before subjecting it to the Joule-Thomson process. By evaporating liquid hydrogen under reduced pressure, a temperature of —259°, or 14° K., was obtained. The inversion temperature of helium is —240°, or 33° K., and H. K. Onnes, in 1908, succeeded in liquefying helium by cooling it below its inversion temperature in liquid hydrogen, and then cooling it still further by the Joule-Thomson process. Helium boils at 4·29° K. under atmospheric pressures; and, by evaporating liquid helium under reduced pressure, H. K. Onnes obtained a temperature 1·48° K., or —271·6°, that is, within less than two degrees of absolute zero.

Preserving liquid air.—There is a far greater difference between the temperature of liquid air (about −190°) and ordinary atmospheric air, than between the temperature of ice and boiling water. The preservation of liquid air is thus a far more difficult problem than would be involved in preventing cold water boiling away while surrounded by a steam jacket at 200°. James Dewar (1892)[14] solved the problem by keeping the liquid air in the double glass flasks with an evacuated space between the inner and outer walls. Vessels similar in principle are said to have been used by L. J. G. Violle in 1882, and by A. d'Arsonval in 1887. Glass is a poor conductor, and a vacuum is a non-conductor. Hence, the liquid in the inner vessel can receive heat only from above, and by radiation. J. Dewar also silvered the glass walls of the evacuated space so as to reduce the effects of radiant heat. Still air is a very bad conductor of heat, so that the open end of the vessel is plugged lightly with cotton wool in order to reduce the ingress of heat from outside to a minimum. In this way, liquid air is transported by rail, etc., with a surprisingly little loss. *En passant*, a similar principle is utilized in the so-called *thermos flasks*, which will not only keep the contained liquids cool, but also retard the cooling of hot liquids; and J. Dewar claimed that he utilized the principle of the vacuum vessel as an insulator in calorimetric experiments in 1874.

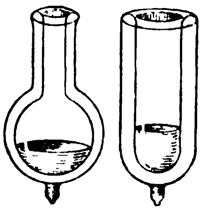

Fig. 24. — Dewar's Flasks.

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§ 26. The Manufacture of Oxygen and Nitrogen from Liquid Air

When a thing is possible according to theory and only practical difficulties oppose its realization, it is infinitely probable that those difficulties are not insurmountable.—G. CLAUDE.

When liquid air evaporates, the nitrogen, boiling at —195·5°, is more volatile than the oxygen, boiling at —182·5°, and escapes first so that the gas which comes from the liquid during the earlier stages of the evaporation contains so little oxygen that it will extinguish a lighted taper; as evaporation continues the liquid becomes richer and richer in oxygen until finally almost pure oxygen separates. If oxygen gas be bubbled through liquid air (—193·5°), the bubbles of gas escaping contain 93 per cent. of nitrogen. The oxygen is condensed from the rising bubbles, and the more volatile nitrogen takes its place. For equilibrium, there is a definite relation between the composition of the liquid mixture and of the rising vapour. This has been investigated by E. C. C. Baly (1900),[1] and the results are illustrated by the curve, Fig. 25, which shows for each proportion of oxygen in the mixed liquid, the corresponding proportion in the vapour which is necessary for equilibrium. Thus, if the *liquid* contains 30 per cent. of oxygen (and 70 of nitrogen), the *vapour* will contain 10 per cent. of oxygen (and 90 of nitrogen). When oxygen is bubbled through liquid air containing 21 per cent. of oxygen (and 79 of nitrogen), then, for equilibrium, oxygen will condense and nitrogen evaporate until the vapour contains 7 per cent. of oxygen (and 93 of nitrogen). E. C. C. Baly's measurements of the percentage composition of liquid air and of the vapour in equilibrium at different temperatures are graphed in Fig. 26. A horizontal line across the curves at any assigned temperature shows the composition of liquid and vapour when in equilibrium. The composition of liquid and vapour in the rectifying columns or scrubbers of Linde's or Claude's apparatus approximate to the values indicated by these curves. These important principles must be clear before the modern method of separating oxygen and nitrogen from liquid air can be understood.

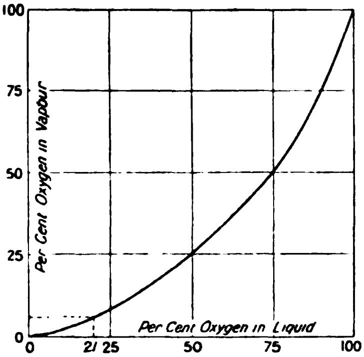

FIG. 25.—Composition of the Liquid and Vapour from Liquid Air (E. C. C. Baly).

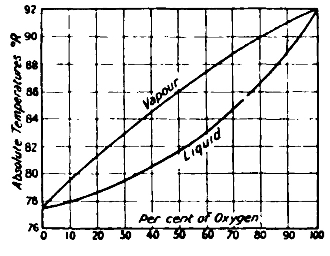

FIG. 26.—The Percentage Composition of Liquid Air in Equilibrium with its Vapour at Different Temperatures.

Linde's process.—J. Dewar noticed that when liquid air boils, the more volatile constituent—nitrogen—is given off preferentially during the first stages of the evaporation, while the residual liquid becomes progressively richer and richer in oxygen. In 1893, J. H. Parkinson[2] patented a proposal to utilize this fact for the commercial production of oxygen, but his apparatus was not satisfactory. It was not until the development of C. von Linde's process[3] in 1895 that it became practicable to manufacture oxygen from liquid air.

A diagrammatic sketch of C. von Linde's apparatus (1895) is indicated in Fig. 27. Purified air is compressed to about 200 atm., and driven along a pipe which divides at *A*, Fig. 27, into two streams and then passes down the interior tubes of a double set of annular or concentric pipes similar to the worm tube, Fig. 23. The two inner tubes finally unite into one single pipe, *B*. The air then passes through a spiral, *S*, *viâ* the regulating valve *R*, and finally streams at *C* into the collecting vessel. The action is here similar to that described in the process for the liquefaction of air, Fig. 23. After a time, the air is liquefied in the collecting vessel, about the spiral *S*. The more volatile nitrogen boils off more rapidly than the oxygen. Hence, a gas rich in nitrogen passes up one of the two annular outer pipes as indicated on the left of Fig. 27. The liquid rich in oxygen is kept at a constant level by means of the valve, and thus the rate at which the liquid air in the collecting vessel is allowed to boil is also regulated. The oxygen passes from this tube on the right of Fig. 27 along the outer annular pipe, and finally emerges from the apparatus, whence it is pumped into cylinders, etc., for use. If the valves are all properly regulated, the inrushing air is cooled by the counter currents of oxygen and nitrogen. The two latter gases pass along the tubes as indicated in the diagram. The tubes, etc., are all well insulated with non-conducting materials—feathers, wool, etc.

In the 1895 apparatus for extracting oxygen from the air, the product was not much more than 60 per cent. purity, and it was not until C. von Linde employed the rectifying tower in 1902, that a purer gas was obtained. In C. von Linde's rectifying column, there is a downward stream of liquid air which starts at about 80° K.; and an upward stream of gas which is rich in nitrogen, and which starts at about 91·5° K. The percolation of the reverse streams through the tower changes the descending current into oxygen of 98–99 per cent. purity, and the ascending current into nitrogen of 93 per cent. purity. The reason why the nitrogen is not richer than 93 per cent. purity will be clear from Fig. 26. The ascending vapours are always richer in oxygen than corresponds with the descending liquid, there is a progressive condensation of oxygen from the vapour, and an evaporation of nitrogen from the liquid, to enable that equilibrium to be established. By this process, oxygen can be obtained as pure as is commercially desired, but the escaping nitrogen contains over 7 per cent. of oxygen. The original apparatus has been much improved in recent years, principally with the object of preparing a purer nitrogen for use in the cyanamide process; but, as G. Claude has said: " We must salute in this apparatus the archetype of all the later machines, for it was the first to demonstrate that the manufacture of oxygen from liquid air is commercially possible." The rectification of the nitrogen is effected by condensing the 93 per cent. product, and rectifying it in another tower. A product with two per cent. oxygen is thus obtained. The supplementary rectification by means of a liquid rich in nitrogen was patented by R. J. Lévy and A. Helbrouner in 1903.[4]

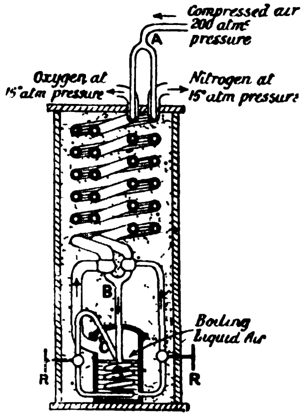

FIG. 27.—Linde's Apparatus for the Separation of Oxygen and Nitrogen from Liquid Air (Diagrammatic).

It must not be assumed that two gases which exert no chemical or physical action on one another, can be separated from a mixture without the expenditure of energy. Each gas in the mixture exerts its own partial pressure, and **the total work required to separate the components of a mixture of gases which exert no chemical or physical action on one another is equal to the sum of the work of isothermal compression of each of the constituent gases from its partial pressure in the mixture to its final pressure.** Lord Rayleigh[5] dealt with the converse problem in 1875 by showing that mechanical work is performed by the simple admixture of two gases without the exercise of chemical affinity.

G. Claude's counter-current process of rectification.—An improvement on Linde's process, by G. Claude (1903), enables practically pure oxygen and nitrogen to be obtained in a simple and effective manner. It is based on the fractional condensation of compressed air. The liquid just formed is drained back through a condenser so that it is scrubbed in contact with the gas which is being condensed. The liquid collects in two portions—one contains about 50 per cent. of oxygen, and the other is almost wholly nitrogen. The two liquids are separately rectified.

A diagrammatic sketch of Claude's apparatus is shown in Fig. 28. The cooled and purified air enters the lower part of the apparatus at a pressure of about 5 atm. and rises through a series of vertical pipes P surrounded by liquid oxygen, where it is partially liquefied. The liquid containing about 47 per cent. oxygen and 53 per cent. of nitrogen drains into the lower vessel A. The vapour which has survived condensation enters B, and then descends through a ring of pipes C arranged concentrically about the set previously described. Here all is liquefied. The liquid which ultimately collects in this vessel D is very rich in nitrogen. The pressure of the vapour in the central receptacle forces the liquid nitrogen to enter the summit of the rectifying column E, and the liquid, containing 47 per cent. of oxygen, is likewise forced to enter the rectifying column at F lower down. The pressure and rates of flow are regulated by the cocks RR'. The liquid nitrogen is 3° or 4° lower in temperature than the liquid rich in oxygen. Nitrogen evaporates from the down-streaming liquid, and oxygen condenses from the up-streaming gases. The heat supplied by the condensation of oxygen helps on the evaporation of nitrogen. Consequently, the descending liquid gets progressively richer and richer in oxygen, and the ascending gases richer in nitrogen. The liquid oxygen drains into the receptacle G, and is there evaporated by the latent heat of the gases condensing in the tubes. Finally, oxygen containing from 2 to 4 per cent. of nitrogen passes from the oxygen exit, and nitrogen containing 0·2 to 1 per cent. of oxygen escapes at the top of the rectifying column.

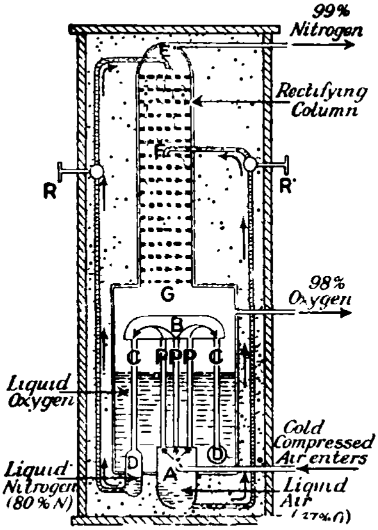

Fig. 28.—G. Claude's Apparatus for the Separation of Oxygen from Liquid Air (Diagrammatic).

These processes enable oxygen and nitrogen to be extracted from atmospheric air comparatively cheaply—one ton of coal for driving the compression apparatus is said to furnish one ton of oxygen and four tons of nitrogen. As C. von Linde has said, "the heat is eliminated from the air exclusively by the expenditure of internal work." The work required for the liquefaction of these gases is solely spent in separating the molecules of the gases from one another against their intermolecular attractions, and in compressing the gases from their partial pressure in the original mixture to their final pressure.

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CHAPTER XIV

OZONE AND HYDROGEN PEROXIDE

§ 1. The Discovery of Ozone and of Hydrogen Peroxide

> In natural philosophy, no observations are trivial, no truths insignificant; that which to us is barren is often so for this reason only, that we do not sufficiently know nor sufficiently examine it.—T. BERGMANN (1779).

IN 1785, eleven years after the discovery of oxygen by J. Priestley, M. van Marum[1] said that he noticed a peculiar smell in the vicinity of electrical machines in motion, but he does not appear to have made any attempt to find the cause of the smell beyond saying that "it seems clearly to be the smell of electrical matter," and noting that the "electrical matter" has the power of acting directly on mercury. A smell, presumably similar, has been noticed from ancient times to accompany thunderbolts, and Homer has made several references to this odour in his *Odyssey* (**12.** 417; **14.** 307), and in his *Iliad* (**8.** 135; **14.** 415).[2] For a time the sulphurous smell was thought to be a popular error in which the blue lurid tint of lightning was connected with the appearance of burning sulphur, and the odour was then imagined. Now, however, there seems no reason to doubt that the peculiar odour which is sometimes perceptible during thunderstorms, and which has been likened to sulphur, is identical with the odour of ozone.

In 1782, T. Cavallo[3] referred to electrified air as the *aura electrica;* he noticed its purifying action on decaying animal and vegetable matter; and he recommended its use as a disinfectant. H. Davy, in his *Lectures on Agricultural Chemistry* (London, 6, 1826), says that

> In 1826 Dr. John Davy recognized the existence of this principle in the atmosphere and published a formula for the preparation of chemical tests to be used in its detection resembling that afterwards adopted by Schönbein.

In 1801, W. Cruickshank also mentioned that a similar odour is produced near one of the electrodes (anode) when acidulated water is electrolyzed. In 1839, C. F. Schönbein's attention was arrested by the similarity in the odour developed during the electrolysis of water and during the working of an electrical machine. The odour emitted by an electrical machine had been explained by assuming that the sensation was due solely to a peculiar action of electricity on the olfactory nerves, and not to the presence of a material substance. In a memoir, *Recherches sur la nature de l'odeur qui se manifeste dans certaines actions chimiques* (1840), C. F. Schönbein[4] claimed that the smell must be due to the formation of a definite substance to which he gave the name *ozone*—from ὄζω, I smell. He said:

> After making many fruitless experiments in order to find the relations between the smell which is developed when ordinary electricity discharges from the points of a conductor in air, and when water is decomposed by a voltaic current, I have finally arrived, not at a complete solution of the problem, but at a point where *le véritable cause de l'odeur électrique* can be recognized more or less clearly.

According to C. F. Schönbein, **ozone is a distinct form of matter with an identity of its own;** ozone is one and the same body from whatever source it be derived; for he found that the same substance was produced when an electrical machine is working; when moist air is passed over oxidizing phosphorus; and when water is electrolyzed. Hence, T. Andrews (1856) could say:

> For the first recognition of ozone and description of its properties, we are indebted to the sagacity of Schönbein, to whom the entire merit of the discovery unquestionably belongs.

Numerous investigations on ozone have proved that the gas is a condensed form of oxygen which can be symbolized by the formula O_3 when ordinary oxygen is symbolized O_2.

Hydrogen peroxide was first described by L. J. Thénard [5] in 1818 in a paper entitled *Observations sur la combinaisons nouvelles entre l'oxygène et divers acides.* The discovery was made while investigating the action of sulphuric, nitric, arsenic, phosphoric, and acetic acids on barium peroxide. He first supposed that the liquids which he obtained were *produits suroxygènés* of the different acids, but he later showed that the liquid, *eau oxygènée,* contains a super-oxide of hydrogen, which is endowed with energetic oxidizing properties, and decomposes when heated into water and oxygen. After analyzing the liquid, he concluded:

> L'eau la plus oxygènée est un bi-oxyde d'hydrogène qui contient, relativement à la même quantité d'hydrogène, deux fois autant d'oxygène que l'eau ordinaire, et que, toutes les fois que l'eau oxygènée ne contient pas cette quantité d'oxygène, elle peut être regardée comme un mélange d'eau pure et de bi·oxyde d'hydrogène.

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§ 2. The Modes of Formation and Preparation of Ozone

When oxygen is heated to an elevated temperature, three endothermal reactions probably occur: (i) $3O_2=2O_3-68{\cdot}2$ Cals.; (ii) $O_2=2O-Q$ Cals.; (iii) $O_3=3O-Q_1$ Cals. Hess' principle shows that $2Q_1-3O_2+2O_3=3Q$, and when the system is in equilibrium $3O_2\rightleftharpoons 2O_3$; $O_2\rightleftharpoons 2O$; and $O_3\rightleftharpoons 3O$. In confirmation it has been shown experimentally that at about 2400°, a great part of the oxygen is dissociated into atoms or associated into molecules of ozone. The formation of ozone, O_3, from oxygen, O_2, is attended by an absorption of energy nearly equivalent to $3O_2=2O_3-68{\cdot}2$ Cals. Consequently, energy is required for the formation of ozone, and this energy must be borrowed from a foreign source, or it may be obtained whenever oxygen is developed at a low temperature by a strongly exothermic reaction. Hence, the various methods of preparing ozone have been arranged in two groups: physical and chemical—

in the former, energy is added to the oxygen directly; in the latter, indirectly. It is, however, not easy to draw a strict line of demarcation.

(1) *The formation of ozone by the action of heat.*—The reputed formation of ozone when hydrogen is burned, and when air or oxygen is passed over glowing platinum, are probably mal-observations; for example, in L. Troost and P. Hautefeuille's oft-quoted experiment (1877), ozone was said to be formed by passing oxygen through a porcelain tube heated above 1400°, but J. K. Clement (1904) [1] could find no ozone under these conditions, not even when a Nernst's filament was heated to over 2000° in oxygen. True, an odour resembling ozone could be detected, and starch and potassium iodide test-paper is coloured blue. These phenomena are a result of the formation of nitrogen oxide, not ozone; this is shown by the fact that the so-called tetra-base test-paper is coloured pale yellow characteristic of the nitrogen oxides; had ozone been present, the paper would have been coloured violet—hydrogen peroxide has no effect.

Ozone seems to be fairly stable at ordinary temperatures, although it gradually decomposes on standing. Low temperatures favour the accumulation of ozone in a system. It also appears to be fairly stable at high temperatures, while at intermediate temperatures it decomposes very rapidly. As a matter of fact, ozone is readily formed at high temperatures. There is a balanced reaction between ozone and oxygen such that the higher the temperature, the greater the proportion of ozone in equilibrium with the oxygen. W. Nernst (1913) estimates that 0·15 per cent. of ozone by weight can exist in equilibrium with oxygen at 1296°, 1·52 per cent. at 2048°, and 16·50 per cent. at 4500°. Hence, if ozone be formed at a high temperature, the hot gas must be cooled more quickly than the ozone can decompose. Ozone decomposes very much more quickly than nitric oxide, so that if both be formed at a high temperature, the latter alone is able to survive if the heated gases are not cooled with very great rapidity. This rapid cooling has been accomplished by F. Fischer and E. Brähmer (1906) by rapidly chilling the heated oxygen in various ways—*e.g.* by burning hydrogen or other substances beneath the surface of liquid air or liquid oxygen; or by plunging a glowing platinum wire or glowing Nernst's filament under the surface of liquid air; or by blowing air or oxygen against a heated Nernst's filament. After hydrogen has burned beneath the surface of liquid air for two or three minutes, the outflowing gas smells like ozone, but it does not give the ozone reaction with the tetra-base test-paper.

The liquid in the tube contains frozen nitric oxides but no hydrogen peroxide. After most of the clear liquid has evaporated, the residue gives all the reactions characteristic of ozone. This shows that nitric oxide and ozone are produced under the conditions of the experiment. Similar results were obtained by burning carbon monoxide, acetylene, hydrogen sulphide, sulphur, or charcoal, but were complicated, of course, by other products of combustion. J. K. Clement's failure to detect ozone in the products of combustion does not prove that ozone is not formed by the heat of the flame, for ozone as well as nitrogen oxide may have been formed, and the latter alone may have survived on cooling. Indeed, the blackening of a silver foil in the hydrogen, or oxy-carbon monoxide blast flame, is taken by W. Manchot (1909) to indicate the presence of ozone, since neither hydrogen peroxide nor nitrogen oxide gives this reaction. To summarize, the effect of heating air to a high temperature:

		Product.		Product.
Time of heating	Short . . .	O_3	Slow cooling	Nil
			Fast cooling	O_3
	Long . . .	O_3+NO	Slow cooling	NO
			Fast cooling	NO+O_3

When a platinum wire at 1700° is plunged beneath the surface of liquid air, ozone but no nitric oxide, is formed, presumably because the temperature required for the production of appreciable amounts of the latter is higher than for ozone. The formation of ozone is not due to the light emitted by the glowing filaments because, if the glower be placed in an evacuated quartz tube plunged in liquid air, no appreciable amount of ozone is formed in the liquid air under the conditions of the experiment so long as the quartz is cool. Nitric oxide, NO, is of course oxidized to nitrogen peroxide, NO_2, in the presence of air or ozone.

(2) *The formation of ozone by the action of ultraviolet and radioactive radiations.*—In 1894, P. Lenard [2] showed that the cathode rays which penetrated an aluminium window in a vacuum tube, ozonized the air through which they passed; but it was not made clear whether the ozone was produced by the cathode rays, or indirectly by the ultraviolet light produced by cathode rays in air. P. Lenard detected no other chemical effects by these rays. Six years later, P. Lenard showed that oxygen is ozonized by ultraviolet light of wave-length between 0·00014 mm. and 0·00019 mm., *i.e.* by rays of great refrangibility to which air is almost opaque. Air is more opaque than rock salt, fluorspar, or quartz to the most chemically active ultraviolet rays. Hence, air-spaces in the path of the rays should be avoided in designing apparatus for ozonizing oxygen by ultraviolet rays. Ozone is produced by the action of radiations of short wave-lengths on oxygen. Cathode rays and ultraviolet light rays, acting on air or oxygen, produce ozone, and this the more the lower the temperature. If liquid or solid oxygen be exposed to ultraviolet light, ozone can be detected in the oxygen obtained by subsequent evaporation. The mercury vapour or uriol lamp is commonly employed for producing ultraviolet radiations; the lamp is made of quartz, not glass, because quartz is transparent and glass is opaque to these radiations. E. Goldstein (1903) passed a discharge through a quartz Geissler's tube, and found that the air in the vicinity was strongly ozonized. If the pressure of the gas in the Geissler's tube be too large, no ozonization occurred. It was assumed that rays of ultraviolet light of small wave-length penetrated the quartz, and ozonized atmospheric oxygen. In H. N. Potter's patented process for ozonizing air, a current of air is conducted spirally about a quartz mercury vapour lamp, within a sheathing of ordinary glass. The mercury lamp gives off a copious stream of ultraviolet light.

There is no definite equilibrium ratio between the rates of formation and decomposition of ozone when air or oxygen is exposed to ultraviolet light; the amount formed increases with fall of temperature, and decreases with fall of pressure. The decomposition of ozone by ultraviolet light is very slow, but is strongly accelerated by small quantities of hydrogen which reacts thus: $H_2+O_3=H_2O+O_2$. No signs of the reaction $2O_3+H_2=H_2O_2+2O_2$ are observed when hydrogen is in excess; the main reaction is $H_2+O_3=H_2O+O_2$, and when ozone is in excess, the main reaction is $2O_3=3O_2$.

According to E. Regener (1906),[3] ozone has a maximum absorptive power for ultraviolet light of wave-length 258$\mu\mu$, and light of wave-length 200–300$\mu\mu$ converts ozone into ordinary oxygen; on the other hand, V. Schumann showed that oxygen absorbs waves below 193$\mu\mu$, and the conversion of oxygen into ozone by ultraviolet light is largely the result of exposure to light of wave-length less than 200$\mu\mu$. There is therefore an equilibrium value for the reaction $3O_2=2O_3$, which decreases with rise of temperature. E. Regener found in one set of experiments 3·4 per cent. of ozone at 20°, 3·15 at 40°, 2·7 at 54°; but the actual proportion of the two gases is also determined by the intensity of the ultraviolet light—*vide* Fig. 6.

The solar spectrum ceases abruptly at 293$\mu\mu$, from which it is inferred that light of shorter wave-length is absorbed by the atmosphere; and further, since oxygen itself does not appreciably absorb light of greater wave-length than 200$\mu\mu$, it follows that the ozone, formed by the absorption of light of wave-length below 200$\mu\mu$, is partially destroyed by light of wave-length approximately 293$\mu\mu$. This is confirmed by the spectroscopic observation that ozone gas has two well-defined absorption bands in the red part of the spectrum, and that the residual transmitted light is markedly blue. These observations are said to favour the hypothesis that the ozone in the atmosphere may have been formed by the action of the ultraviolet rays from the sun, on the oxygen in the upper regions of the atmosphere, and that ozone is formed in the upper atmosphere in sufficiently large quantities to account for the normal blue colour of the sky; this has been rendered further probable by actual determinations of the amounts of ozone in the upper atmosphere. At a mean altitude of 15·2 kilometres, for instance, J. N. Pring (1914) found a mean of $2{\cdot}1\times10^{-6}$ volumes of ozone per volume of air.

The action of the radiations from radium or other radioactive substances[4] on air or oxygen furnishes some ozone. If radium be enclosed in a tube with oxygen, ozone is formed, but not if the radioactive substance is in a separate glass vessel which in turn is placed in a tube of oxygen. The radiations from radium, polonium, etc., can produce ozone. S. C. Lind (1911)[5] showed that the amount of ozone formed by the action of α-rays on oxygen is such that one molecule of ozone is formed for two pairs of gaseous ions. F. Krüger and M. Möller found that in the passage of electrons of high velocity through gaseous oxygen, one pair of ions is concerned in the formation of each molecule of ozone.

(3) *The formation of ozone by electrolysis.*—In 1840, C. F. Schönbein[6] observed the presence of ozone in the gases evolved during the electrolysis of acidulated water and salt solutions. Ozone can generally be detected in the oxygen gas obtained during the electrolysis of acidulated water with non-oxidizable electrodes—*e.g.* gold, platinum, etc. The yield of ozone in the electrolysis of acidulated water is very small, but is increased by reducing the temperature and by increasing the current density—*i.e.* by increasing the intensity of the current or reducing the surface of the anode. By the electrolysis of sulphuric acid of a specific gravity between 1·075 and 1·1, with an anode made by imbedding platinum foil in glass and grinding away the edge so that a line of platinum 0·1 mm. broad and 11·5 mm. long, is exposed, F. Fischer and K. Bendixsohn (1909)[7] prepared oxygen containing 17 to 28 per cent. of ozone. This form of anode prevents long contact between the platinum surface and the gas. The curve, Fig. 1, shows the relation between the yield of ozone by weight and the concentration of the sulphuric acid. With a current density of 65 amps. per sq. cm., the maximum yield is obtained with an acid of specific gravity 1·1. An acid of specific gravity 1·22 has a maximum electrical conductivity, so that the best conducting acid does not give the maximum yield of ozone. Solutions of phosphoric, chromic, nitric, perchloric, or hydrofluoric acid; ammonium or potassium sulphate, potassium hydrogen carbonate; or of sodium or potassium hydroxide do not give such good yields as sulphuric acid. Platinum-iridium electrodes give the best results—lead or lead peroxide electrodes are rapidly destroyed. The cell should be immersed in water cooled to 0°, and the anode should be internally cooled by a freezing mixture to about —14°. The method of making ozone by the electrolysis of sulphuric acid is dearer than the electrical discharge process; but it is an advantage that the gas is free from nitrogen, and that the hydrogen obtained as a by-product may be utilized.

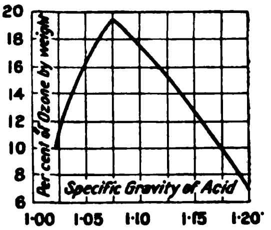

FIG. 1.—Yield of Ozone with Sulphuric Acid of Different Concentrations.

(4) *The formation of ozone by the action of an electrical discharge.*—The electrical discharge through air as dielectric produces a variety of effects: luminous, thermal, chemical, mechanical, and magnetic. In the production of ozone by the electric discharge, chemical action is alone wanted, and accordingly the conditions should be such as to keep the waste of energy expended in producing other effects as low as possible.

The relations between the current *C* and voltage *V* in a gaseous discharge are somewhat complex.[8] If the current from a positively charged point, passing through the air to the earth, be gradually increased, the voltage rises rapidly and very small currents pass as a *non-luminous or invisible discharge* which produces no chemical effects; finally, Fig. 2. there is a slight discontinuity in the voltage-current curve, and the discharge becomes luminous—*glow or silent discharge.* This is a high tension discharge of little energy. Very little electricity leaks during the so-called invisible and glow discharges. For an air-gap a few centimetres in length, there are very high voltages and small currents of a few amperes; as the voltage increases, the conductivity of the air increases, and the voltage rapidly falls, the current increases, and the so-called *brush discharge*, more luminous than the glow discharge, is developed. The appearance and nature of the brush discharge varies considerably with the conditions and the shape of the electrodes; it develops very little light and heat, and it acts almost exclusively on the oxygen—very little nitrogen is oxidized. The conditions favourable for the formation of the brush discharge are important since the production of ozone by the electrical discharge is largely the result of its work. The brush discharge is sometimes called *silent, or dark discharge.* These terms are misnomers; the brush discharge is neither silent nor dark, for it is attended by a peculiar sound, and it is coloured bluish-white. The German equivalent is *Bueschelentladung*; the French equivalents are *l'effluve électrique* and *l'aigrette électrique* according as the discharge shows a narrowed stem or is expanded fan-wise. The transition from one form of high tension discharge to another may be accompanied by sparking, where the discharge is characterized by a loud snapping noise and a yellow colour. The spark and brush discharges may be mixed. Sparking is very detrimental to the formation of ozone. At −194°, E. Briner and E. Durand (1907) [9] found that 99 per cent. of oxygen is converted into ozone with the silent discharge, and only 1 per cent. with the spark discharge; and even this was considered to be produced by the silent discharge which occurred simultaneously with the sparking.

There is another discontinuity in the voltage-amperage curve of electrical discharge as the brush discharge changes into the *electrical flame*—the precursor of the *high-tension arc.* When the arc has been established, the path of the discharge is strongly luminous, and the ratio C/V is higher than before; but instead of the voltage increasing with current, it now decreases owing to the fact that the resistance of the air-gap decreases faster than the increase of current. The high-tension arc in air at ordinary pressure corresponds with the glow-discharge in a gas at a low pressure. The electric arc is active in producing nitric oxide in air. The temperature is different in different parts of the arc and depends on the current and voltage; it approximates 2200° or 2500° in the positive column. As the current increases still further, the temperature rises, and another discontinuity occurs as the discharge passes into the *low-tension or lighting arc.* The low-tension arc is used in steel and carbide furnaces; the temperature is very high; and the electrode material is largely vaporized. The temperature with carbon electrodes is about 3500°. With a negatively charged point, the results are similar but rather less complex. If the electric discharge takes place between parallel conductivity plates, with one or both covered by a solid dielectric, the phenomenon is rather more complex. The brush discharge then changes its character, but it still retains its valuable property of converting oxygen into ozone. As a matter of fact, a series of electric sparks in oxygen will form ozone, and in air a mixture of nitrogen oxide and ozone [10]—all depends on the rate of cooling as indicated previously.

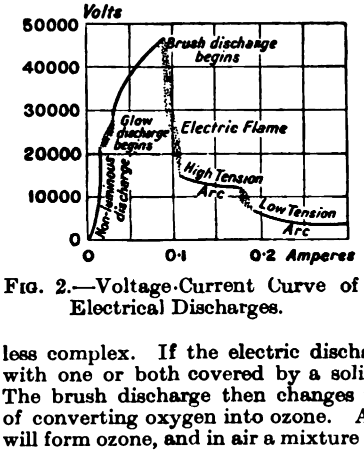

FIG. 2.—Voltage-Current Curve of Electrical Discharges.

The brush discharge is most favourable for the production of ozone.[11] In the arc and spark discharges much heat and light are developed, and energetic chemical action occurs; ozone is formed, but the nitrogen of the air also reacts with the oxygen under this stimulus. The fact that nitrogen oxides are often produced when ozone is made from atmospheric oxygen rather confused the minds of the early investigators as to the real nature of ozone, for the two products were not always clearly discriminated by the tests employed—usually, the bluing of starch and potassium iodide test-paper.

E. Warburg [12] found that under different conditions, the electrical discharge produces from 93 to 1000 times as much ozone as would have been obtained by electrolysis. One equivalent of hydrogen reduces 24 grms. of ozone, and therefore the equivalent of ozone is taken to be 24. E. Warburg and G. Leithäuser obtained between 0·003 and 0·1 grm. of ozone per coulomb, so that between 240 and 8000 coulombs are required to produce 24 grms. of ozone; these numbers are not at all equivalent to the electrochemical equivalent, 96,540 coulombs. The energy required is greater than the heat of the reaction. The highest yield of ozone, 70 grms. per kilowatt hour, is equivalent to 589 Cals. per gram-molecule—nearly 20 times the energy equivalent to the heat of the reaction. Hence it was inferred that the formation of ozone by the silent discharge is not a direct electrolytic action, but is rather a secondary effect of the ultraviolet and cathode rays generated in some profusion by this discharge. Quartz plates are virtually transparent to ultraviolet light, so that if the discharge passes inside a quartz vessel surrounded by oxygen, ozone is formed; while if under similar conditions, the discharge passes inside a glass vessel, which is almost opaque to ultraviolet rays, there is little or no ozonization of the oxygen. E. Warburg assumes that the electrons, generated by the ultraviolet and cathode rays which have a velocity as high as that required for the production of luminosity, are effective in forming ozone either directly by impact with oxygen molecules, or indirectly by the intermediate production of short æther waves.

The amount of ozone obtained per coulomb of electricity follows no known law, and it is therefore necessary to find the yield of ozone under different conditions empirically. The silent discharge has a deozonizing as well as an ozonizing effect on oxygen. The speed of the ozonization is proportional to the amount of oxygen present, and the speed of the deozonization is proportional to the amount of ozone present. In other words, the reaction follows the law of opposing reactions. If the discharge be passed an infinite time, a certain definite limiting concentration of ozone will be reached when the rate of decomposition is equal to the rate of formation of the ozone: $3O_2 \rightleftharpoons 2O_3$.

E. Warburg[13] obtained the results shown in Table I. with an apparatus containing oxygen, and fitted with a small pointed platinum wire (0·05 mm. diameter) connected to the negative pole of an electrostatic machine, and discharging on to another platinum wire (0·05 mm. diameter) connected to earth. The results show that the maximum concentration of ozone decreases as the *temperature* rises, owing to an increase in the speed of decomposition of ozone, and not to a marked reduction in the speed of formation of ozone. The spontaneous decomposition of ozone was negligibly small.

TABLE I.—MAXIMUM CONCENTRATION OF OZONE.

Temperature.	Ozone—per cent. by volume.	A constant proportional to the rate of formation.	A constant proportional to the rate of decomposition.
−71	5·74	0·0232	0·380
0	4·19	0·0219	0·503
17	3·53	0·0225	0·616
50	2·22	0·0214	0·939
93	1·23	0·0277	1·420

E. Goldstein's[14] experiment shows how a low temperature favours the formation of ozone. He introduced oxygen into an evacuated Geissler's tube until the pressure registered a few centimetres. The tube was partially immersed in liquid air, and electrical discharge passed through the tube. In about half a minute, the pressure sank to about 0·1 mm. Oxygen was again introduced until the pressure reached a few centimetres, and the process repeated again and again. In this way, E. Goldstein claimed 100 per cent. conversion of oxygen into dark blue liquid ozone.

In general, the greater the *pressure* of the gas, the greater the yield. In E. Warburg's experiments, the yield at a pressure p—between 460 and 780 mm.—was $(0·32360+0·00089p)$ times the yield at a pressure of 760 mm.—temperature between 17° and 23°. According to E. Warburg, the decrease in the yield with a rise of temperature is largely due to the decrease in the density of the oxygen.

E. Warburg's experiments further showed that the maximum concentration with a positive discharge is one-third the value obtained with a negative discharge owing to the greater ozonizing effect of the latter, while the speed of deozonization and the temperature effect is nearly the same with both a positive and a negative discharge. E. Bichat and A. Guntz (1888) [15] also testified to the greater efficacy of the negative discharge in the formation of ozone, but A. Vosmaer (1916) maintains that this is an error probably due to a reversal of the poles during the working of the electrostatic machine, so that what was thought to be the negative pole was really positive.

The yield of ozone decreases with increasing *current* up to a certain point; thus with oxygen of 98·5 per cent. purity:

Volts	7230	8800	12500
Ampères . . .	0·00000883	0·0000175	0·0000523
Ozone (grms. per coulomb)	0·0950	0·0908	0·0485

If the current be increased still more, the yield reaches a minimum, and then increases with the current. Thus, with oxygen of 96 per cent. purity:

Volts	6080	7000	9610	12510
Ampères . . .	0·00000146	0·0000219	0·0000524	0·0001307
Ozone (grms. per coulomb)	0·0423	0·0375	0·0307	0·0422

The effect of variations of temperature and pressure is complicated, because not only is the substance itself altered, but the reagent which brings about the reaction is also modified. According to A. Chassy [16] the amount of ozone formed is proportional to the *voltage*, but there is a doubt about this since it is very difficult to vary the voltage in electrical discharges through gases without at the same time varying the energy. The formation of ozone, after all, is a question of the transformation of electrical into chemical energy. The quantity of available electrical energy may be regarded as a product of the voltage and amperage, and since the voltage for a given apparatus does not change very much, the yield of ozone must depend on the amperage, and bear no special relation to the voltage.[17] The voltage can be regarded only as a force which can neither be under nor over a certain limiting value consistent with the apparatus. If the voltage be too high there is a danger of sparking through the air, or of cracking or piercing a solid dielectric. Hence, the voltage is run as high as is consistent with safety in order to keep the product—voltage × amperage—high. The yield is then large, not because the voltage is high but because a large amount of electrical energy is available. Most experiments on high-tension currents have been made with alternating currents. A higher frequency than 100 is favourable to the brush discharge. M. W. Franklin [18] says that the yield of ozone is proportional to the periodicity of the current. According to E. Warburg, the yield with an alternating current is not so good as with a direct current, but this has not been definitely accepted.

According to E. Warburg and G. Leithäuser, the presence of *water vapour* in the oxygen to be ozonized reduced the yield nearly proportional to the pressure of the water vapour.[19] With a negative discharge, a reduction of 7 mm. in the pressure of the water vapour reduced the yield to 94 per cent. of its value for dry oxygen. The effect of moisture is greater with air, and greater still with a positive discharge. The retardation with moisture is greater with oxygen than with air. E. P. Perman and R. H. Greaves also find water vapour accelerates the decomposition of ozone. Even when extreme precautions are taken to dry the gas thoroughly, W. A. Shenstone and T. A. Cundall still found that oxygen is ozonized by the silent discharge, and they also obtained a *greater* yield with moist than with the thoroughly dried gas. H. B. Baker then stated that "ozone is formed as rapidly in oxygen dried with phosphorus pentoxide as it is in the same tube when the oxygen is dried by sulphuric acid." W. A. Shenstone (1897) then showed that a high percentage of ozone is formed by the action of the silent discharge on oxygen saturated with water vapour and the ozone produced is remarkably stable; while on partially drying the gas, the percentage of ozone produced is considerably reduced, and the gas is singularly unstable." W. A. Shenstone's result has not been confirmed, and it is probably a mal-observation due to the presence of nitrogen peroxide in the dry gas, derived from the action of the discharge on slight trace of nitrogen in the oxygen gas. E. Warburg, and D. L. Chapman and H. E. Jones found that the velocity of decomposition of ozone at 100° is virtually the same whether water vapour be present or absent.

According to E. Warburg (1904), no nitrogen oxide is formed when the oxygen is mixed with 7 per cent. of nitrogen, but this is doubtful since with air, nitrogen oxides are formed. A spark discharge produces oxides of nitrogen alone; these oxides prevent the formation of ozone. A little nitrogen or hydrogen favours the production of ozone,[20] but if sparking occurs, the hydrogen unites with the oxygen—explosively if sufficient be present. According to P. Hautefeuille and J. Chappius, a little silicon tetrafluoride or hydrogen fluoride does not affect the yield of ozone; but a trace of chlorine or nitrogen oxide hinders the ozonization of oxygen.[21]

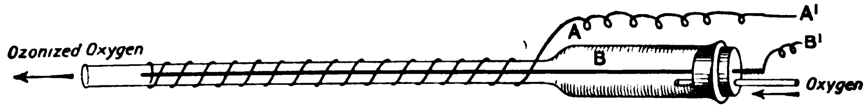

FIG. 3.—L. von Babo's *Tube Ozoniseur.*

The brush discharge may be produced from a static electric machine, from a battery of cells or a dynamo and an induction coil; or from an alternating current from a dynamo of high periodicity, and transformed up to several thousand volts. The latter is the means employed in the commercial production of ozone, while the induction coil furnishes a useful ozonizing discharge in common use for demonstrations and other purposes. L. von **Babo's ozonizer** modified by A. Houzeau,[22] is one of the oldest, and simplest. It is illustrated in Fig. 3. The discharge takes place between two platinum wires, one of which, *B*, Fig. 3, is fitted axially in the narrow tube—this wire is about one or two mm. thick and 40 cm. long; the other wire is rather thin, and is wound around the outside of the narrow tube. The ends of these wires, *A'B'*, are put in communication with the two poles of an induction coil (*G*, Fig. 4). A slow current of oxygen is passed into tube at one end; ozonized oxygen escapes at the other end. The ozonizer illustrated at *A B*, Fig. 4, is

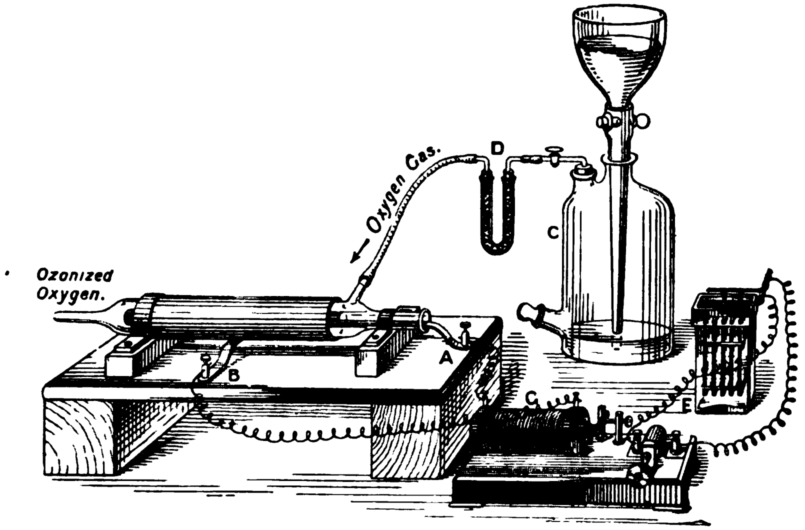

FIG. 4.—Preparation of Ozone with Siemens' Tube.

virtually the one devised by W. von Siemens (1857).[23] **Siemens' ozonizer** (or *ozonator*, or *electrizer*), as it is called, consists of two concentric tubes. The inner tube is coated on its inner surface with tinfoil in metallic contact with the terminal *A*; and the outer tube is coated on its surface with tinfoil in metallic contact with the terminal *B*. This forms the so-called *Siemens' induction tube*. The two terminals are connected with an induction coil. A slow stream of oxygen is led from the gasholder *C* through the calcium chloride drying tube *D*, and then through the annular space between the concentric tubes, and is there exposed to the action of the silent discharge of electricity, operated by the induction coil *G*, and battery *E*. Ozone is decomposed by cork and indiarubber. In consequence, these materials should not be used for any part of the ozonizer in contact with the gas. The gas issuing from the ozone tube, or ozonizer, is charged with 3 to 8 per cent. of ozone. If the oxygen contains traces of chloride, the gas should be washed in dilute alkali before drying. In some forms of ozonizer there are three concentric tubes, and cold water circulates in the inner tube while the discharge is passing so as to prevent a rise of temperature, and thus increase the yield of ozone.

The ozonizer devised by B. C. Brodie in 1872—**Brodie's ozonizer**[24]—is usually called *Berthelot's ozonizer*, though the latter designed it some years after B. C. Brodie. Here the tinfoil coatings are replaced with sulphuric acid as illustrated in Fig. 5. It consists of two concentric thin glass tubes with an annular space from 1 to 4 mm. There are inlet and egress tubes as shown. The inner tube is about 30 mm. diameter and 30–35 cm. long. This apparatus is suspended in a cylinder of water acidulated with sulphuric acid (1 : 10), and the inner tube likewise contains the same liquid. Platinum wires dip in the liquids. The wires *A* and *B* are connected with the induction coil and a slow current of oxygen is sent through the apparatus—ozonized oxygen escapes. The quantity of ozone per coulomb increases with the potential.[25] According to F. Russ, the yield of ozone with an ozonizer of vitreous quartz is but half that obtained with a glass ozonizer. The yield of ozone per kilowatt hour is greater when one electrode is not covered with an insulator (glass). The parts of the tube which do not dip in the dilute acid are covered with shellac varnish in order to prevent external sparking. The gas circulates in the annular space between the inner and outer tubes. If the gas travels through the apparatus too quickly some escapes the action of the discharge; and if too slowly, the ozone may be decomposed. About one bubble of gas per second gives good results. The cooler the vessel, the better the yield; at −23°, oxygen containing 21 per cent. of ozone can be obtained.

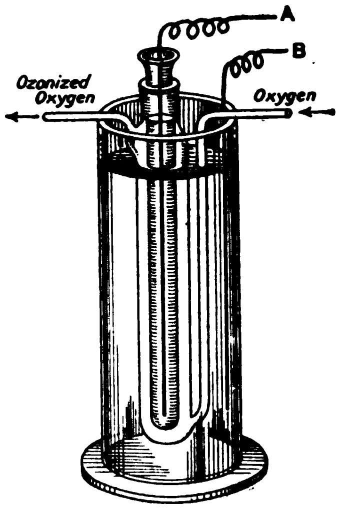

FIG. 5.—B. C. Brodie's Ozone Tube.

It will be observed that in W. von Siemens' or in M. Berthelot's ozonizer there are three dielectrics in the path of the discharge—two layers of glass, and one of gas; in L. von Babo's ozonizer there is one layer of glass, and one of gas. Neglecting the gas to be ozonized which must necessarily be present in all ozonizers, there are two types of ozonizers in use, for the ozonization of air or oxygen on a large scale: those which have dielectrics in the path of the discharge—*e.g.* E. W. von Siemens and J. G. Halske's, Abraham and Marmier's, and Linder's ozonizers[26]—and those which have no dielectric—*e.g.* A. Schneller's, A. Vosmaer's, and H. Tindal's ozonizers.[27] In the so-called *ozonair system*, a series of mica plates, covered on both sides with a metal alloy, are mounted side by side in a box. The plates serve as electrodes. Air passes into the box between the plates. It is claimed that the gauze promotes the formation of a sparkless brush discharge, and that the open arrangement of the plates suffices to keep them cool without the aid of water cooling.

Ozone is said to be produced by the violent mechanical disturbance of air[28]—say, when grinding wheels are being tested for bursting speed. This may be an effect of heat or of electrification or both. Ozone is also said to be formed during the evaporation of water. This statement may be regarded as not proven; nor is the evidence satisfactory as to the formation of ozone when water or a salt solution—*e.g.* sea water—is splashed about,[29] although these statements have been cited to explain the greater ozone content of air in the vicinity of the sea, waterworks, irrigation plants, and waterfalls; and for the bleaching of linen, etc., spread on lawns. The electrification of air by the splashing of liquids is, however, a well-known phenomenon investigated by P. Lenard,[30] Lord Kelvin, etc.

(5) *The formation of ozone in chemical reactions.*—Ozone is usually present in the oxygen obtained by low temperature exothermal reactions; but not if the temperature of the reaction be high, because the ozone, if it be formed, is at once transformed into oxygen. Potassium chlorate gives ozone-free oxygen, but if the chlorate be mixed with catalytic agents which lower the temperature of the reaction, ozone may be found in the resulting oxygen (*q.v.*). Crystallized iodic or periodic acid decomposes between 130°–135° giving off strongly ozonized oxygen; and, according to C. F. Rammelsberg,[31] aqueous solutions of periodic acid or periodates smell of ozone; but A. R. Leeds has shown that what C. F. Rammelsberg thought to be ozone is really chlorine or nitrous acid, present as an impurity in the periodate. Ozonized oxygen is also formed when many oxidizing agents are heated alone or mixed with acids. For instance, ozonized oxygen is obtained from silver peroxide (C. F. Schönbein, 1855), lead peroxide (C. F. Schönbein, 1855), and mercuric oxide (C. T. Kingzett, 1872). As previously indicated, A. R. Leeds contended that C. F. Schönbein mistook chlorine for ozone in assuming that ozonized oxygen was formed by heating these oxides—both gases affect a solution of starch and potassium iodide in the same way; but O. Brunck[32] showed that manganese dioxide, chromium, nickel, cobalt, and gold sesquioxides, silver mono- and dioxide, mercuric oxide, and chromium and uranium trioxides give ozonized oxygen if heated in an atmosphere of oxygen, but not if heated in an atmosphere free from oxygen. Ozonized oxygen is formed by the decomposition of hydrogen peroxide (A. Riche, 1860), not only with sulphuric acid, but also with dilute sulphurous acid, with finely divided metals, and with all substances[33] which stimulate the decomposition of this compound. F. Raschig also detected ozone in gas obtained by dissolving nitrogen peroxide in sulphuric acid in the lead-chamber process.[34] Ozonized oxygen is also obtained by the action of sulphuric acid on barium peroxide (A. Houzeau, 1861), sodium peroxide (C. Arnold and C. Mentzel, 1902), persulphuric acid and the persulphates (A. von Baeyer and V. Villiger, 1901, and P. Malaquin, 1911), percarbonic acid and the percarbonates (C. Arnold and C. Mentzel, 1902), perborates (S. Tanatar, 1898), per-monophosphates (J. Schmidlin and P. Massini, 1910), permanganates (G. Bertazzi, 1855), bichromates (C. Weltzien, 1867), peruranic acid (P. G. Melikoff and L. Pissarjewsky, 1897), fluovanadic compounds (P. G. Melikoff and P. Kasanezky, 1901), barium ferrate (A. Baschieri, 1906), per-pyrosulphates (W. Traube, 1909), acetone peroxide (A. von Baeyer and V. Villiger, 1900), performic acid (J. d'Ans and A. Kneip, 1915), etc.[35]

H. Moissan[36] (1891) found that when drops of water are allowed to fall into a vessel containing fluorine gas, the water is decomposed, and hydrogen fluoride and deep blue vapours of ozonized oxygen are produced. At 0°, oxygen containing up to 21 per cent. of ozone by weight was obtained. The lower the temperature of the reaction, the greater the yield of ozone. O. Ruff and F. W. Tschirch[37] obtained ozonized oxygen by the action of osmium octafluoride on soda lye. L. Gräfenberg[38] obtained ozonized oxygen by the electrolysis of hydrofluoric acid—with the 40 per cent. acid, a maximum yield of 5·2 per cent. of ozone was obtained.

E. B. R. Prideaux also electrolyzed saturated solutions of alkali fluorides, and obtained a yield never exceeding 1 per cent. of ozone.

(6) *The formation of ozone during slow oxidations.*—Ozone is formed during the slow oxidation of many substances; C. F. Schönbein [39] detected it in the atmosphere of a flask containing a couple of sticks of clean phosphorus, and J. C. G. de Marignac prepared ozonized air by aspirating atmospheric air through a flask or tube containing a few pieces of clean phosphorus partly submerged in water. According to C. F. Schönbein, one part of phosphorus converts $\frac{1}{1300}$th part of oxygen into ozone. The resulting gas should be washed to free it from phosphoric oxide. The action is very slow at the freezing point of water, but between 15° and 20°, the action is fairly quick, and at 38° but little ozone is formed; according to A. R. Leeds, the optimum temperature is 24°, but even then, the yield is very small—say about 2 mgrm. of ozone per litre of air. According to R. Engel, reducing the pressure favours the formation of ozone; thus, the action does not occur with appreciable velocity below 6°, but under reduced pressure, the action may occur at 9°. Since ozone is decomposed in contact with phosphorus, a rapid current of air is desirable. According to A. R. Leeds and R. Böttger, the addition of sulphuric acid and potassium permanganate or potassium dichromate to the water is said to increase the yield of ozone; but C. Arnold and C. Mentzel found no advantage in the use of chromic acid.

Instead of air, a mixture of oxygen and carbon dioxide can be used. J. C. G. de Marignac found that a mixture of oxygen and hydrogen sometimes exploded. Minute traces of ammonia, sulphur dioxide, nitrogen peroxide, alcohol, ether, ethylene, and ethereal oils retard the action. The liquid in the flask [40] contains phosphorous and phosphoric acids, hydrogen peroxide, and ammonium nitrite. According to C. T. Kingzett, the ratio of ozone to hydrogen peroxide formed in the reaction is 1 : 2·4; and according to A. R. Leeds, 1 : 1. The evidence is not quite satisfactory since H. McLeod failed to find hydrogen peroxide, but his tests were not very delicate.

P. Villard [41] has suggested that the oxidation of oxygen to ozone in this reaction is produced by radiations of short-wave length generated during the phosphorescence of the phosphorus. The phosphorescence of phosphorus is probably an ozonizing action; similarly, according to L. Bloch, when sulphur is heated to about 200°, the luminescence is accompanied by the formation of ozone. According to J. H. van't Hoff [42] and W. P. Jorissen, only half an atom of oxygen is available for the oxidation of oxygen to ozone per atom of phosphorus oxidized. Ozone is not formed when a substance is present capable of giving rise to the formation of hydrogen—*e.g.* hydrogen peroxide is formed by the oxidation of water when zinc, lead, etc., is substituted for the phosphorus. During the oxidation of phosphorus the ambient air becomes electrically conducting.

Many other substances also furnish ozone or activate oxygen during their oxidation. Ozone is said to be formed during the combustion of ether as well as during the combustion of hydrogen compounds generally. At any rate, the potassium iodide test indicates the formation of ozone (or hydrogen peroxide) when a spiral of hot platinum is placed above the surface of a little ether in the bottom of a beaker. The ether burns on the surface of the platinum, and the platinum remains incandescent as long as any ether remains in the beaker. The alleged formation of ozone during the evaporation of alcohol, ether, ethereal oils, hydrocarbons, etc.,[43] may be an effect of an analogous phenomenon—*autoxidation*. By exposing *p*-diacetyldiamino-stilbene-*o*-disulphonic acid, or many of its salts, in glass vessels to sunlight, the colour changes from bright yellow to reddish-brown, and the reverse change takes place in darkness. The glass cuts off the rays below 350μ wave-length. The presence of oxygen is necessary, and ozone is simultaneously formed. This may be a kind of autoxidation phenomenon.

According to C. F. Schönbein,[44] ozone is formed when turpentine, benzene, petroleum, aldehyde, coal tar, many hydrocarbons, mineral and essential oils—

eucalyptus, lavender, cinnamon, etc.—are oxidized. Acids and resinous matter are formed at the same time. There are ozonators on the market which contain an essential oil—say cinnamon oil—which slowly evaporates; they do not give ozone at all. C. Engler[45] has shown that it is not ozone which is produced by these organic compounds, but rather an unstable peroxide, or ozonide, which can act as a powerful oxidizing agent. For instance, when turpentine is agitated with a large volume of air, oxygen is absorbed, and part of the substance is oxidized, and it is this oxide which has led to the assumption that ozone is formed and dissolved by the hydrocarbon—for it can colour starch and potassium iodide test-paper blue, decolorize indigo blue, colour tincture of guaiacum blue, etc. When a 5 to 7 per cent. benzene solution of dimethylfulvene, C_8H_{10}, is agitated with air[46] for a few days, a precipitate of a peroxide, $C_8H_{10}O_4$, is formed which detonates at 120°, and which gives the usual reactions for peroxides only when a little ether, alcohol, ethyl acetate, or chloroform is present.

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§ 3. The Occurrence of Ozone and Hydrogen Peroxide

According to A. Houzeau (1867), country air contains about one volume of ozone per 700,000 volumes of air; but a maximum of one part in ten millions would be nearer the mark. The maximum amount of ozone in the atmosphere is said to occur during the spring months, and to diminish gradually, reaching a minimum in winter. The air over the sea is usually, but not always, richer in ozone than air over land.[1] Ozone is absent in the air of towns and dwelling-houses, over marshes, and wherever organic matter is present. It is really extraordinary the number of determinations which have been made in order to find if the amount of ozone predominates in spring, summer, autumn, winter, or at any particular part of the day. Attempts have been made to show the effect of the electrical and hygrometric state of the atmosphere; the force and direction of the wind; the intensity of the sunlight; the geographical and geological formation of particular districts; etc. A. Houzeau himself is responsible for 4000 observations; and many others have been published. In some cases, the results are contradictory; and most of them should be discarded because much of what was formerly alleged to be ozone may not be ozone at all. This is due to the imperfection of the tests employed. For example, T. Andrews found that the oxidizing matter in the air was destroyed by heating the air to 260°. This would not be the case if the oxidizing matter was chlorine, nitrous acid or sulphur oxides; but Andrew's test does not discriminate between ozone and hydrogen peroxide. The old starch and potassium iodide test-papers did not discriminate between ozone, hydrogen peroxide, nitrogen oxide, or other oxidizing agents, hence there is some uncertainty about many of the reports of the occurrence of ozone, and more particularly those referring to the proportion of ozone in the atmosphere. For example, C. F. Schönbein gave about 0·0043 mgrm. of ozone per 100 litres of air; J. Pless and V. Pierre, 0·008 mgrm.; C. W. Zenger, 0·002 to 0·01 mgrm.; A. Houzeau, 0·0029 mgrm.; M. de Thierry, 0·0035 to 0·0094 mgrm.; and R. Lespieau, 0·00052 mgrm.[2]

The more recent determinations by E. H. Kaiser and L. McMaster, and by W. Hayhurst and J. N. Pring,[3] have satisfactorily established the presence of ozone in atmospheric air. The atmosphere of the Alps at an elevation of 6·5 kilometres contains 1·2 volumes of ozone per million parts of air; and at an altitude of 20 kilometres, 5·4 volumes per million. No hydrogen peroxide or nitrogen peroxide was detected. There is also a quite adequate explanation of the formation of atmospheric ozone. The dark electrical discharges from clouds, etc., and lightning, and the action of ultraviolet radiations from the sun must all ozonize atmospheric oxygen. W. N. Hartley[4] showed that from spectroscopic observations ozone must be a regular constituent of the upper regions of the atmosphere where it is present in larger proportions than nearer sea-level. The ozone formed in the upper regions is decomposed by oxidizable substances in the lower regions, C. Fabry and H. Buisson emphasize the fact that although the assumption that the high ozone content of the upper atmosphere is not proved, the deduction is very probable from the blue colour of the sky, and the abrupt break in the solar spectrum for rays of wave-length 293$\mu\mu$ corresponding with the break in the absorption spectrum of ozone. G. D. Liveing and J. Dewar question whether the blueness of the sky can be justly attributed to ozone because the absorption spectrum of oxygen exhibits certain bands identical with those of the solar spectrum, which K. Angström[5] found to be equally strong whether the atmosphere be wet or dry; and that daylight possesses a blue tint when observed through a 18-metre layer of oxygen compressed at 90 atm.

The presence of ozone in solution in certain spring waters has been established by R. Nasini and M. G. Levy, and C. Porlezza.[6] The spring at Fiuggi and the *aqua forte della Bagnori* of Monte Amiata, gave the qualitative reactions of ozone with starch and potassium iodide, and litmus-potassium iodide test papers; guaiacum test paper; acid-free gold chloride, manganous chloride, C. Arnold's tetramethyl base test paper; and with silver foil. At 21·50°, a litre of the water contained 0·135 c.c. of ozone in solution. It is suggested that the ozone may be due to the action of radioactive rocks, or to the autoxidation of ferrous carbonate, or to sulphur bacteria. A. Schrötter[7] (1860) reported 0·02 per cent. of ozone—identified by the smell—occluded in the blue fluorspar of Wölsendorf and Joachimsthal, but A. Houzeau and O. Loew considered this inference to be wrong because the smell attributed to ozone is retained after fluorspar has been heated to 300°. C. F. Schafhäutel attributes the smell to the presence of inclusions containing free hypochlorous acid; and J. Meyer supposes the mineral contains free fluorine as an inclusion, and this, with traces of moisture from the air, forms ozone. Reports of the presence of ozone in blood (A. Schmidt, 1862), in milk (C. Arnold, 1881), and in respired air (A. Struve, 1871) are probably wrong, and they are based only on old and fallacious tests. Some physiologists assert that the oxygen given off by green plants in light contains ozone,[8] but G. Bellucci contradicts this statement.

The occurrence of hydrogen peroxide.—There is a similar uncertainty about the alleged occurrence of hydrogen peroxide in the atmosphere and rain, snow and in dew, as in the case with early reports on the occurrence of ozone in air. C. F. Schönbein, E. Schöne,[9] and others claim hydrogen peroxide to be present in the atmosphere and in rain water; A. Houzeau[10] and L. I. de N. Ilsova say that no hydrogen peroxide is present, and the latter adds that what was thought to be hydrogen peroxide is really an oxide of nitrogen. It is too true that much of the published work does not clearly discriminate hydrogen peroxide from other oxidizing substances. In any case the amount of hydrogen peroxide must be very small—between 0·04 and 1·00 mgrm. per litre of rain water. In a year's observation at Moscow, E. Schöne reported 110 mgrm. of hydrogen peroxide in the rain and snow which fell per sq. metre. According to A. Bach,[11] when the chlorophyll of plants acts on carbon dioxide and water in sunlight, formaldehyde, CH_2O, and percarbonic acid, H_2CO_4, are formed, $3H_2CO_3=2H_2CO_4+CH_2O$; and the percarbonic acid breaks down into carbon dioxide and hydrogen peroxide, $H_2CO_4=CO_2+H_2O_2$; and the

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latter in turn forms water and oxygen gas. A. Bach recommends the following reagent for detecting peroxides in plants : 5 c.c. of a solution of 0·03 grm. potassium dichromate and 5 drops of aniline with sufficient water to make a litre of solution. Treat 5 c.c. of the solution to be tested with one drop of a 5 per cent. solution of oxalic acid and the given reagent. A reddish-violet colour will be obtained if peroxides are present. Of 25 plants examined, 18 gave the reaction for peroxides. J. Cho (1896) obtained the coloration only where leaves were damaged. The existence of hydrogen peroxide in vegetable juices has been reported by many observers,[12] but G. Bellucci could not confirm this by the chromic acid reaction, and he attributes the results obtained to the presence of oxydases in vegetable sap. C. Wurster made similar remarks with respect to the alleged presence of hydrogen peroxide in animal fluids.[13]

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§ 4. The Physical Properties of Ozone

Ozonized air has a strong characteristic smell, which reminds some people of sulphur dioxide, others of garlic, and others of chlorine. The amount of ozone which can be detected by the olfactory sense is extremely small; one part in a million parts of air can be readily perceived. Indeed, ozone can be detected by smell before starch and potassium iodide paper turns blue. If air highly charged with ozone be breathed for any length of time, it produces headache; but in minute quantities the odour is pleasing and refreshing. In large quantities, ozonized air acts as an irritant poison causing headache and coughing, and finally inflammation and death; in small quantities, ozonized air has been recommended medicinally for pulmonary complaints. According to D. Labbe and S. M. Oudin, air containing one part of ozone in 20,000 may be breathed half an hour without ill effects. L. E. Hill and M. Flack[1] say that a concentration of one part in a million irritates the respiratory tract; exposure for two hours to a concentration of 15 to 20 per million is not without risk of life. In concentrations even less than one per million, it reduces respiratory metabolism, and rapidly causes a fall of body temperature. Its beneficial effect, as popularly believed, is a myth. The irritation of the olfactory nerves may relieve the monotony of close air, and in concentrations of more than 1 per million for brief periods may be of therapeutic value by acting in appropriate cases as a sort of " blister " to the respiratory tract.

Ozone at ordinary temperatures is a gas with a pale blue **colour.** Oxygen with 10 per cent. of ozone has a blue tinge when viewed through a tube a metre long.[2] Liquid ozone is dark indigo-blue. C. F. Schönbein[3] wrote to M. Faraday (1852) to the effect that he had made experiments supporting the hypothesis that the colour of oxy-compounds is due to the contained oxygen, or to a peculiar condition of that body. To this M. Faraday replied:

> Your letter quite excites me and I trust you will establish undeniably your point. It would be a great thing to trace the state of combined oxigen by the colour of its compound, not only because it would show that the oxigen had a special state, which could in the compound produce a special result—but also because it would, as you say, make the optical effect come within the category of scientific appliances and serve the purpose of a philosophic induction and means of research, whereas it is now simply a thing to be looked at. Believing that there is nothing superfluous, or deficient, or accidental, or indifferent, in nature I agree with you in believing that colour is essentially connected with the physical condition and nature of the body possessing it, and you will be doing a very great service to philosophy if you give us a hint, however small it may seem at first, in the development, or as I may even say in the perception of this connexion.

A litre of ozone weighs 2·1445 grms. at n.p.t.; and a gram of ozone under the same conditions occupies 466·3 c.c. The **specific gravity** is 1·5 (oxygen unity), or 1·62 (air unity). P. Hautefeuille and J. Chappius (1880) liquefied ozone by gradually compressing the gas in Cailletet's apparatus, at —23°, if the compression be sudden, or without cooling, the ozone is converted into oxygen with a yellow flash. P. Hautefeuille and L. Chappius liquefied ozone under a pressure of 125 atm. at —100°; K. Olschewsky[4] under atmospheric pressure at —181°. By passing ozonized oxygen through a tube cooled by immersion in boiling liquid oxygen, or by ozonizing oxygen in a tube kept at this temperature, a solution of ozone in liquid oxygen is obtained. By allowing the liquid to boil, most of the oxygen is removed, and a deep indigo-blue, almost black, liquid remains, which is opaque in layers of 2 mm. thick. By allowing the blue liquid to vaporize, A. Ladenburg (1898) obtained a gas containing about 86 per cent. of ozone. The liquid is particularly liable to explode when it reaches the boiling point of ozone, or when it is brought in contact with oxidizable substances. According to H. Erdmann, pure liquid ozone is not explosive, and he ascribes the explosibility to the presence of highly concentrated ozone gas; he says liquid ozone is harmless, and he obtained Leidenfrost's phenomenon with a drop of the liquid on a porcelain plate. The indigo-blue vapour of ozone in a test tube explodes if a little turpentine is introduced. G. D. Liveing and J. Dewar attributed the explosion of liquid ozone at —181° to the presence of the vapour.

The **boiling point** of ozone under atmospheric pressure is —106° (K. Olzschewsky);

—116° (L. Troost); or —125° (A. Ladenburg). The ratio of the two **specific heats** C_p/C_v for ozone is 1·29 as determined[5] by extrapolation from the value 1·396 for oxygen, and the observed values of mixtures of oxygen and ozone. G. N. Lewis and M. Randall[6] say that although the heat capacity of ozone has not been accurately determined, no great error will be involved by assuming that the relation which holds good for the triatomic gases, CO_2 and SO_2, is applicable, and therefore $C_p = 7{\cdot}0 + 0{\cdot}0071T - 0{\cdot}00000186T^2$. Subtracting the heat capacity for $1\frac{1}{2}$ gram-molecules of oxygen from $C_p + 6{\cdot}50 + 0{\cdot}0010T$ leaves for the heat Q of the reaction $1\frac{1}{2}O_2 = O_3$, at constant temperature: $Q = Q_0 - 2{\cdot}75T + 0{\cdot}0028T^2 - 0{\cdot}00000062T^3$.

According to M. Berthelot (1876), the **heat of formation** of a gram-molecule of ozone, O_3, is —29·6 Cals.; —36·3 to —36·65 Cals., according to H. G. L. van der Meulen (1883); and —34·5 Cals., according to S. Jahn (1908). The reported heats of the reaction thus range from 29 to 36 Cals.; if 34,600 cals. be the best representative value, the heat of the reaction at T will be $Q = 34600 - 2{\cdot}75T + 0{\cdot}0028T^2 - 0{\cdot}00000062T^3$; and the increase in free energy $34600 + 2{\cdot}75T \log T - 0{\cdot}0028T^2 + 0{\cdot}00000031T^3 + IT$, where the integration constant I can be evaluated very crudely from F. Fischer and F. Brähmer's work, $K = p_1/p^{1{\cdot}5}$, where p_1 denotes the partial pressure of ozone, and p that of oxygen; at 2300°, $K = 0{\cdot}01$. Hence, the increase in free energy at 2300° is $-RT \log K + 21000$ cals. When this is substituted in the preceding equation $I = -22{\cdot}4$, and at 298° K. the increase in free energy is 32,400 cals.

R. Luther and H. J. K. Inglis studied the potential of the ozone electrode by means of a platinum electrode surrounded by ozone, but they were unable to determine definitely the nature of the electrode reaction; and with an iridium electrode, R. Luther obtained values differing by 0·2 volt from those with the platinum electrode. S. Jahn found the **free energy** of the decomposition of ozone, determined from measurements of the potential of the cell O_3 | electrolyte | H_2, which is 1·90 volts at 0°; and of the cell O_2 | electrolyte | H_2, which is 1·25 volts. In the former case, the free energy of the reaction is $2O_3 + 2H_2 = 2O_2 + H_2O + (4F \times 1{\cdot}90)$ joules; and in the latter case, $O_2 + 2H_2 = 2H_2O + (4F \times 1{\cdot}25)$ joules, when F denotes the electrochemical equivalent, 96,540 coulombs. By subtraction, eliminating H_2O, there remains $2O_3 - 3O_2 + (4F \times 0{\cdot}65)$ joules; or $O_3 = \frac{3}{2}O_2 + 30$ Cals. nearly.

Ozone has a high absorptive and emissive power for ultra-red heat radiations; according to J. Tyndall,[7] its absorption power is 136 times as great as oxygen. K. Angström found that there is a sharp ultra-red absorption band at 4·8μ; a feeble one at 5·8μ; an uncertain one at 6·7μ; and a strong—perhaps double—band at 9·1 to 10·0μ. The first and last occur in the solar spectrum. J. Chappius and E. Schöne found that the **absorption spectrum** of ozone shows thirteen bands and lines: (1) A narrow band of wave-length 628·5μμ in the red; (2) a very large band from 609·5 to 593·5 in the orange; (3) a very large band, 577 to 560, and (4) one at 547 to 544·5 in the yellow; (5) a large one between 535 to 527; (6) one at 508·5 to 502, and (7) one at 492·5 to 491 in the green; (8) one at 484·5 to 479, and (9) one at 470 to 468; (10) one at 464·5 to 460, and (11) at 444 in the blue. There is also one at (12) 452 and (13) one at 516. Nos. 2 and 3 are very marked; Nos. 5, 6, and 8 are less characteristic; Nos. 10 and 11 still less characteristic; Nos. 12 and 13 still less so; Nos. 1, 4, 7, 9, 12, and 13 can be recognized only under special conditions. Liquid ozone does not show any absorption bands in the visible spectrum, but there is a masking in the region at about 500μμ; there are no bands in the ultraviolet, and the absorption extends into the visible region as the concentration increases, but not so far as in the case of the gas. The absorption spectrum of the gas in the ultraviolet is so marked that, as previously indicated, W. N. Hartley supposed that in passing through the atmosphere the 293μμ radiations from the sun are suppressed. The hypothesis was confirmed by the work of E. Meyer and A. Lévy. From Lambert's law, $I = I_0 \times 10^{-al}$, when I_0 denotes the intensity of the incident energy, and I that after traversing a layer of ozone of thickness l, the absorption constant a of ozone at 0° and 760 mm. in H. Kreusler's photometer is, for light of wave-length λ, and with the centimetre as unit of length, E. Meyer found :

λ	193	200	220	240	260	280	300$\mu\mu$
a	11·7	7·8	19·2	105	126	73·4	30·3

There is thus a maximum near $\lambda=260\mu\mu$, and a minimum near $\lambda=7{\cdot}8\mu\mu$. A. Lévy estimated that the atmosphere contains $0{\cdot}7696\times10^{-6}$ per cent. of ozone by volume. The corresponding absorption can be calculated. E. Meyer found for I_0 the intensity of the incident radiant energy before it enters the atmosphere, and I, the intensity at the earth's surface, on the assumption that for $\lambda=300\mu\mu$, the intensity of the radiant energy=100,

λ	193	200	220	240	260	280	300$\mu\mu$
I_0	16·76	20·75	34·36	50·43	67·54	76·07	100
I	14·21	18·59	26·19	11·46	11·28	14·73	65·10

These curves are plotted in Fig. 6. The intensity of the radiant energy received at the earth's surface owing to absorption by ozone rapidly falls from 300$\mu\mu$ down to about 260$\mu\mu$, and then rises again. The beam of radiant energy from the sun is assumed to be directed normally to the earth's surface; in reality, the beam is more or less slanting, this could make the absorption greater than the calculated value—even if the data were otherwise correct. The absorption band commencing near $\lambda=200\mu\mu$ is probably responsible for the de-ozonizing effect of ultraviolet rays; and the rays below 170$\mu\mu$, which V. Schumann found to be entirely absorbed by a layer of air 1 mm. thick and 760 mm. pressure, are probably responsible for the formation of ozone, so that the stability of ozone is a function of the active mass of oxygen, and of the intensity of the ultraviolet rays beyond, say, 180$\mu\mu$. K. Stuchtey examined the spectrum of the luminous glow on an ozone tube.

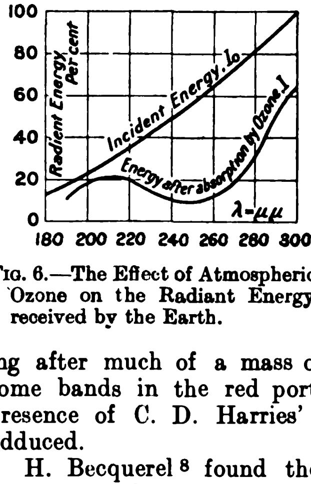

FIG. 6.—The Effect of Atmospheric Ozone on the Radiant Energy received by the Earth.

E. Ladenburg and E. Lehmann have observed a second absorption spectrum in the ozone remaining after much of a mass of liquid ozone has evaporated; this spectrum has some bands in the red portion. It has been suggested that this is due to the presence of C. D. Harries' *oxozone*—but no satisfactory proof has been yet adduced.

H. Becquerel[8] found the **specific magnetism** of ozone to be very high. M. Berthelot found that ozone is stable under the influence of sound waves.

Solubility.—H. Erdmann[9] found that liquid nitrogen dissolves ozone,[2] forming a clear sky-blue liquid. M. A. Hunter attempted to measure the molecular weight of ozone dissolved in liquid oxygen and in liquid nitrogen. The last-named solution was too explosive. He found that solutions of ozone in oxygen have a minimum boiling point, −183·3°, when 4 to 5 per cent. of ozone is present—thus :

Ozone . .	0	2	4	5	6·5	7·5 per cent.
Boiling point .	−182·8°	−182·85°	−183·3°	−183·25°	−182·75°	−182·63°

Many measurements have been made of the solubility of ozone in water. C. F. Schönbein[10] said that ozone is not perceptibly soluble in water—this statement is incorrect, since ozone is appreciably soluble in this menstruum; E. Schöne (1873) found that when ozonized oxygen is passed into distilled water, the concentration of the ozone remains constant, although about one-fourth of the ozone is decomposed; hence, H. J. K. Inglis argues that the concentration of the ozone must depend on the rate the gas is passed through the solvent, and consequently the solubility coefficient cannot be accurately determined. However, many determinations of the solubility have been attempted. According to A. Ladenburg, a litre of water at 0° dissolves 20 mgrm. of ozone; at 2°, 10 mgrm.; at 28°, 1·5 mgrm. A. Mailfert's results for the equilibrium conditions in the partition of ozone between gas and liquid are indicated in Table II.

TABLE II.—SOLUBILITY OF OZONE IN WATER.

Temperature.	Mgrm. ozone per litre solvent.	Mgrm. ozone per litre gas.	Ratio.	Temperature.	Mgrm. ozone per litre solvent.	Mgrm. ozone per litre gas.	Ratio.
0°	39·4	61·5	0·641	27°	13·9	51·4	0·270
6°	34·3	61·0	0·562	33°	7·7	39·5	0·195
11·8°	29·9	59·6	0·500	40°	4·2	37·6	0·112
13·0°	28·0	58·1	0·482	47°	2·4	31·2	0·077
15·0°	25·9	56·8	0·456	55°	0·6	19·3	0·031
19·0°	21·0	55·2	0·381	60°	0·0	12·3	0·000

The solubility decreases with a rise of temperature; and according to O. Fröhlich, increases with an increase of pressure. L. Carius reported that the absorption coefficient of ozone prepared by electrolysis is 0·834 at 1°; and for ozone prepared by the electric discharge 0·635 at 1°. A. Mailfert, E. Moufang, F. Bürger, and V. Rothmund and A. Burgstaller found that the solubility of ozone in water is augmented by the addition of acids.[11] The presence of oxidizable substances must be avoided. R. Luther and J. K. H. Inglis find that the absorption coefficient for water at 0° is 0·494; and for $\frac{1}{10}N$-H_2SO_4, at 0°, 0·487, so that the solubility appears to decrease slightly with increasing concentration of the acid; but the rate of decomposition of ozone in water increases with decreasing acid concentration. The solution of ozone in water soon decomposes, so that aqueous solutions cannot be used for the determination of the molecular weight of this gas. Solutions of ozone in $\frac{1}{10}N$-H_2SO_4 follow Henry's law. The solubility of ozone in neutral *salt solutions*—*e.g.* sodium or magnesium chloride—is in many cases greater than in water, and the solutions are more stable. B. Graf's patent for stabilizing aqueous solutions of ozone is based on this fact. The solubility diminishes in feebly *alkaline solutions*—say 0·005 and 0·00002 *N*-solutions of sodium carbonate; in concentrated solutions of the alkalies, the ozone is rapidly decomposed. No signs of the formation of hydrogen peroxide has been observed in the decomposition of acid or alkaline solutions of ozone. E. Langheld [12] recommends quinine salts for increasing the solubility and stability of aqueous solutions of ozone. Contrary to F. Jeremin's views, R. Böttger holds that oxalic acid does not make ozone solutions more stable, since it is readily oxidized by ozone. Acetaldehyde and, better still, paraldehyde have been recommended by S. Fraser for stabilizing solutions of ozone.

Ozone is apparently dissolved by *essential oils*—turpentine, thyme, cinnamon oil, etc. According to J. L. Soret,[13] these oils absorb ozone from ozonized oxygen and leave the oxygen unaffected. B. Stelzer found ozone is copiously absorbed by *fats*, C. T. Kingzett by *ethereal oils*. C. D. Harries assumes that the action is here not a true solution, but rather a case of chemical combination; addition compounds are formed called **ozonides**. According to E. Molinari (1906), unsaturated carbon compounds with a double or ethylene bond between the carbon atoms appear to absorb ozone quantitatively forming ozonides, whereas those with a triple or acetylene bond do not combine with ozone. C. D. Harries, however, does not accept E. Molinari's conclusion, since some compounds with a triple bond combine with ozone more rapidly than some with a double bond. C. D. Harries used ozonized oxygen, E. Molinari ozonized air. C. D. Harries and R. Koetschau, H. Erdmann, and F. Fischer and H. Tropsch [14] find that a blue solution is obtained when ozonized oxygen is passed into acetic acid, acetic anhydride, ethyl acetate, chloroform, or carbon tetrachloride. The colour persists for 15 to 20 hrs. with acetic acid and carbon tetrachloride, but disappears more rapidly with the other solvents. Water and formic acid do not form coloured solutions; the latter is oxidized to carbon dioxide. Carbon tetrachloride dissolves seven times as much ozone as an equal bulk of water.

The so-called *ozone water* of commerce usually contains no ozone at all. R. Böttger[15] found nitrous acid; E. A. Behrens and G. Sonntag, hypochlorous acid; C. F. Rammelsberg, L. Keutmann, H. Thoms, and C. G. Egeling, chlorine; and G. Vulpius, chloride of lime in commercial ozone water.

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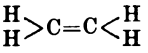
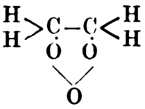
§ 5. Oxozone, Ozonides, and Oxozonides

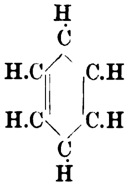
It was thought for some time that ordinary oxygen is a compound of negative and positive oxygen, the former was called by C. F. Schönbein *ozone* and symbolized ⊕, and the latter *antozone*, symbolized ⊖; so that ordinary oxygen—ozone ⊖ +antozone ⊕. The existence of the two different forms has not been satisfactorily proved, and the term ozone is reserved for polymerized oxygen O_3, while the term antozone is not used. C. F. Schönbein used the term **ozonides** for certain peroxides which gave off ozone when decomposed; this term was then extended to certain compounds formed by the action of ozone on various derivatives of unsaturated organic compounds; and it is now applied to compounds formed by direct union with ozone, and which contain the, presumably dyad, radicle O_3. Thus, ethylene $CH_2 : CH_2$ forms *ozoethylene* or *ethylene ozonide*, $C_2H_4O_3$, where the group O_3 is thought to act as a dyad, $-O.O.O-$, or $-O:O:O-$; and benzene, C_6H_6, forms *ozobenzene*, $C_6H_6O_9$, where three dyad O_3 groups are united to the benzene. The graphic symbols of these two ozonides are considered to be respectively



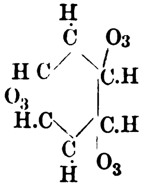
Ethylene.



Ozoethylene or ethylene ozonide.



Benzene.



Ozobenzene or benzene ozonide.

The ozonides are usually prepared by slowly passing oxygen containing 3 to 18 per cent. of ozone over the dry substance or into a solution of the substance in an inert solvent—methyl or ethyl chlorides—free from water. Solvents, like acetone, chloroform, hexane, and carbon tetrachloride, are more or less attacked by the ozone; benzene forms ozobenzene. The ozonides are usually decomposed by water, and they are often explosive.

Some evidence has been cited to show that a still more condensed form of oxygen, O_4, and called **oxozone**, is present in the residues obtained when liquid ozonized oxygen—prepared by a brush discharge of high voltage, say 8000 volts—is fractionally distilled. The alleged oxozone has not been isolated, although compounds called **oxozonides** containing the group O_4 are known; as well as ozonides with the group O_3. Thus, the hydrocarbon butylene, C_4H_8, forms both ozobutylene, $C_4H_8O_3$, and oxozobutylene, $C_4H_8O_4$. Indeed, said C. D. Harries (1911), "experimental results in ozonization lead to the conclusion that all organic compounds containing an ethylene linkage (double bond) add one molecule of ozone, and give rise to ozonides." Thus, ozone may oxidize in one of two ways: (i) One atom of oxygen per molecule of ozone is given up to the reducing agent, and the other two atoms unite to form a molecule of oxygen, and (ii) the whole molecule may unite with the reducing agent to form an ozonide.

C. D. Harries (1911)[1] claims that oxozone has an identity of its own on the following grounds: (1) The specific gravity of the gas from the last fraction of liquid ozonized oxygen to evaporate, is less than corresponds with the amount of iodine it liberates from potassium iodide. C. D. Harries takes this to mean that some O_4, as well as O_3, is present, and that the former on decomposition furnishes two atoms of oxygen: $O_4 \rightarrow O_2+2O$; and the latter, one such atom: $O_3 \rightarrow O_2+O$. This inference is not an adequate explanation of the alleged discrepancy because a mixture of the two should give the same result if determined gravimetrically as if determined iodometrically. (2) Moderately ozonized oxygen can be passed through potassium hydroxide solution or through sulphuric acid without appreciable loss of ozone, but with very concentrated ozonized oxygen or with oxygen ozonized by means of a high voltage, there is a 3 to 4 per cent. loss of ozone in the potassium hydroxide solution, and a 2 to 3 per cent. loss of ozone in the sulphuric acid. This may or may not show that there is an equilibrium condition between the ozone and the solutions in question. (3) C. D. Harries and his co-workers (1912) have shown that washed ozonized oxygen in contact with butylene, C_4H_8, produces the ozonides $C_4H_8O_3$ and the polymer $(C_4H_8O_3)_2$, while the unwashed gas produces the oxozonide $C_4H_8O_4$ and the polymer $(C_4H_8O_4)_2$. They also found that when washed ozonized oxygen is passed into a solution of tetrahydrobenzene, C_6H_{10}, in hexane, it gives the solid ozonide $C_6H_{10}O_3$, while the unwashed gas gives a mixture of the ozonide and oxozonide; and similarly, with caoutchouc, the compounds $C_{10}H_{16}O_6$ and $C_{10}H_{16}O_8$ are formed. Hence, argues C. D. Harries, the so-called ozone in ozonized oxygen with which this work was done contained about one-third of oxozone. (4) E. Ladenburg and E. Lehmann found some absorption bands in the red portion of the spectrum of liquid ozone which are only visible in the fractions remaining when three-quarters has evaporated; these bands are the first to disappear, and the pressure increases when this occurs. (5) E. Ladenburg and E. Lehmann consider that the changes of the pressure, and also of the density of liquid ozone —1·78, 1·75, 1·83—indicate the presence of a higher molecular modification of ozone. According to E. H. Riesenfeld and F. Bencker, although the reaction between potassium iodide and ozone starts instantaneously, the final equilibrium resulting in the formation of potassium hydroxide, iodide, hypoiodite, iodate, and periodate, is attained only after some days. The *oxidation number of ozone*, that is, the number of oxygen atoms consumed per gram-molecule of ozone, in a neutral solution of potassium iodide is unity; in acid solutions the oxidation number ranges from 1·0 to 2·7—it is not affected by the concentration of ozone, and increases with decreasing temperatures; and in alkaline solutions also the oxidation number increases. The greater the concentration of the ozone in the oxygen, the greater the influence of the hydroxyl ions, resulting in the formation of iodate or hydrogen peroxide. The differences observed by C. D. Harries are to be attributed to the action of the hydroxyl ions of the alkali and not to the existence of a modification of oxygen containing more than three atoms. C. D. Harries used a concentrated solution of potassium iodide and concentrated ozone, so that the oxidation number was increased by the potassium hydroxide which was formed. In conclusion, E. H. Riesenfeld and F. Bencher say that there is no evidence of the existence of a modification of ozone containing more than three atoms per molecule. To this, C. D. Harries replied that the explanation suggested by E. H. Riesenfeld and F. Bencher is wrong; a 2·5 per cent. solution of potassium iodide was used; and moreover the action of crude and washed ozone on butylene is evidence of the presence of more than one compound in ordinary ozone.

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§ 6. The Chemical Properties of Ozone

Ozone slowly and spontaneously passes into ordinary oxygen at ordinary temperatures. L. von Babo[1] kept a sample for a week over concentrated sulphuric acid and found some undecomposed ozone. The gas seems to be more stable in contact with acid than with water. C. D. Harries found that ozonized oxygen lost one per cent. of ozone by bubbling through sulphuric acid. The decomposition of ozone gives ordinary oxygen, and is attended by an expansion corresponding with $2O_3$ (2 vols.) $=3O_2$ (3 vols.).[2] The speed of the spontaneous decomposition of ozone in ozonized oxygen is greater the more concentrated the ozone.[3]

The rate of the decomposition is accelerated by reducing the pressure. According to D. L. Chapman and H. E. Jones, the presence of oxygen, carbon dioxide, nitrogen, and moisture do not appreciably affect the rate of decomposition, while the presence of traces of nitrogen peroxide, chlorine, and phosphorus pentoxide accelerate the rate of decomposition. The effect of moisture has been previously discussed. Ozone is said to be decomposed by agitation with powdered glass, by passage through a long glass tube[4]—though this is doubtful—and by mere contact with certain agents:[5] finely divided platinum and other metals; silver foil; the rare earths; dioxides of manganese, lead, nickel, and cobalt; oxide of iron, silver, or copper; mercury; soda lime; etc. The ozone is converted into ordinary oxygen without decomposing the oxides. Hence, the reactions are grouped among catalytic reactions. The effect can be shown by passing ozonized air through a tube containing copper oxide and testing the issuing gas by ozone test paper. No indication of ozone is obtained. The action is probably due to the cyclic formation and decomposition of the higher oxides: with silver foil, the alternate formation and decomposition of silver oxide can be observed. According to D. L. Chapman and H. E. Clarke the effect of the surface of the glass on the decomposition of the contained ozone is so slow that even in moderately small globes, the amount of ozone destroyed on the internal surface of the vessel may be neglected in comparison with that decomposed in the interior of the gas; and that the conversion of ozone into oxygen may be regarded as a homogeneous reaction. C. F. Schönbein[6] found that if clean and dry plates of gold or platinum be placed in ozonized oxygen, the metal becomes negatively polarized, and an electric current can be obtained by connecting up these plates with plates of ordinary gold or platinum—the polarization disappears on heating the plates.

The action of heat is very peculiar, as previously discussed. In every case, the decomposition and formation of ozone by ultraviolet light, electrical discharge, and heat, a balanced reaction is involved, and the conditions of equilibrium are in accord with the law of mass action. According to S. Jahn,[7] and E. P. Perman and R. H. Greaves, the rate of decomposition varies inversely as the pressure of the oxygen; but D. L. Chapman and H. E. Jones found the velocity of decomposition not to be affected by increasing the partial pressure of the oxygen mixed with the ozone at 100°, the reaction is almost irreversible, and the rate of decomposition at 127° is bimolecular, so that if C denotes the number of gram-molecules of ozone per litre, and k is a constant, t the time, the velocity of the decomposition is $dC/dt=kC^2$; if C is unity, k represents the number of gram-molecules of ozone which would decompose in one minute if the initial concentration of the ozone were one gram per litre. E. Warburg found at 16°, $k=0{\cdot}0000492$; at 100°, $k=0{\cdot}157$; and at 126·9°, $k=1{\cdot}77$. The water had a pressure of 0·0021 mm. of mercury; when the water pressure was 0·154 mm., the velocity of decomposition was 22 per cent. faster than the results just recorded. In order to explain this result, it has been assumed that a rapid reversible change $O_3 \rightleftharpoons O_2+O$ occurs, and this is followed by a relatively slow reaction $O_3+O=2O_2$. This latter reaction is alone accessible to measurement.

The decomposition of ozone at high temperatures is accompanied by phosphorescence or **luminescence**—this is shown by holding a hot glass rod near the surface of liquid ozone (M. Beger, 1910), or by passing ozonized oxygen through a tube with a capillary opening into an evacuated vessel (J. Dewar, 1888).[8] When ozone is aspirated with a water pump, the water becomes luminous, and retains its luminosity for five or six seconds. Flasks filled with the issuing water are distinctly luminous, and when water is shaken with ozonized oxygen, the phenomenon of luminescence can be reproduced five or six times and then ceases ; it can be reproduced with the same gas if fresh water be introduced. Variations of pressure had no appreciable effect on the luminosity. If ozonized oxygen be shaken with alcohol, the luminescence is feebler but more persistent ; with benzene it is very feeble, and the ozone is absorbed or decomposed. If the water be carefully freed from organic matter it shows no luminescence even with highly concentrated ozone. The luminescence with ordinary tap water is therefore due to the action of organic matter on the ozone. According to M. Otto, the luminescence always appears on contact of ozone with organic bodies. The decomposition of ozone gives gaseous ions which discharge a charged electroscope. According to R. Schenck,[9] ozone acts on a photographic plate, and makes zinc blende, but not zinc oxide or barium platinocyanide fluorescent. These statements have also been denied ; others say the fluorescence of zinc blende is an effect which attends its oxidation to sulphate, and the action on a photographic plate is due to the chemical action of ozone on the organic matter.

Ozone is a very powerful oxidizing agent. B. C. Brodie[10] (1872) has made an interesting study of its action with different substances. Let the so-called *oxidation number* represent the number of atoms of oxygen [O] taken up by the oxidized compounds, per molecule of ozone, then

(1) If the ozone is catalytically decomposed, say by concentrated alkali lye at not too low a temperature, $2O_3=3O_2$, the oxidation number is zero, and the increase in volume is equal to half the volume of the ozone employed.

(2) If the ozone gives up one atom of oxygen per molecule, as is the case when it acts on ferrous sulphate, manganese sulphate, potassium ferrocyanide, or potassium iodide, $O_3=O_2+[O]$, and there is no change of volume. The oxidation number is unity.

(3) If the ozone gives up all three oxygen atoms to the oxidized substance as is the case with turpentine, sodium thiosulphate in neutral solution, the oxidation of sulphur dioxide : $3SO_2+O_3=3SO_3$, sodium sulphide : $Na_2S+O_3=Na_2SO_3$, and in the formation of ozonides, $O_3=[3O]$; the oxidation number is 3, and the decrease in volume is equal to the volume of the ozone.

According to E. H. Riesenfeld and T. F. Egidius (1913),[11] it is probable that the ozone does its work in one of two ways : (i) One atom of oxygen per molecule of ozone is given up to the reducing agent, and the remaining two atoms form a molecule of gaseous oxygen ; or (ii) the whole molecule may be added or coupled with the compound oxidized, as in the formation of ozonides, and the oxidation number is 3. The more complicated reactions are probably the result of a combination of these two. Thus, the reaction $2O_3=O_2+[4O]$ observed by B. C. Brodie in the oxidation of sodium thiosulphate, is a combination of $O_3=O_2+[O]$ and $O_3=[3O]$. In the oxidation of sodium thiosulphate in neutral solution, Y. Yamauchi found that the main reaction is symbolized $Na_2S_2O_3+O_3=SO_2+Na_2SO_4$, with a side reaction $Na_2S_2O_3+O_3=Na_2S_2O_6$ (sodium dithionate). In *alkaline* solutions, sodium thiosulphate seems to unite directly with ozone, forming an ozonide, $Na_2S_2O_3.O_3$ which subsequently decomposes, giving off ordinary oxygen, forming as principal products : sodium sulphate, sulphite, and dithionate—with sulphate as the end-product. Similar remarks apply to the oxidation of sulphides and sulphites. The result may be complicated by the catalytic decomposition of the ozone or of the thiosulphate ($Na_2S_2O_3=S+Na_2SO_3$) itself.

Ozone oxidizes **hydrogen** very slowly. Although C. F. Schönbein and M. Berthelot failed to obtain any evidence of combination, others[12] have found that by exposing electrolytic gas to the brush discharge—either under reduced pressure, or by diluting the gas with argon or carbon dioxide so as to avoid an explosion, or by heating the gaseous mixture—water is formed. Thus, F. Fischer and M. Wolf, by heating electrolytic gas containing ozone, for an hour, at 100°, obtained 3·7 mgrm. of water and 4·45 mgrm. at 174°. According to F. Weigert, when electrolytic gas is exposed to ultraviolet light, larger quantities of water are formed than corresponds with the ozone produced. H. Thiele says that the action is not to be ascribed to the primarily formed ozone, as in the case of other reactions in ultraviolet light.

C. F. Schönbein, G. Meissner, and L. von Babo [13] supposed that when a solution of ozone in **water** decomposes, hydrogen peroxide, H_2O_2, is formed, but many investigators—C. Engler and A. Nasse, L. Carius, E. Schöne, C. Gianetti and A. Volta, and M. Berthelot—have denied this reaction, and claim that the solution decomposes into oxygen and water. There is no reliable evidence of the alleged formation of hydrogen peroxide. The difficulty arose because of the confusion of ozone reactions with those of hydrogen peroxide, and C. Arnold and C. Mentzel, V. Rothmund and A. Burgstaller, and P. Jannasch and W. Gottschalk, have employed tests which leave no ambiguity. The latter have shown that neither hydrogen peroxide nor persulphuric acid is formed in solutions of ozone in sulphuric acid. Ozone precipitates manganese dioxide quantitatively from a solution of manganous sulphate, but if a trace of hydrogen peroxide were formed the reaction would not be quantitative since the precipitate is dissolved in the presence of that reagent. The stability of a solution of ozone decreases as the concentration of the acid decreases, but no relation between the concentration of the acid and the velocity of decomposition has been discovered. Alkaline solutions of ozone are very unstable. Colloidal platinum, copper sulphate, stannous sulphate, etc., do not accelerate the speed of decomposition of aqueous solutions of ozone. V. Rothmund also found that in $0{\cdot}01N$-acid solutions the speed of decomposition of ozone is bimolecular, and in weaker acid and in alkaline solutions the speed is between a bi- and uni-molecular process; they therefore assume that a uni-molecular reaction is superposed on a bimolecular one, and this furnishes the velocity equation $dx/dt=k_1(a-x)^2+k_2(a-x)$, where k_1 and k_2 are constants—in acid solutions the first term is the more important, and in alkaline and weakly acid solutions the second term is the more important.

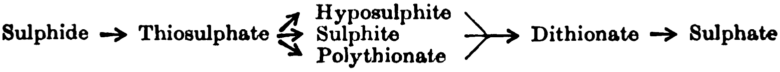
C. D. Harries found almost all ozonides react with water forming hydrogen peroxide. M. Berthelot and C. T. Kingzett also found ozonized ether, and many other substances after treatment with ozone, give hydrogen peroxide when shaken with water. The hydrogen peroxide may be formed by the autoxidation of these substances, and the ozone may act indirectly as a carrier of oxygen. C. F. Schönbein, L. von Babo, E. Schöne, A. Schmidt, etc., have reported that commercial ether nearly always contains hydrogen peroxide, and this may mean that an ozonide has been formed. Ozone and **hydrogen peroxide** react slowly: $H_2O_2+O_3=H_2O+2O_2$. H. J. K. Inglis found the reaction is catalytically accelerated by manganese salts. So slow is this reaction in aqueous solutions that C. Arnold and C. Mentzel believed the mixture to be *Beständigkeit*, and C. Engler and W. Wild [14] applied the same remarks to the gaseous mixture. It is very remarkable that the reaction between a vigorous oxidizing agent like ozone, and a reducing agent like hydrogen peroxide, should be so slow. Theoretically it might have been anticipated that $O : O : \boxed{O+H_2} : O : O \rightarrow H_2O+2O_2$ would readily occur. In concentrated solutions this is probably what happens, because, in F. Fischer and M. Wolf's experiments on the synthesis of hydrogen peroxide by the action of the brush discharge on mixtures of hydrogen and oxygen at low temperatures, it was found that a mixture with 97 per cent. of oxygen and 3 per cent. of hydrogen gave much ozone and the merest traces of hydrogen peroxide, while if these proportions were reversed, a highly concentrated form of hydrogen peroxide was obtained. It is assumed that the trace of hydrogen peroxide, in the former case, represents what has escaped decomposition in the reaction between ozone and hydrogen peroxide. V. Rothmund and A. Burgstaller measured the velocity of the reaction between hydrogen peroxide and ozone in $0{\cdot}01N$-sulphuric acid at 0°, and found that in the presence of a large proportion of hydrogen peroxide the decomposition of the ozone follows the course of a unimolecular reaction: $H_2O_2+O_3=H_2O+2O_2$; but if a less proportion of the peroxide be present, the ozone disappears more rapidly than the peroxide, and this the more the lower the ratio of peroxide to ozone. Hence it was inferred that the interaction of hydrogen peroxide and ozone is accompanied by the spontaneous decomposition of ozone, and that hydrogen peroxide catalyzes the latter reaction. According to H. McLeod (1880), if the hydrogen peroxide be in an alkaline or neutral solution, the ozone is destroyed very quickly; the reaction is slow only in acid solutions. In some cases, therefore, **ozone acts as a reducing agent.** Thus, barium peroxide is reduced to the monoxide, and hydrogen peroxide to water. When ozone is brought into contact with sodium peroxide, the two substances mutually decompose and oxygen is liberated: $O_3+Na_2O_2+H_2O=2NaOH+2O_2$.

There are very uncertain signs of the formation of a very unstable compound of ozone with **fluorine.**[15] H. Moissan postulated the possible formation of an intermediate compound of fluorine and ozone when fluorine acts on water; but O. Ruff and J. Zedner could detect no signs of such a compound by the action of fluorine on oxygen under the influence of an electric arc, or in the induction coil. G. Gallo, however, believed that he did prepare an unstable endothermal compound by the action of ozone on fluorine at low temperatures, and that above $-23°$ this compound is liable to decompose explosively. E. Comanducci claims to have converted a mixture of **chlorine** and oxygen into chlorine dioxide by treating the mixed gases in Siemens' ozonizer.[16] D. L. Chapman and P. S. McMahon found that the presence of ozone retards the photochemical action between chlorine and hydrogen. No reaction was observed with **bromine** and oxygen. C. F. Schönbein found that **iodine** is oxidized in a stream of ozonized oxygen to I_2O_3 or I_4O_9, and according to H. B. Baker and R. J. Strutt, the oxidation [17] is accompanied by an orange-coloured glow. By exposing a mixture of iodine vapour and oxygen to the brush discharge in an ozonizer, J. Ogier obtained different oxidization products in different parts of the tube. F. Fichter and F. Rohner passed 8 per cent. of ozonized oxygen into a chloroform solution of iodine, and obtained a yellowish-white oxide, I_4O_9, and the same product was obtained by the action of ozone on dry iodine. By treating a solution of iodine in acetic anhydride and concentrated sulphuric acid with ozonized oxygen, M. Beger obtained a white substance which unites with sulphuric acid forming a citron-yellow hygroscopic powder, $I_2O_3SO_3\frac{1}{2}H_2O$, analogous to the substance prepared by P. Chrétien by the action of iodine on a solution of iodic acid in sulphuric acid. Ozone decomposes all the **hydrogen haloids** with the exception of **hydrogen fluoride**: $2HCl+O_3=Cl_2+H_2O+O_2$; and E. Comanducci claims to have made hypochlorous acid by the action of ozone on **hydrogen chloride** in an ozonizer.

The action of ozone on potassium iodide.—Unlike oxygen, ozone liberates iodine from a **neutral solution** of potassium iodide, KI. This can be shown by dipping paper in a solution of potassium iodide and holding it at the exit tube of the ozonizer. The paper turns brown owing to the liberation of iodine. If a little starch be mixed with the potassium iodide, the paper will appear blue if ozone be present. The reaction is usually represented $O_3+2KI+H_2O=O_2+I_2+2KOH$. The solution is then alkaline in virtue of the potassium hydroxide. Hence, if red litmus paper be steeped in water containing a trace of potassium iodide, the moist paper, when exposed to ozonized air, will be coloured blue owing to the action of the potassium hydroxide on the red litmus. The simple equation just indicated gives no idea of the great complexity of this reaction. According to O. Brunck [18] and others, there is a slow reaction between the iodine and the potassium hydroxide which results in the formation of potassium hypoiodite, KIO, which, in consequence of another consecutive reaction, slowly forms potassium iodate, KIO_3, and iodide, $3KIO=2KI+KIO_3$. E. Péchard believes that potassium periodate is formed at an intermediate stage in the oxidation of potassium iodide by ozone, and that the periodate then reacts, $3KIO_4+2KI+3H_2O=KIO_3+2K_2H_3IO_6+I_2$, and the two constituents last symbolized react $2K_2H_3IO_6+I_2=3KIO_3+KI+3H_2O$, which form a neutral solution. Some periodate and peroxide have also been reported to be produced by a reaction between the iodide and ozone. According to J. N. Pring, the ratio of iodate and periodate to free iodide and hypoiodite increases with the amount of ozone which acts on the solution. With a dilution less than 160 parts of ozone per million of air, no iodate is formed, but only iodine and hypoiodite. If the temperature is less than —24°, and the ozone acts on the solid salt, the smallest quantity of ozone gives more iodate than free iodine and hypoiodite. If ozone acts upon an **acid solution** of potassium iodide, the result is different [19] from that which occurs with a neutral solution, for there is a side reaction resulting in the formation of hydriodic acid: $KI+HCl=HI+KCl$, in addition to the normal reaction for neutral solutions. The ozone reacts with the hydriodic acid, HI, forming hydrogen peroxide, possibly by the side reaction: $4HI+O_3=H_2O+H_2O_2+2I_2$. The resultant equation is represented: $4O_3+10HI=H_2O_2+5I_2+4H_2O+3O_2$. The hydrogen peroxide can be detected with titanium sulphate which gives a yellow coloration. It therefore follows that a gram-molecule of ozone gives more iodine in an acid than in a neutral solution. According to G. Lechner (1911), an **alkaline solution** of potassium iodide reacts with ozone forming potassium iodate, KIO_3, thus $KI+O_3=KIO_3$. If the mixed solution of iodine and iodate be acidified, iodine is liberated: $KIO_3+5KI+3H_2SO_4 =3K_2SO_4+3H_2O+3I_2$. The free iodine can then be determined by titration with a standard solution of sodium thiosulphate. In this way, E. Czako (1912) has shown that it is possible to determine 0·00002 grm. of ozone in 100 c.c. of ozonized air. According to C. Engler and A. Nasse, dry ozone and dry potassium iodide do not react. H. Riesenfeld and F. Bencker found that ozone has no action on neutral or acid solutions of potassium iodate, but it oxidizes alkaline solutions to periodate; and it is without action on potassium periodate—*vide* oxozone.

The white mist—*ozone fog*—produced when ozone acts on iodides, sulphur dioxide, etc., was thought by C. Meissner to be the antozone of C. F. Schönbein. V. Rothmund [20] noted that analogous fogs are produced in many other reactions—*e.g.* ammonium chloride fogs, fogs from fuming acids, fogs produced by the action of radium emanation on sulphur, carbon disulphide, etc.—and that it is caused by water in which a small quantity of the products of the reaction are dissolved. The fogs with ozone are produced only when the reducing agent is of a volatile nature and the reaction products are soluble in water. The size of the mist spheres were found to be practically the same in a number of very different reactions, and from their rate of subsidence they are approximately 10^{-4} cm. in diameter.

The reports which have been published to the effect that **sulphur** is not attacked by ozone are probably based on experiments in which the concentration of the ozone was very small. E. Pollacci [21] has shown that at ordinary temperatures sulphur is oxidized by ozone, but not by oxygen; and H. B. Baker and R. J. Strutt observed that a blue luminescence is obtained when ozonized oxygen is passed over sulphur. A. Malfert supposed that sulphur dioxide is formed if moisture be excluded; sulphuric acid if moisture be present; and alkali sulphates if alkalies be present. T. Weyl obtained sulphuric acid by leading ozonized oxygen into hot water with finely divided sulphur in suspension, but there were no signs of oxidation if oxygen alone be used. A. Stock and K. Friederici also found that sulphur dissolved in carbon tetrachloride was oxidized by ozone to sulphur dioxide. C. D. Harries looks upon sulphur trioxide as a kind of ozonide, SO_3. **Hydrogen sulphide** is oxidized by ozone to sulphur. and D. Helbig found that hydrogen sulphide can be oxidized to sulphur when passed into a solution of potassium permanganate and sulphuric acid, which furnishes ozonized oxygen. **Sulphur dioxide** and **sulphurous acid** are oxidized to sulphur trioxide and sulphuric acid respectively: $3SO_2+O_3 =3SO_3$. P. V. Langlois and L. S. Thomassin, and E. H. Riesenfeld have suggested technical processes for the oxidation of sulphur dioxide based on this reaction. With the same object in view, A. Reynoso and B. Hunt proposed to pass electric sparks through a strongly compressed mixture of sulphur dioxide and air at a low temperature. A. Borchers assumes that an ozonide, $(SO_2)_3O_3$, is first formed as an intermediate product which decomposes into $3SO_3$. The action of ozone on **sodium sulphide,** hydrosulphide, or polysulphide; **sodium thiosulphate**, sodium sulphate, and sodium bisulphite, gives sodium sulphate as an end-product when an excess of the oxidizing agent is used; when the ozone is not in excess, intermediate products are formed. With sodium sulphide, E. H. Riesenfeld and T. F. Egidius detected the intermediate products:



Ozone is dissolved by **sulphuric acid**; and some unknown change occurs, for J. Brand and L. Gräfenberg found that the sulphuric acid possesses oxidizing properties—*e.g.* it blues starch and potassium iodide test paper. These qualities are not lost by boiling, or by leading air through the liquid. The titanic acid reaction for hydrogen peroxide does not occur. The presence of platinum sponge favours the oxidation.

The solution gives a similar precipitate with acetone as does Caro's acid, but, according to J. Brand and L. Gräfenberg, neither persulphuric nor Caro's acid appears to be present.[22] The electrical conductivity of the dilute acid seems to be lowered by the presence of the unknown oxidizing substance which is present, and which some have supposed to be an unknown **ozonic acid.** Persulphuric acid has not yet been formed by oxidizing **sulphuric acid** with ozone. M. Berthelot obtained a persulphuric anhydride by subjecting a mixture of sulphur dioxide and oxygen to the brush discharge, and J. Schmidlin and P. Massini obtained persulphuric acid by treating the product of the action of ozone on **sulphur trioxide** or fuming sulphuric acid and with water. The presence of sulphur trioxide seems to be necessary, since no persulphuric acid is obtained with sulphuric acid alone. It is thought that the reaction involves the formation of sulphur heptoxide as an intermediate product. The salts of persulphuric acid with concentrated sulphuric acid give ozonized oxygen. **Selenium** and **tellurium,** like sulphur, are oxidized by ozone. Attempts by J. Jannek and J. Meyer to make pure selenium dioxide and selenium trioxide by this method have not yet been successful.

It has not been definitely proved that ozone can react directly with **nitrogen.** L. Carius and M. Berthelot[23] said not. C. F. Schönbein stated that a mixture of ozonized oxygen and nitrogen furnishes calcium nitrate with lime water, but M. Berthelot says that the nitrate was due to an impurity in the lime water, and that nitrates or nitrogen oxide may be produced as a by-product in the formation of ozone by the phosphorus process. However, there is no doubt that, as shown by J. Chappius and P. Hautefeuille, nitrogen is oxidized when air is exposed to the brush discharge in the ordinary method of preparing ozone;[24] but, as E. Fonrobert remarks, this does not prove that ozone can react with nitrogen. C. Montanari obtained no signs of the oxidation of nitrogen by leading a mixture of nitrogen and ozonized oxygen over platinized lime. The chemically active variety of nitrogen obtained by R. J. Strutt[25] by the action of a spark discharge on nitrogen gives no trace of nitrogen oxide after it has been mixed with ozone, and cooled with liquid air, but T. M. Lowry has shown that air which has been subjected to the brush discharge and afterwards sparked gives a greater yield of nitrogen oxides than when the air supply has not been previously ozonized. Hence, it is inferred that in the sparking the nitrogen in the air is converted into a form which enables it to unite rapidly with the ozone. **Nitric oxide** once formed can be oxidized to a higher oxide, which is decomposed by ozone to oxygen and nitric oxide.[26] While two volumes of nitric oxide and one volume of oxygen unite to form nitrogen peroxide, the reaction is not complete if the oxygen employed be previously ozonized—this may be due to the direct retarding action of ozone, or to the destruction by ozone of some catalytic agent necessary for the reaction between nitric oxide and oxygen. Ozone oxidizes **nitrogen trioxide** to the tetroxide, and **nitrogen tetroxide** to the pentoxide; in aqueous solution, nitrous acid is first formed and then nitric acid. The reaction is very much faster with ozone than with oxygen.[27] D. Helbig obtained a volatile substance by the action of ozone on nitrogen trioxide at the temperature of liquid air;

it is possible an ozonide, N_2O_6, identical with E. Müller's nitrogen hexoxide. The oxidation of the tetroxide to the pentoxide by ozone has been recommended as a method of making nitric anhydride.[28]

L. Carius, and L. I. de N. Ilosva failed to obtain evidence of any combination between dry **ammonia** and ozone; but G. Baumert and C. F. Schönbein [29] noted the formation of a cloud immediately moisture was added, and the ammonia was oxidized to ammonium nitrite and nitrate. L. Carius reported that some hydrogen peroxide was formed at the same time: $2NH_3+4O_3=NH_4NO_2+H_2O_2+4O_2$; and $NH_4NO_2+H_2O_2=NH_4NO_3+H_2O$. If the gases are very dilute, the reaction is so slow that it is not thought the occurrence of ammonium nitrite and nitrate in the atmosphere can be explained by the oxidation of ammoniacal products by atmospheric ozone. D. Helbig reported the oxidation of ammonia with incandescence when the gas is passed over a mixture of potassium permanganate and sulphuric acid; while P. Jannasch and W. Gottschalk found a cloud is formed by leading ozone into aqueous ammonia, and the cloud condenses to a white film on the walls of the vessel. E. Warburg also obtained a very marked contraction by exposing a mixture of ammonia and oxygen to ultraviolet rays. A. W. Browne and F. F. S. Netterly [30] reported that if ozone be passed into a boiling alkaline solution of **hydrazine sulphate,** a small quantity of azoimide, HN_3, but no ammonia, NH_3, was formed.

Dry yellow and red **phosphorus** are oxidized to phosphorus pentoxide by ozone; if water is present phosphorous acid is first formed and afterwards phosphoric acid. Ozone oxidizes **arsenic** in presence of water to arsenic acid, but **antimony** is not so easily oxidized, and C. F. Schönbein (1847) proposed to distinguish the two latter elements by this reaction. J. Schmidlin and P. Massini[31] tried to convert **phosphorus pentoxide** into a higher state of oxidation by means of ozone, but without result. **Arsenious oxide** is oxidized quantitatively to arsenic acid by ozone, and C. F. Schönbein [32] proposed to determine ozone by the reaction: $As_2O_3+2O_3=As_2O_5+2O_2$, but Y. Yamauchi found that one gram of ozone oxidized 2·14 grms. of arsenic trioxide while theoretically 2·06 grms. passes into the pentoxide. **Phosphine** and **arsine** are immediately decomposed by ozone; and A. Stock and W. Siebert found that **stibine** at —90° explodes in contact with ozone. A solution of ozone in liquid oxygen does not attack solid stibine, but as the temperature is allowed to rise slowly an explosion occurs. According to A. Besson,[33] ozone in sunlight acts on **phosphorus trichloride** forming the oxychloride; with **phosphorus tribromide,** the pentabromide and trioxide are formed, but no oxybromide; and with **arsenic trichloride,** at 50°, chlorine is liberated and arsenic oxide formed. **Phosphorous iodide** is decomposed with the liberation of iodine and the formation of complex oxyiodide. Ozonized oxygen has no action in the cold on solutions of **phosphorus pentachloride or pentabromide** in carbon tetrachloride. A. Stock and K. Friederici [34] find that when solutions of phosphorus trisulphide, P_4S_3, are treated with ozone a yellowish-white oxysulphide, $P_4S_3O_4$, which with further treatment forms $P_4S_3O_7$, is precipitated.

Ozone is destroyed by **carbon,** the smell disappears, but no oxidation has been detected. A. R. Leeds and F. Baumann stated that ozone oxidizes **carbon monoxide,** while according to I. Remsen and M. S. Southworth, and E. H. Keiser,[35] ozone does not oxidize this gas, but the negative results are possibly due to the use of ozone of too great dilution. M. Berthelot has shown that there is a kind of equilibrium between ozone and carbon monoxide since a mixture of the two gases in the brush discharge forms about 90 per cent. carbon dioxide, while carbon dioxide is partially decomposed under similar conditions into carbon monoxide and ozone. E. Goldstein found that when sparks were passed through a Geissler's tube filled with oxygen and carbon monoxide, at the temperature of liquid air, the spectrum of carbon monoxide gradually disappeared. R. Clausmann exposed a mixture of ozonized oxygen and carbon monoxide in sunlight for eight days and found 2·83 parts of carbon dioxide were formed, in darkness only 0·88 part was formed. J. Thiele also exposed a similar mixture to ultraviolet radiations and obtained small quantities of carbon dioxide. According to W. A. Jones and C. E. Waters,[36] the oxidizing power of ozonized oxygen on carbon monoxide is greater the higher the temperature, and the greater the concentration of the ozone. The action is appreciable in the cold if the concentration of the ozone be high. A. Besson and L. Fournier[37] converted **silicochloroform** into a volatile oxychloride, Si_2Cl_6O, by the action of ozone.

With the exception of **gold** and the metals of the **platinum** family, moist ozone oxidizes all the metals which have been tried—copper, **iron,** nickel, etc. In some cases the metals require heating at ordinary temperatures. Copper, nickel, and tin withstand the gas fairly well; **aluminium, zinc, brass,** and lead are quickly corroded. Iron is not so readily oxidized if the carbon-free metal be alloyed with chromium, and the use of **ferrochromium** containing 25 per cent. of chromium has been patented[38] for chemical apparatus required to resist the fumes of ozone or nitric oxide. A coating of shellac varnish as well as many of the acid-proof paints of the graphite or asphalt type protects the metals quite well. Silver and lead form the higher oxides. If the gas and metal be thoroughly dried, C. F. Schönbein[39] found that in many cases no reaction occurs; the presence of moisture is necessary to start the oxidation. C. F. Schönbein found that similar remarks apply to the action of ozone on several other substances—metal sulphides, iodides, manganese and lead salts, potassium cyanide, organic colouring agents, etc. W. Manchot and W. Kampschulte hold that dry ozone can react with the metals forming ozonides under certain conditions. These ozonides are usually very unstable and only a very small quantity is formed.' If, however, water be present, or the system be heated, the ozonide is formed in greater proportions and decomposed into the metal oxide and oxygen.

The many analogies between ozone and sulphur suggest the hypothesis that ozone and sulphur dioxide, SO_2, are related as indicated in the respective graphic formulæ $O=O=O$, and $O=S=O$; and that just as sulphur dioxide is the anhydride of sulphurous acid, so is ozone the anhydride of an **ozonic or ozonous acid.** Although ozonic acid is unknown, it is supposed that the well-known potassium tetroxide, K_2O_4—that is, $K_2O.O_3$—is the corresponding salt analogous with potassium sulphite, say $K_2O.SO_2$. The argument, though very feeble, has been pushed still further. C. F. Schönbein (1844) found that when ozone is passed through an aqueous solution of, say, 40 per cent. potassium hydroxide, something is formed which gives a blue coloration with a mixture of potassium iodide and starch; and A. von Baeyer and V. Villiger (1902)[40] showed that if the potash lye be strongly cooled, the ozone forms an orange-brown solution, and the colour disappears when the lye is removed from the freezing mixture. In these experiments, it was assumed that *ozonsäures Kalium*—**potassium ozonate**—is formed, and that the salt is more stable at low temperatures than it is at ordinary temperatures. A. von Baeyer and V. Villiger also obtained a coloured product with solid potassium hydroxide. Similar results were obtained with the other four **alkali hydroxides,** and the stability of the product decreased with decreasing atomic weight in passing from cæsium to lithium. Indications of the formation of an analogous unstable product were obtained with dry liquid ammonia.[41] Again, according to L. Gräfenberg, the **hydroxides of the alkaline earths** form coloured peroxidized compounds; when ozone is passed into lime water under the same conditions, a granular precipitate is formed which does not colour a mixture of potassium iodide and starch blue; but does so if it be acidified. The acidified liquid does not smell of ozone. The corresponding product with magnesium hydroxide is not coloured.

It is further assumed, without proof, that potassium tetroxide and potassium ozonate are the same, and hence, ozonic acid, H_2O_4, is regarded as a **hydrate of ozone,** O_3H_2O, or $(HO)_2O_2$, *i.e.* $(HO)_2=O=O$ by analogy with the corresponding sulphur compound, $(HO)_2=S=O$. Against this assumption it has been urged: (1) Ozonized oxygen led through water does not make the liquid appreciably more conducting, electrically, which it probably would do if traces of an acid were formed; and (2) no appreciable difference has been detected in the solubility of ozone in water and in normal acids—if an acid were formed in water, the solubility in that menstruum would probably be the greater. The latter argument has not much weight.

W. A. Shenstone and J. T. Cundall found that although dried ozone is destroyed by mercury, the metal is not attacked as it is by imperfectly dried ozone. The action of ozone on **mercury** is superficial.[42] Put a globule of mercury in a small flask, pass ozonized air into the flask and shake the globule of mercury about. The mercury loses its lustre, and spreads a film over the walls of the flask. The globule of mercury is restored when the film is shaken up with water. According to W. Manchot and W. Kampschulte, the mercury is but slightly attacked at ordinary temperatures by oxygen with 1·5 per cent. of ozone by volume; at 55°, a brown film is formed which becomes deeper and deeper in colour as the temperature is raised, and attains a maximum at 180° to 190°. The surface of the mercury then acquires a deep steel-blue colour and begins to develop a brown vapour. At higher temperatures the action becomes less marked; at 238°, only a yellow film is perceptible, and at 250° there is no apparent action. There appears to be a higher oxide, or an ozonide of mercury formed in this reaction, but the product has not been isolated. Polished **silver** foil is attacked by moist ozone, and, according to A. Volta,[43] negatively polarized; dry ozone also polarizes the metal, and the ozone is at the same time decomposed. If a piece of silver foil cleaned with silver sand be heated in a Bunsen's burner for a moment, and while still warm, held in a stream of ozonized air, the silver is browned or blackened, owing, it is said, to the formation of a higher oxide of silver. E. Frémy recommended the reaction as a test for ozone, but A. Houzeau considered it not sufficiently delicate. Ozone can be recognized by its smell long before the silver is coloured. If the silver is dirtied by contact with the fingers the test is not so good. If the surface of the silver be not specially purified it will be darkened by ozone at the ordinary temperature. Thus, if a plate which has once been blackened be strongly heated, the colour disappears, but the plate is blackened by ozone at ordinary temperatures, owing, it is supposed, to the presence of a trace of undecomposed oxide; similarly, a plate which has been dipped in dilute nitric acid, washed, and dried, is blackened at ordinary temperatures. Scouring the plate with sand destroys its activity at ordinary temperatures. Minute traces of the oxides of the heavy metals—*e.g.* nickel, cobalt, lead, chromium or iron oxide—or the platinum metals—*e.g.* ruthenium, palladium, or platinum—act as catalytic oxygen carriers and enable the silver to be blackened by—say, 0·2 per cent. of ozone—at ordinary temperatures. To clean the metal surface, it is washed a few times with benzene, polished with moist sand, and rubbed with a clean dry cloth. The sensitiveness gradually diminishes when the plate is kept. Ozone produces a white iridescent film on a clean silver plate at 100°; a steel blue film at 154°; a pronounced blackening between 220° and 240°; this is an optimum temperature since at higher temperatures the effect becomes more and more feeble, until at 450° no change can be observed—*vide* silver.

Copper is attacked by ozone, but reactions analogous with those presented by mercury have not been observed because air itself oxidizes the heated metal. As in the case of mercury, W. Manchot found that molten **tin** at 500° is attacked by ozonized air (1 per cent. of ozone). Ozonized air slowly attacks metallic **lead** forming a layer of brown dioxide; in the presence of water, A. R. Leeds found that lead hydroxide is formed, W. Manchot observed only a slight reaction on lead at 100°, with rising temperatures the attack is more marked; at 227°, the metal is steel-blue like silver; at 385° it is brownish-blue and the action cannot then be distinguished from that of ordinary oxygen. **Nickel** is not perceptibly attacked by ozone at 240°; at 300° a yellow film is formed; at 415° the film is golden yellow. This change occurs more quickly with ozonized oxygen than it does with ordinary oxygen; at higher temperatures, the difference is inappreciable. The action of ozone on **silver sulphide** is very slow; **cobalt and nickel sulphides** first form sulphites and then the dioxides; **lead, manganese, and palladium sulphides** give the dioxides and sulphuric acid without the intermediate formation of the sulphite being perceptible; and **gold sulphide** gives metallic gold.

Ozone oxidizes **mercurous salts** to the mercuric state:[44] $2HgNO_3+O_3=HgO+Hg(NO_3)_2+O_2$; mercurous chloride or bromide also forms some oxyhalide. Similarly **thallous salts** are oxidized to thallic salts; and at the same time the colour turns brown; this was proposed as a test for ozone by R. Böttger (1865) and E. Schöne (1879). According to Y. Yamauchi, the reaction, $2TlOH+2O_3=Tl_2O_3+H_2O+2O_2$, is quantitative. Ozone precipitates dark-brown lead dioxide from solutions of **lead salts,** slowly in neutral solutions, rapidly in basic solutions; hence, basic lead acetate test papers have been recommended as a test for ozone. Ozone converts dark-brown lead sulphide into white lead sulphate: $PbS+4O_3=PbSO_4+4O_2$. This can be shown by holding a strip of paper which has been steeped in a solution of lead acetate and browned by hydrogen sulphide, in a stream of ozonized oxygen or ozonized air. Many other sulphides—copper, antimony, zinc, cadmium—behave in a similar manner. Attempts by L. Moser to oxidize **cupric salt** solutions by the action of ozone on neutral or alkaline, hot or cold, solutions have given no result. Ozone acts on Fehling's solution like chlorine or hypochlorites. Feebly acid solutions of **bismuth nitrate** gave P. Jannasch and W. Gottschalk no precipitate, but alkaline solutions are coloured yellow or brown. C. F. Schönbein and A. W. Williamson represented the oxidation of **stannous chloride** to stannic chloride by the equation: $3SnCl_2+6HCl+3O_3=3SnCl_4+3H_2O+3O_2$; but Y. Yamauchi has shown that the relation between the ozone and the stannous chloride oxidized corresponds with $3SnCl_2+6HCl+O_3=3SnCl_4+3H_2O$. This latter equation is unusual in that the whole of the oxygen of ozone is consumed by the oxidation.

The action of ozone on **manganous salts** is peculiar, and is largely determined by the concentration and acidity of the solution. With *neutral* solutions, a brown precipitate of **manganese dioxide** is formed; paper soaked in a solution of manganous sulphate and dried was recommended by D. Huizinga as a test for ozone; and paper similarly made with manganous chloride was recommended by C. Engler and W. Wild. The test papers are not very sensitive. A solution of manganous sulphate can be used in place of ink, and the writing is turned brown by exposure to ozone owing to the formation of a brown manganese dioxide. C. F. Schönbein wrote M. Faraday a letter to this effect, soon after he had discovered ozone. According to L. Maquenne, in *feebly acid* solutions of manganous sulphate, the solution which remains after the separation of the manganese dioxide has a rose-pink colour, and this is the more intense, the greater the acidity of the solution, until, with 10 per cent. of sulphuric acid, no dioxide is precipitated, and the manganese is converted into **permanganate**. Ozone does not carry the oxidation further. If the concentration of the acid exceeds 30 per cent., **manganic sulphate,** not a permanganate. is formed. The greater the concentration of the manganous sulphate, the more the sulphuric acid required. Analogous results are obtained with manganous nitrate and nitric acid, and with hydrochloric acid and manganous chloride. The fact that the higher manganese oxides give ozone, led O. Brunck, as we have seen, to postulate an ozonide structure for these compounds, and the conversion of the lower mangansese salts into the higher oxides, by ozone, is taken to confirm this. P. Jannasch and W. Gottschalk[45] have studied the use of ozone as a reagent for the qualitative detection and the gravimetric precipitation of manganese salts in analysis. Colourless glass, in which the colour of the iron salts has been bleached by manganese oxide, is slowly coloured violet by exposure to ozone or to ultraviolet rays. According to F. Fischer, this transformation does not occur so readily in the near sea-level, as on high mountains where the ozone and the ultraviolet rays of the sun are more prevalent.

Ozone oxidizes **ferrous salts** to ferric salts[46] in neutral and acid solutions. The reaction, according to R. Luther and H. J. K. Inglis is in accord with $2Fe(NH_4)_2(SO_4)_2+O_3=Fe_2O(SO_4)_2+2(NH_4)_2SO_4+O_2$, but Y. Yamauchi found rather more ferrous iron was oxidized than corresponds with this equation, and hence he inferred that some of the oxygen also does work in oxidation. **Ferrocyanides** are oxidized to ferricyanides. **Potassium carbonyl ferrocyanide,** $K_3FeCOCy_5$, is not oxidized to the ferri-salt by ozone. In alkaline solutions **ferri-salts** are oxidized to ferrates by ozone: $Fe_2O_3+O_3+2H_2O=2H_2FeO_4$, which suggests an ozonide structure for the ferrates. P. Jannasch and W. Gottschalk could not oxidize **nickel nitrate** solutions by ozone, but **cobalt sulphate** gave a dark-brown precipitate. Cobalt and nickel sulphides or hydroxides are immediately oxidized to the peroxide—the sulphur of the sulphide forms sulphuric acid. Ozone oxidizes **chromic salts** to chromates or dichromates, but it does not carry the oxidation further.

Ozone precipitates gold from acid-free solutions of **gold chloride** or colours the solutions dark-violet. This was therefore recommended as a test for ozone by R. Böttger.[47] Ozone precipitates palladium dioxide from **palladium salt** solutions, and it forms complex salts, palladiates, in alkaline solutions. E. Schneider recommended palladous chloride for making test papers for ozone. The reaction is usually represented by the equation: $H_2PdCl_4+4H_2O+O_3=Pd(OH)_4+4HCl+H_2O+O_2$.

Ozone rapidly corrodes **rubber** and rubber compounds; concentrated ozone will eat through rubber tubing in a few moments; **cork** withstands dilute ozone for a short time, but its use should be avoided. Ozone attacks many organic compounds in the cold. **Methane** gives formaldehyde and formic acid; ethylene forms acetaldehyde and acetic acid; **ethylene** reacts explosively, giving carbon and water; **alcohol** forms aldehyde and acetic acid; ether forms aldehyde and acetic acid and a syrupy liquid **ethyl peroxide.** $(C_2H_5)_2O_2$, which is explosive, and which forms alcohol and hydrogen peroxide with water. **Nitroglycerol, dynamite, nitrogen chloride,** and **nitrogen iodide** explode in an atmosphere rich in ozone. **Benzene** forms formic, acetic, oxalic, and other acids as well as a white gelatinous explosive compound called **ozobenzene.** The **phenols** are slowly attacked; **aniline** forms ozobenzene, etc. The **vegetable colours** are quickly bleached by ozone—indigo blue forms colourless isatine. Tincture of guaiacum is coloured blue by ozone. The two last-named reactions have been used as tests for ozone. The colouring matter of blood as well as the albumins are destroyed by ozone.

The uses of ozone.—Ozone is used for the purification of water. Its function is to oxidize the organic matter, and sterilize the water. So satisfactory is the ozone treatment in the sterilization of water that it is declared by recognized authorities: "The purification of drinking water has ceased to be a problem." Water of average quality can be satisfactorily treated with ozonized air containing one part of ozone per million, and the cost of treatment lies between 4*s*. 0*d*. and 8*s*. 0*d*. for 1,000,000 gallons per hour. There are not far from 100 ozone water-plants giving satisfactory results. Ozonized air is also used in ventilation. The ozone treatment of air is not intended to supplant ventilation, but is to supplement it, by providing an agent which destroys bad odours, and the feeling of closeness experienced when a number of people are in a confined space. The concentration of the ozone for this purpose should be smaller than can be recognized by smell—say less than a milligram per cubic metre. Ozone or galvanized air, said Leuch, in 1849, is a most powerful bleaching agent. It is now used for bleaching purposes particularly for paper pulp; starch; oils; and for oxidizing oil in the manufacture of linoleum, etc. H. de la Coux[48] has given a long list of possible applications, but many have been reported failures on trial—sometimes because the ozone has been wrongly applied, *e.g.* in too concentrated a form for bleaching certain textiles; and sometimes because some unexpected complication has arisen, *e.g.* in bleaching flour where the taste is affected, and in bleaching dextrine and glue where the adhesive properties are impaired by ozone bleaching. The industrial applications have stimulated inventors, and accordingly, a number of fairly efficient ozonizers have been placed on the market. In most of these, a high tension alternating electric discharge is sent across a space through which the air to be ozonized passes.

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§ 7. The Constitution of Ozone

The nature of ozone was the subject of much discussion soon after C. F. Schönbein had established the individuality of the gas. At first, C. F. Schönbein seems to have thought the gas was a new elementary body which belonged to the same class of electronegative elements as chlorine and bromine; later on, he suggested that it may be an elementary substance which, when united with hydrogen, forms the nitrogen of the atmosphere.[1] Henry Cavendish had proved, in 1784, that nitrates are produced when electric sparks pass through air; and L. Rivier and L. R. de Fallenberg (1845) showed that nitrous acid is formed during the oxidation of phosphorus. Nitrous acid like ozone colours starch paper blue; it was at first supposed that the reactions ascribed by C. F. Schönbein to ozone were really produced by traces of nitrous acid. Ozone can be produced under conditions where no nitrogen is present; consequently, it follows that **ozone contains no nitrogen.** Oxygen is an invariable antecedent when ozone is formed, and an invariable consequent when ozone is decomposed.

Is ozone a condensed form of oxygen or an oxide of hydrogen?—About 1845, J. C. G. de Marignac and A. de la Rive showed that moist silver, when exposed to ozone, forms a silver oxide, and that potassium iodide—KI—can be oxidized by ozone to potassium iodate—KIO_3; but there is never any sign of the formation of any nitrogen compound. This narrowed the question, for it appeared that ozone is either (1) a form of matter identical with oxygen—J. C. G. de Marignac and A. de la Rive (1845); or (2) oxidized water, that is, a peroxide of hydrogen—C. F. Schönbein and A. W. Williamson (1845). On the one hand, J. C. G. de Marignac and A. de la Rive, in their memoir, *Sur la production et la nature de l'ozone*,[2] showed that ozone can be obtained by the electrolysis of water free from nitrogen, and that ozone containing nothing but oxygen must be an allotropic form of that element. This conclusion was supported by J. J. Berzelius. On the other hand, C. F. Schönbein (1847) contended that ozone is a higher oxide of hydrogen than L. J. Thénard's *bioxyde d'hydrogène*. This view was supported by A. W. Williamson because he obtained water by passing ozonized oxygen over heated copper oxide. A. W. Williamson's gas was obtained by electrolysis. E. Frémy and E. Becquerel demonstrated in their memoir, *Recherches électrochimque sur les propriétés des corps électrisés*, that pure oxygen can be converted into ozone by the prolonged action of electricity; they also found the ozone to be absorbed by mercury or by potassium iodide, as fast as it was produced. G. Baumert then suggested that the ozone obtained by the electrolysis of acidulated water is different from that obtained by the electrical discharge in oxygen, or by the action of phosphorus on moist oxygen, because the electrolytic ozone always contains hydrogen and the other form of ozone contains nothing but oxygen. In 1856, in a paper, *On the constitution and properties of ozone*, T. Andrews showed that the difficulty with electrolytic ozone was due to the presence of impurities in the gas, and if proper precautions be taken :

> No gaseous compound having the composition of a peroxide of hydrogen is formed during the electrolysis of water; and that ozone, from whatever source derived, is one and the same body, having identical properties and the same constitution, and is not a compound body, but oxygen in an altered or allotropic condition.

About this time, ozone was variously styled *nascent oxygen*, implying that it was oxygen in an atomic condition ; *active oxygen* or *erregter Sauerstoff*, in reference to its great chemical activity ; and *polarized oxygen* or *electrisierten Sauerstoff*.

The hydrogen oxide theory was not given up until 1860, when T. Andrews and P. G. Tait[3] proved in their paper, *On the Volumetric relations of ozone*, that if an electric discharge—brush or spark—be passed through pure dry oxygen, a contraction occurs amounting to about one-twelfth of the original volume. The oxygen was sealed in a tube, shaped as indicated in Fig. 7, *Q*, and subjected to the brush discharge, *via* the platinum wires sealed into the glass. In T. Andrews and P. G. Tait's experiment the contraction in volume was measured by attaching to the tubes a small manometer, *a* and *b*, charged with concentrated sulphuric acid. A duplicate tube, *Q*, Fig. 8, containing air was treated along with the tube containing the oxygen, *R*, Fig. 7, so that any changes due to variations of pressure or temperature during the experiment could be corrected. The tubes, during the experiment, were placed in a water tank as indicated in Fig. 8, to keep the temperature uniform. When ozonized oxygen is heated to 270°, and allowed to cool, the original volume of oxygen is obtained ; and when a thin glass bulb, *c*, Fig. 7, *R*, of potassium iodide is sealed in the tube along with the oxygen, and after ozonization, broken by shaking the bulb against a piece of glass tubing *d*, iodine is liberated without any perceptible change in volume. If the gas which has been treated with potassium iodide be heated to 270° as before, no change in volume can be detected. Hence, T. Andrews and P. G. Tait concluded that **ozone is a condensed form of oxygen.** This statement, however, gives no information about the weight of oxygen in a given volume of ozone, *i.e.* the number of atoms in the molecule of ozone.

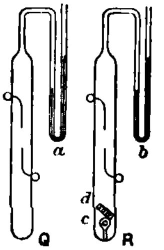


FIG. 7.—Andrews and Tait's Ozone Tubes.

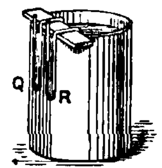


FIG. 8.—Andrews and Tait's Experiment.

The absence of hydrogen in ozone was further confirmed by A. Houzeau (1866), L. von Babo (1863) and by J. L. Soret (1863)[4] in an experiment in which ozone was thoroughly dried, and then decomposed by heat. No trace of any compound of hydrogen—*e.g.* water—could be detected in the products of decomposition. Hence, it is inferred that **ozone is not a compound of hydrogen with oxygen ; ozone contains nothing but oxygen ;** it is a kind of oxidized oxygen. A similar experiment was made by C. F. Schönbein in 1849, but its importance does not appear to have been appreciated at that time.

Ozone is a form of oxygen in which three volumes of oxygen are condensed to two volumes.—Since the volume of ozonized oxygen undergoes no change when mixed with a solution of potassium iodide, it is inferred that the oxidation of potassium iodide can only be effected by so much oxygen in ozone as has been condensed with ordinary oxygen to form ozone. This excess of oxygen is absorbed by the solution of potassium iodide, and the ordinary oxygen which remains has the same volume as the ozone present before the action of the potassium iodide. Hence, no new contraction occurs with potassium iodide. In symbols, the formula for ozone is O_{2+n}. T. Andrews and P. G. Tait did not determine the numerical value of n. The formula for ozone might be O_3, O_4, O_5, . . . The special difficulty involved in this determination arises from the fact that ozone cannot be obtained free from oxygen; and, accordingly, the regular methods of determining the molecular weights—vapour density, etc.—cannot be applied. W. Odling (1861)[5] proposed to take the simplest possible formula, O_3, thus assuming that three volumes of oxygen are condensed to form two volumes of ozone; he said:

> If we consider ozone to be a compound of oxygen with oxygen, and the contraction to be consequent upon their combinations, then, if one portion of this combined or contracted oxygen were absorbed by the reagent, the other portion would be set free, and by its liberation might expand to the volume of the whole. Thus, if we suppose three volumes of oxygen to be condensed by their mutual combination into two volumes, then on absorbing one-third of this combined oxygen by mercury, the remaining two-thirds would be set free and consequently expand to their normal bulk, or two volumes:

$$\overset{-}{O}\overset{+}{O}\overset{-}{O}+\overset{+}{Hg_2}=\overset{+}{Hg_2}\overset{-}{O}+\overset{+}{O}\overset{-}{O}$$

Interpreting this assumption in the light of Avogadro's rule:

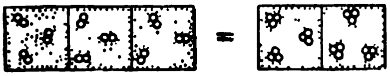
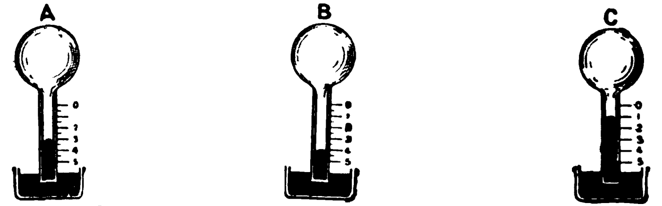


FIG. 9.—3 Volumes of Oxygen give 2 Volumes of Ozone.

This beautiful hypothesis, said C. W. Heaton (1868), although accounting perfectly for all known facts, is yet but a probability. One link in the chain of evidence is lacking. True, J. Tyndall[6] inferred that ozone contains more atoms per molecule than does ordinary oxygen because the former has much greater absorptive power for heat than the latter; but the missing link was not supplied until J. L. Soret described some happily devised experiments in his memoir, *Recherches sur la densité de l'ozone* (1866).

J. L. Soret's experiments.—J. L. Soret (1866)[7] took advantage of the fact, known to C. F. Schönbein, that essential oils absorb ozone without absorbing any marked quantity of oxygen. Hence a sample of ozonized oxygen was introduced into two flasks, A, Fig. 10, and A_1. The vessel A was heated so as to decompose the ozone. The gas now occupied a greater volume than before—B, Fig. 10. The expansion was measured when the gas had cooled to its former temperature. The vessel A_1, containing the same mixture of ozonized oxygen, was treated with cinnamon oil; the contraction due to the removal of ozone was measured—C. J. L. Soret (1866) found the following data with measured volumes of a given sample of ozonized oxygen:



(A) Ozonized oxygen.

(B) After the ozone has been converted into oxygen by heat.

(C) After removal of ozone with cinnamon oil.

FIG. 10.—Soret's Experiments with Ozone (Diagrammatic).

Expansion after heating	3·45 c.c.
Contraction after treatment with cinnamon oil . .	6 90 c.c.

Consequently, the ozonized oxygen contained 6·90 c.c. of ozone; and 6·90 c.c. of ozone becomes 10·35 c.c. of ordinary oxygen when heated; or 2 c.c. of ozone becomes 3 c.c. of oxygen. In another set of experiments:

Contraction after treatment with turpentine oil . . .	8·0 c.c.
Oxygen absorbed by treatment with potassium iodide . .	3·9 c.c.

Hence 8·0 c.c. of gas gave up 3·9 c.c. of oxygen to potassium iodide solution without change of volume. This means that 8 c.c. of ozone is equivalent to 8·0–3·9 c.c. of oxygen within the limits of experimental error. L. von Babo and C. E. Claus,[8] in 1863, also found the decrease in the volume of oxygen on ozonization to be equal to the volume of oxygen calculated from the quantity of iodine liberated by the action of the ozone on potassium iodide. Hence, it was inferred that **three volumes of oxygen produce two volumes of ozone.**

J. L. Soret's work was rather crude, but, in 1872, B. C. Brodie[9] repeated the experiments with cinnamon oil, turpentine, and stannous chloride in such a way that the above conclusion was the only possible interpretation of the experiment. A. Ladenburg[10] extended J. L. Soret's work to a mixture containing a large proportion of ozone, and calculated the relative density of ozone—assumed unknown—from the density of a sample of ozonized oxygen, and the amount of iodine liberated by the gas when in contact with potassium iodide, taken in conjunction with the fact that the gas undergoes no change in volume during the reaction. A. Ladenburg tacitly assumed that a molecule of iodine is liberated by a molecule of ozone. The argument is accordingly fallacious because if the molecule of ozone be represented by O_2+nO, each molecule of ozone will liberate n molecules of iodine. The excess of the density of ozonized oxygen over that of pure oxygen represents the weight of oxygen available for the liberation of iodine, and this is not necessarily dependent on the molecular weight of ozone.

EXAMPLE.—If 100 c.c. of ozonized oxygen are converted into oxygen by passage through a hot tube, what was the composition of the original mixture if 110 c.c. of oxygen remained? The mixture contained x c.c. of ozone, and $(100-x)$ c.c. of oxygen, and since x volumes of ozone yield $\frac{3}{2}x$ c.c. of oxygen, the original mixture contained the equivalent of $\frac{3}{2}x+(100-x)=110$ c.c. of oxygen. Hence, $x=20$, or the mixture contained 20 per cent. of ozone and 80 per cent. of oxygen.

M. Otto (1897)[11] determined the density of ozone by weighing a bulb filled with oxygen, and again when filled with ozonized oxygen. The increase in weight gave the weight of the active oxygen in ozone. The amount of ozone was determined by means of an acidified solution of potassium iodide. A. Ladenburg (1901) measured the total volume of ozone by absorption with turpentine. The mean of A. Ladenburg's five determinations was 47·78—with 45·3 and 50·4 as extreme values. J. L. Soret (1867) confirmed his determination of the molecular weight of ozone by assuming T. Graham's relation between the speed of the diffusion of a gas and its density. He allowed vessels of chlorine and oxygen to be in communication for a given time; and likewise vessels of ozonized oxygen and oxygen. The amounts of chlorine and ozone which diffused in a given time were as 0·227 : 0·271. Consequently, if the density of chlorine is 2·49, and D, the density of the ozone, air unity, by Graham's law, $D:2{\cdot}49=(0{\cdot}227)^2:(0{\cdot}271)^2$; hence, D is nearly 1·5. A. Ladenburg obtained the density 1·3698 by Schilling's apparatus. All these numbers are in accord with a molecular weight 48 (oxygen 32) for ozone.

The frequent formation of dimeric (doubled) ozonides at low temperatures, suggested to C. D. Harries the possibility that ozone may be itself dimeric, $(O_3)_2$; at low temperatures and monomeric, O_3, at higher temperatures: $(O_3)_2 \rightleftharpoons 2O_3$; nitrogen peroxide behaves similarly, $(NO_2)_2 \rightleftharpoons 2NO_2$.

Newth's experiment.—Many neat ways of illustrating the volume relations of oxygen and ozone have been devised.[12] G. S. Newth's apparatus (1896), slightly modified, consists of two concentric tubes, Fig. 11. The inner tube has a hollow stopper ground to fit the outer tube ; it contains dilute sulphuric acid. The inner tube has two little projections, *A*, and the outer tube has three projections, *B*, in such a position that a sealed thin glass tube containing cinnamon oil can be broken, when desired, by twisting the stopper of the inner tube. The outer tube is fitted with a three-way cock, *D*, connected with a manometer charged with concentrated sulphuric acid. The apparatus is placed in a cylinder containing, say, ice and water. The annular space between the two tubes is filled with oxygen, *via* the cocks *E* and *D*. The manometer is then put in communication with the annular space between the two tubes. Note the level of liquid in the manometer. Pass a current from an induction coil, so as to ozonize the oxygen sufficiently to give, say, a one-centimetre contraction on the manometer. Note the contraction. Give the stopper a twist so as to break the glass tube containing the cinnamon oil; the contraction which occurs will be twice the former contraction, namely 2 cm. more. It may be advisable to level the liquid in the manometer, after the first contraction, by admitting either air or oxygen, before breaking the capillary tube. The same or a similar apparatus can be employed for showing the contraction which occurs when ozone is treated with potassium iodide by using a tube *C* with this substance in place of cinnamon oil.

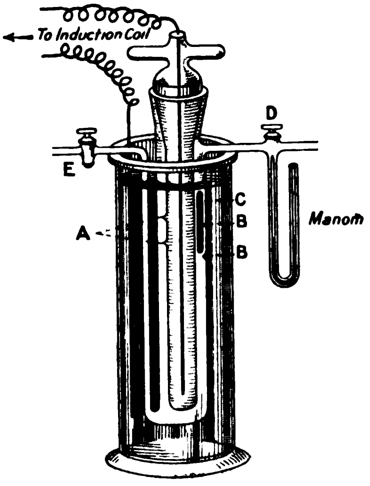
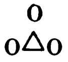
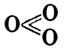


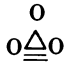
Fig. 11.—Newth's Apparatus (Modified).

The graphic or constitutional formula of ozone.—If it be assumed that all three atoms of oxygen are bivalent, the only possible formula for ozone is the ring structure indicated in formula I. Owing to the peculiar oxidizing qualities of the odd oxygen atom, some consider that the three oxygen atoms cannot


I

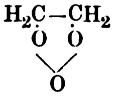

II

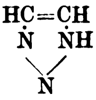

III


IV


V

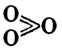
be symmetrically placed in the molecule, and this has given rise to other suggestions. For example, M. Traube[13] assumes that two of the oxygen atoms in the ozone molecule are tervalent and one bivalent, as indicated in formula II. The evidence for the tervalency of oxygen is very weak since there are few compounds in which such an assumption can be accepted ; nor does it correspond with the position of oxygen in the periodic system. A. Angeli has drawn attention to the relationship between ozone, O_3, and azoimide, N_3H ; both compounds are endothermal, explosive, poisonous, and react with unsaturated compounds forming addition products—ozone gives ozonides ; azoimide gives triazoles :


Ozonide.

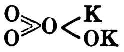

Triazole.

From observations on the molecular refraction of hydrogen peroxide, J. W. Brühl[14] inferred that this compound contains quadrivalent oxygen, and he also assumed that ozone has one or more quadrivalent oxygen atoms as illustrated in formulæ III to V ; J. W. Brühl favoured formula IV or V. Formula V is related to I in the symmetrical arrangement of its atoms. J. W. Brühl favoured IV, but gave no particularly strong evidence in its support. It will be observed that even though one atom in the ozone molecule appears to behave differently from the others, this does not prove a dissymmetrical molecule, for the trinity is possibly unstable because it is overloaded with atoms, and as soon as *any one* atom has been ejected, the remaining pair is stable. On this hypothesis the greater chemical activity of the odd oxygen atom is not due to its being oriented differently from the other two, but rather to the molecule containing one atom too many for stability.

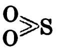
There is no objection to the assumed quadrivalency of oxygen. In fact, it is highly probable that oxygen, like its companions—sulphur, selenium, and tellurium—in the periodic system can be bi-, quadri-, or sexi-valent. O. Wolkowicz[15] concludes that ozone has the constitution O=O=O, indicated in formula III, by analogy with sulphur dioxide O=S=O. This would make ozone the anhydride of ozonous acid, H_2O_4, analogous with sulphurous acid, H_2SO_3; and the so-called tetroxides —*e.g.* K_2O_4—analogous to the sulphites:


$\begin{matrix}O\\O\end{matrix}\!\gg O$

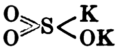
Ozone.


$\begin{matrix}O\\O\end{matrix}\!\gg O<\begin{matrix}K\\OK\end{matrix}$

Potassium ozonate.


$\begin{matrix}O\\O\end{matrix}\!\gg S$

Sulphur dioxide.

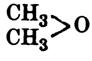

$\begin{matrix}O\\O\end{matrix}\!\gg S<\begin{matrix}K\\OK\end{matrix}$

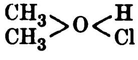
Potassium sulphite.

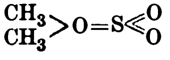
Both series of salts reduce the permanganates. There is no decisive evidence in favour of any one formula for ozone. The question cannot be answered by far-fetched analogies, or by pen- and paper-abstractions. Accordingly, the graphic or structural formula for ozone is still *sub judice*.

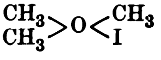
The quadrivalency of oxygen.—The idea that oxygen may be quadrivalent was suggested by A. Naquet[16] in 1864 because of the analogy between oxygen and the elements of the sulphur family—sulphur, selenium, and tellurium—where the compounds SCl_4, $SeCl_4$, TeI_4, etc., show that these elements are quadrivalent. Two years later H. Buff applied the idea to hydrogen and barium dioxides, for he explained the composition of these compounds by the formulæ $H_2=O=O$ and $Ba=O=O$ respectively. A. W. Williamson (1869) suggested that oxygen is quadrivalent in carbon monoxide, $C\equiv O$; and about the same time, S. M. Jörgensen assumed that in virtue of the quadrivalency of oxygen in water, the H_2O-group can act as a bivalent radicle analogous to the bivalency of the NH_3-group—nitrogen quinquevalent. J. Thomsen (1873) also explained the constitution of periodic acid, by assuming that oxygen is quadrivalent, and S. M. Jörgensen's idea was employed by W. A. Tilden (1876) to explain the constitution of crystallized zinc sulphate, $ZnSO_4.7H_2O$; and by A. Wurtz (1879), the constitution of potassium magnesium sulphate, $K_2Mg(SO_4)_2$.

The investigation of C. Friedel,[17] in 1875, on the compounds of methyl ether, $(CH_3)_2O$, with hydrogen chloride, sulphur dioxide, SO_2, methyl iodide, CH_3I, established the existence of a series of compounds:

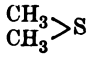

$\begin{matrix}CH_3\\CH_3\end{matrix}\!>O$

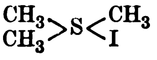

$\begin{matrix}CH_3\\CH_3\end{matrix}\!>O<\begin{matrix}H\\Cl\end{matrix}$


$\begin{matrix}CH_3\\CH_3\end{matrix}\!>O=S\ll\begin{matrix}O\\O\end{matrix}$

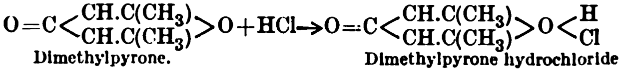

$\begin{matrix}CH_3\\CH_3\end{matrix}\!>O<\begin{matrix}CH_3\\I\end{matrix}$

in which it appears highly probable that in addition to the two ordinary valencies of oxygen, two others are wakened into activity. In an analogous manner, A. A. T. Cahours found that methyl sulphide, $(CH_3)_2S$, reacts with methyl iodide, CH_3I, to form a compound—trimethylsulphonium iodide with quadrivalent sulphur, $(CH_3)_2S.CH_3I$,


$\begin{matrix}CH_3\\CH_3\end{matrix}\!>S$


$\begin{matrix}CH_3\\CH_3\end{matrix}\!>S<\begin{matrix}CH_3\\I\end{matrix}$

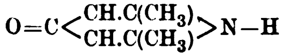
The oxygen compounds are called **oxonium salts** on account of their analogy with **ammonium salts,** say ammonium chloride, H_4NCl, formed by the direct coupling of ammonia, NH_3, and hydrogen chloride, HCl. Instead of C. Friedel's formula for the hydrochloride, A. Wurtz suggested the alternative $(CH_3)_2O : Cl{\cdot}H$, where the oxygen is still quadrivalent and the chlorine tervalent. C. Friedel cited Rose's quadrantoxides, Ag_4O and Cu_4O, as further evidence of a quadrivalent oxygen. In 1888, J. F. Heyes,[18] like H. Buff, in 1866, argued that one of the oxygen atoms in the dioxides of barium, lead, manganese, etc., corresponds with quadrivalent oxygen, and he attributed the ready polymerization of the aldehydes, cyanates, and metaphosphates to the presence of oxygen potentially quadrivalent. J. F. Heyes also referred the formation of compounds with water of crystallization to the same cause. A great number of organic compounds have been discovered in which the most satisfactory formulæ are based on the quadrivalency of oxygen.[19] In 1899, J. N. Collie and T. Tickle[20] showed that hydrochloric acid unites with dimethylpyrone forming dimethylpyrone hydrochloride:



$$O{=}C{<}\begin{matrix}CH.C(CH_3)\\CH.C(CH_3)\end{matrix}{>}O+HCl\rightarrow O{=}C{<}\begin{matrix}CH.C(CH_3)\\CH.C(CH_3)\end{matrix}{>}O{<}\begin{matrix}H\\Cl\end{matrix}$$

Dimethylpyrone. Dimethylpyrone hydrochloride.

This compound acts as an easily dissociated salt of a strong base and a weak acid; it contains a quadrivalent oxygen atom which must play a similar part to that of the nitrogen atom in the salts of dimethylpyridone, and this quadrivalent oxygen



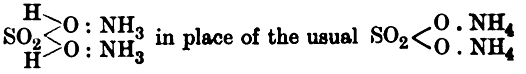
$$O{=}C{<}\begin{matrix}CH.C(CH_3)\\CH.C(CH_3)\end{matrix}{>}N{-}H$$

imparts a basic character to the salts in question. By analogy with ammonium, phosphonium, sulphonium, and iodonium bases, he supposed these salts to be derivatives of an hypothetical **oxonium hydroxide,** $H_3O.OH$. A. von Baeyer and V. Villiger (1901)[21] further argued that the simple oxygen atom, in every form in which it appears in organic chemistry, can form salts with the proper acids under suitable conditions. While a few oxygen compounds give well-characterized salts with the simpler acids, it is usually better and surer to work with the complex acids—*e.g.* hydroferricyanic, hydroferrocyanic, hydrocobalticyanic, phosphotungstic, chloroplatinic, or, above all, perchloric acid. In these salts there is usually little room for doubting the interpretation of their constitution based upon the quadrivalency of oxygen. The same influences which increase or diminish the basicity of nitrogen similarly affect the basicity of oxygen, and also, but to a limited extent, the basicity of sulphur:

NH_3, base	OH_2, neutral	SH_2, acid
$N(C_2H_5)_3$, strong base	$O(C_2H_5)_2$, weak, base unknown	$S(C_2H_5)_2$, neutral
$N(C_2H_5)_4$, OH, very strong base		$S(C_2H_5)_3OH$, base

The entrance of a positive alkyl radicle group renders the oxygen of neutral water basic although this is not the case with negative groups like phenyl, C_6H_5—*e.g.* in triphenylamine, $N(C_6H_5)_3$, the basic character of ammonia has virtually disappeared. Oxygen is an amphoteric element in that it can form both acids and bases. The base-forming qualities of oxygen are comparable with those of nitrogen, phosphorus, sulphur, and iodine, for when united with certain base-forming organic groups, the resulting compound has well-defined basic qualities. Oxygen has not so strong a tendency as nitrogen to pass from a lower to a higher valency.

When the tendency of oxygen to act as a quadrivalent element was generally recognized, and chemists ceased to be restricted to a bivalent oxygen, many compounds previously represented by graphic formula with oxygen bivalent were remodelled on the assumption of the higher valency. For example, following A. W. Williamson's suggestion that oxygen is quadrivalent in carbon monoxide, F. Goldschmidt (1904)[22] used the formula $R{-}C\equiv O{-}OH$ in place of $R{-}CO{-}OH$ for the organic acids and esters; and for ammonium sulphate, J. C. Cain (1904) used:



$$SO_2{<}\begin{matrix}{}^{H}{>}O:NH_3\\{}_{H}{>}O:NH_3\end{matrix}\text{ in place of the usual }SO_2{<}\begin{matrix}O.NH_4\\O.NH_4\end{matrix}$$

Ammonium hydroxide[23] is also regarded as a compound $H_3N:OH_2$ rather than the usual $H_4N.OH$.

E. H. Archibald and D. McIntosh (1904)[24] studied the compounds formed by the liquid hydrogen halides with ether or acetone, and assumed that the valency of oxygen increases as the temperature diminishes. While ethyl oxide, $(C_2H_5)_2O$, forms a compound $(C_2H_5)_2O.HI$ with hydrogen iodide, HI, analogous with the oxonium salts, where the oxygen is quadrivalent, they assume that oxygen is sexivalent in $C_3H_7OH.2HBr$, and dodecavalent in the compound $C_3H_7OH.5HCl$. There is here no reason for assuming these abnormally high valencies for oxygen if the halogen be taken tervalent. J. I. Kanonnikoff (1901) thought that the spectrometric constants of certain organic compounds containing oxygen better agreed with sexivalent oxygen than with either quadri- or bi-valent oxygen; and F. Flavitzky[25] used sexivalent oxygen atoms to explain the union of water of crystallization of a salt. If the tendency of water to crystallize in union with salts as water of crystallization is to be ascribed to the tendency of oxygen to pass from the bi- to the quadrivalent condition, other substances, built on the water type with bivalent oxygen, might be expected to act in a similar manner. Examples are common. Methyl alcohol, $CH_3.OH$, unites with calcium chloride as alcohol of crystallization to form $CaCl_2.4CH_3OH$. Similarly, the unsaturated character of the oxygen in water, H_2O, and of nitrogen in ammonia, NH_3, is employed to explain how ammonia and water are frequently interchangeable in chemical compounds; thus, $CuSO_4.5H_2O$ and $CuSO_4.5NH_3$, etc.

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§ 8. The Modes of Formation and Preparation of Hydrogen Peroxide

At first sight hydrogen peroxide, H_2O_2, is related to water much as ozone is related to oxygen; while the latter can be regarded as oxidized oxygen, so the former can be regarded as oxidized water. Consequently, the term *eau oxygènée*, applied to this compound by its discoverer L. J. Thénard in 1818, is singularly appropriate. Just as ozone is obtained from oxygen by the expenditure of energy equivalent to 30 Cals. per gram-molecule of O_3, so is hydrogen peroxide formed from water by the expenditure of 21·5 Cals. per gram-molecule of H_2O_2. As in the case of ozone, the various methods of preparing hydrogen peroxide may be classed as physical or chemical—in the one case, energy is added in the form of heat, electricity, or ultra-violet radiations; and in the other case, energy is added indirectly or through the mediation of a chemical reaction.

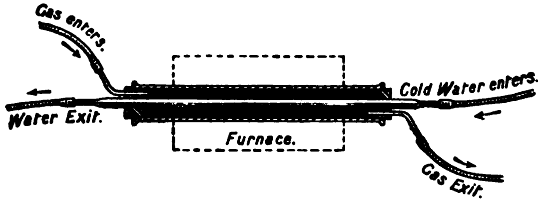


FIG. 12.—Deville's Tube Chaud et Froid.

(1) *The formation of hydrogen peroxide by the action of heat.*—Hydrogen peroxide can be formed by passing a current of moist oxygen through a tube at about 2000° and rapidly chilling the issuing gases. In **H. St. C. Deville's**[1] **hot and cold tube**—*tube chaud et froid*—method of conducting the experiment, a narrow silver or platinum tube is kept cool by a current of cold water. This tube is placed in the centre of a porcelain tube, Fig. 12. A current of gas is placed along the annular space between the two tubes. This arrangement is placed in a furnace so that the gas is heated to a very high temperature. The products of decomposition are suddenly chilled by the cold tube and partially prevented from recombining as they are carried out of the hot zone. The products of many high temperature reactions can thus be examined at ordinary temperatures. According to W. Nernst, the formation of hydrogen peroxide cannot be observed by passing a mixture of steam and oxygen through a hot platinum or iridium tube and cooling the products rapidly, presumably because of the extremely rapid rate of decomposition which W. Nernst found to be nearly the same as with ozone. The formation and decomposition of hydrogen peroxide is a balanced reaction $2H_2O+O_2 \rightleftharpoons 2H_2O_2$; and W. Nernst (1905) estimates that the percentage amount of hydrogen peroxide which can coexist in equilibrium with steam and oxygen under 0·1 atm. pressure, at different temperatures, is as follows:

Temperature . . .	650°	867°	1220°	1881°	2511°
Per cent. of hydrogen peroxide .	0·00036	0·0032	0·028	0·24	0·66

Hence, the rate of cooling must be exceedingly fast if hydrogen peroxide formed at a high temperature is to survive undecomposed. For example, W. Nernst prepared hydrogen peroxide by spraying water on to a glowing Nernst's filament, F. Fischer and O. Ringe made it by passing steam, at 40 mm. of mercury pressure, through a tube of fused magnesia nearly white hot. A large block tin condenser was placed as near as possible to the hottest zone. The condensed liquid contained 0·0045 per cent. of hydrogen peroxide. The magnesia tube was 0·6 mm. diameter, and the yield was very much reduced with tubes 0·3 mm. or 1·0 mm. diameter. F. Fischer and O. Ringe also obtained hydrogen peroxide by blowing steam from a sloping quartz capillary tube into a flame of hydrogen 4 to 6 cm. in height. The jet of steam, at 7 mm. pressure, was between 4 to 6 mm. from the flame, and so directed that the products were driven into the neck of a tin condenser. Although the condensation was incomplete owing to the velocity of the gaseous stream, 0·067 per cent. of hydrogen peroxide was found in the condensed liquid.

(2) *The formation of hydrogen peroxide by exposure to ultraviolet radiations.*—Water confined in a quartz vessel, permeable to ultraviolet rays, is decomposed by exposure to ultraviolet radiant energy furnished by a mercury lamp; hydrogen and hydrogen peroxide are formed: $2H_2O = H_2O_2 + H_2$; and, according to K. V. Charitschkoff,[2] hydrogen peroxide can be detected in water, with a little oxygen in solution, which has been exposed to bright sunlight at 9°–22° for 12 days; at 19°–31°, after 8 days; and at 20°–41°, after 7 days. If the oxygen be replaced by air, no hydrogen peroxide was observed. According to A. Tian (1915),[3] ultraviolet rays of short wave-length (λ2500–3000) decompose solutions of hydrogen peroxide at a measurable rate, but water is decomposed only by the rays in the extreme ultraviolet (less than λ1900). The water is decomposed in accord with the reversible reaction: $2H_2O = H_2O_2 + H_2$; the hydrogen peroxide is subsequently decomposed in accord with the equation $H_2O_2 = H_2O + O$; and after the lapse of sufficient time, the hydrogen and oxygen evolved by these two reactions are in the proportions which would occur if the water alone were directly decomposed into its elements. If the water contains dissolved oxygen it may unite with the hydrogen evolved in the primary reaction and form hydrogen peroxide, some of the dissolved oxygen forms ozone which in turn reacts with the hydrogen peroxide. No reaction between water and ozone has been observed under the influence of ultraviolet light. The conditions which favour the formation of hydrogen peroxide are (i) the use of ultraviolet light rich in rays of very short wave-length; (ii) the exposure of thin layers of water; and (iii) eliminating the conditions which favour the decomposition of hydrogen peroxide. Radioactive barium bromide produced a negative result in darkness, but a positive result in light, hence K. V. Charitschkoff assumes that it is not the radium emanation *per se* which produces the hydrogen peroxide, but that the radium salt acts as a catalytic agent.

(3) *The formation of hydrogen peroxide by electrolysis.*—The water which collects about the anode or positive electrode during the electrolysis of water acidulated with sulphuric acid possesses oxidizing properties which are usually attributed to the presence of hydrogen peroxide.[4] The formation of hydrogen peroxide by electrolysis is favoured by high acid concentration, low temperature, strong current, and small electrode surface. Its formation is prevented if the acid be dilute and the temperature exceeds 60°. According to M. Traube,[5] hydrogen peroxide is formed in small quantities at the cathode, not the anode, during the electrolysis of aqueous solutions, provided oxygen is bubbled about the cathode from which hydrogen is being evolved during the electrolysis of dilute sulphuric acid. If air or oxygen be carefully excluded from the cathode, no hydrogen peroxide is formed. According to M. Traube, this shows that hydrogen peroxide can be regarded as an intermediate product in the reduction of oxygen, where the end-product is water. Indeed, M. Traube draws the extraordinary conclusion that *hydrogen peroxide is always a product of the reduction of molecular oxygen, and is never produced by the oxidation of water.* M. Traube (1887) explains the formation of hydrogen peroxide by the electrolysis of water by assuming that the hydrogen liberated at the cathode immediately unites with the oxygen of the air to form the compound in question, and that this compound is reduced to water by the further action of hydrogen. F. Richarz,[6] on the contrary, shows that hydrogen peroxide is also formed at the anode, and assumes with M. Berthelot that persulphuric acid is primarily formed during the electrolysis of water acidulated with sulphuric acid, and hydrogen

peroxide is formed by the secondary reaction between the water and the acid. Persulphuric acid appears during the electrolysis of sulphuric acid more concentrated than $H_2SO_4.2H_2O$; and when this acid reacts with water, a certain amount of hydrogen peroxide is formed. According to M. Traube, if a plate of hydrogenized palladium be used as anode, the oxygen developed is absorbed without forming a trace of hydrogen peroxide.

(4) *The formation of hydrogen peroxide by the electric discharge.*—Although W. Nernst[7] failed to obtain hydrogen peroxide by passing a stream of electric sparks through a mixture of steam and oxygen, F. Fischer and O. Ringe found that hydrogen peroxide is formed under these conditions provided the stream of gas passes quickly enough to allow the escaping gases to be rapidly cooled. W. Nernst, however, did find that if electric sparks are passed through liquid water, hydrogen peroxide is formed, for the rate of cooling is then fast enough to prevent its complete decomposition.

When a mixture of hydrogen and oxygen is exposed to a brush electrical discharge, while the gas is passing through a U-tube cooled by liquid air, a yield of about 2·5 per cent. of hydrogen peroxide is obtained, but none is formed if the experiment be conducted at ordinary temperatures. The mixed gases must be under reduced pressure—say 3 cm. of mercury—to prevent explosion. At ordinary pressures when the mixed gases contain less than about 5 per cent. or more than 95 per cent. hydrogen, a yield of 87 per cent. has been obtained at the temperature of liquid air; and at 22°, a yield of 6·4 per cent. resulted. F. Fischer and O. Ringe obtained traces of hydrogen peroxide by subjecting steam to the brush discharge of an ozonizer at a temperature of 130°, so as to prevent the condensation of water within the instrument. Better results were obtained with a mixture of steam and oxygen or air. Hydrogen peroxide is also formed when the Tesla brush discharge,[8] or the discharge in an ozonizer, is passed through a mixture of oxygen and water vapour at pressures between 385 and 770 mm.; no hydrogen peroxide was observed with water vapour alone; and nitrogen oxides are simultaneously produced if moist air be used in place of moist oxygen. Hydrogen peroxide is also said to be formed by blowing moist air against a spark or arc discharge—this may be purely a temperature effect.

(5) *The formation of hydrogen peroxide during oxidation processes.*—Both hydrogen peroxide and ozone have been detected in the flame of burning hydrogen by O. Loew (1870) and by W. Manchot (1909). The latter considers that these substances do not take part in the processes of combustion, but are an effect of the high temperature of the flame. Hydrogen peroxide is produced during the explosion of hydrogen with an excess of oxygen,[9] and it has been recognized among the products of various types of combustion in air—*e.g.* hydrogen, carbon monoxide, cyanogen, etc.[10] Since the temperature of the hydrogen flame exceeds 2000°, it is natural to expect that this flame will contain appreciable amounts of hydrogen peroxide; and this was demonstrated by M. Traube, who allowed a jet of burning hydrogen to impinge on the surface of cold water in which ice was floating or on ice itself, and detected the hydrogen peroxide in the water. M. Traube thus obtained an aqueous solution containing 0·74 per cent. of hydrogen peroxide. This compound has also been reported in the water produced during the combustion of hydrogen in air; in the flames of alcohol, ether, coal gas, or carbon disulphide.

It might be asked why no trace of hydrogen peroxide was detected by F. Fischer and F. Brähmer (1906) in the products obtained when hydrogen, etc., is burned under liquid air (*vide supra*). It is supposed that the formation of ozone is preceded by the dissociation $O_2 \rightleftharpoons O+O$; that the speeds of formation of ozone and hydrogen peroxide are approximately equal, and therefore in the presence of a large excess of oxygen, more atoms of oxygen will be oxidized to ozone than water molecules to hydrogen peroxide; and further, that at the moment of cooling the ozone reacts with the relatively small quantity of hydrogen peroxide—$O_3+H_2O_2 \rightarrow H_2O+2O_2$. Hydrogen peroxide is formed when ozonized oxygen or air is passed through water on the surface of which a little ether floats. If a little water is placed in a beaker containing ether, and the latter is burnt by placing a spiral of hot platinum wire just over the surface of the liquid, hydrogen peroxide can be detected in the water after all the ether has burnt away. It is supposed that the ozone first produced forms a peroxide with the ether and that this is decomposed by the water forming ether and hydrogen peroxide. According to this view, the ether acts as a catalytic agent. K. V. Charitschkoff and M. Ambardanoff[11] reported the formation of hydrogen peroxide in water containing oxygen, during exposure to bright sunlight.[12]

According to A. Richardson, hydrogen peroxide is produced by exposing urine to direct sunlight, and also by exposing ether, amyl alcohol, and certain organic acids—*e.g.* oxalic acid—to sunlight. W. R. Dunstan and T. S. Dymond, however, were unable to detect hydrogen peroxide in pure ether—dry or moistened with water—after exposure to sunlight. Some specimens of less pure ether—*e.g.* methylated ether—did develop hydrogen peroxide in light. Hydrogen peroxide is also formed when turpentine or other oils containing terpenes are oxidized by air or ozone in the presence of water. C. T. Kingzett (1878) claims to have made a solution of hydrogen peroxide of 2-vol. strength in this way. Moist bone-black, when exposed to air and light, rapidly forms appreciable quantities of hydrogen peroxide.

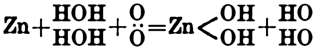
Hydrogen peroxide is often formed when metals, and particularly their amalgams, are slowly oxidized in the presence of water—*e.g.* by shaking zinc amalgam with water—a better yield is said to be obtained if an alkaline earth be present. Hydrogen peroxide, says M. Traube (1893),[13] is formed only when the oxidation is effected by ordinary oxygen; oxidizing agents, other than ozone, do not give rise to this compound—*e.g.* hydrogen peroxide is obtained when finely divided zinc, magnesium, aluminium are shaken with water, but not if all traces of free oxygen are excluded. In 1859 E. von Gorup-Besanez[14] reported that an oxidizing substance, probably hydrogen peroxide, is formed during the evaporation of water, but N. Smith could detect this compound only when the evaporation took place in the presence of the metal zinc. When zinc, copper, or lead is shaken up with air and dilute sulphuric acid (1 : 55), the reactions symbolized: $Zn+2H_2O+O_2=Zn(OH)_2+H_2O_2$; and $Zn(OH)_2+H_2SO_4=ZnSO_4+2H_2O$ occur. It will be observed that twice as much oxygen is required for the oxidation process as is actually consumed in oxidizing the zinc: $Zn+O_2=ZnO+O$; $H_2O+O=H_2O_2$. One half of the oxygen is said to be used in the primary process and the other half in the secondary reaction. The reaction is a concurrent or side reaction, but since half a molecule of oxygen is used in each, the two concurrent reactions are not independent of one another. This particular type of reaction is known as **auto-oxidation.** There is a considerable difference of opinion as to the mechanism of auto-oxidation. The oxygen used in the secondary reaction—formation of hydrogen peroxide—is said to be " rendered active " by the primary reaction. The formation of ozone during the oxidation of phosphorus is another example. W. R. Dunstan, H. A. D. Jowett, and E. Goulding[15] consider that hydrogen peroxide is an intermediate stage in the rusting of iron.

In certain cases, if a substance undergoing slow oxidation at ordinary temperature be mixed with another substance which is not oxidized when alone, both substances are simultaneously oxidized. This phenomenon was noticed by C. F. Schönbein[16] in 1858. For example, (1) Ozone is formed during the oxidation of phosphorus; (ii) hydrogen peroxide is formed during the oxidation of zinc, lead, etc.; (iii) indigo blue is simultaneously oxidized to colourless isatin when benzaldehyde or turpentine is oxidized; sodium arsenite is likewise oxidized in the presence of oxidizing sodium sulphite, etc.

That part of the oxygen which unites with the substance undergoing oxidation is sometimes called **bound oxygen,** while the oxygen which is consumed in the formation of ozone, hydrogen peroxide, is called **active oxygen,** and the oxygen is said to be *activated* or *rendered active* during the process of oxidation. C. Engler calls the substance undergoing oxidation the *autoxidizer*, and the substance which unites simultaneously with the active oxygen, the *acceptor*.

C. F. Schönbein still further demonstrated that just so much oxygen is rendered active as is consumed by the oxidizing substance; or, in all slow oxidations the same amount of oxygen is required for the oxidation of the substance as is consumed in the formation of hydrogen peroxide from water, ozone from oxygen, etc. The hydrogen peroxide is generally decomposed into water and oxygen, so that an exact proof of the above deduction can be obtained only under favourable conditions.

C. F. Schönbein obtained a confirmation of the hypothesis by the slow oxidation of lead amalgam in the presence of dilute sulphuric acid. Almost the same amount of oxygen was rendered active in the form of hydrogen peroxide, as is used in the formation of lead sulphate. Similar results were obtained by M. Traube in the oxidation of zinc in the presence of water, whereby zinc hydroxide and hydrogen peroxide are formed in equi-molecular proportions. The reaction was symbolized:



$$Zn+\begin{matrix}HOH\\HOH\end{matrix}+\begin{matrix}O\\\ddot{O}\end{matrix}=Zn<\begin{matrix}OH\\OH\end{matrix}+\begin{matrix}HO\\HO\end{matrix}$$

C. F. Schönbein's observation has also been verified by J. H. van't Hoff, W. P. Jorissen, and by C. Engler and his co-workers.[17]

(6) *The formation of hydrogen peroxide in chemical reactions.*—If a peroxide, MO_2, be treated with such an acid that the base radicle is precipitated as a salt of the acid, hydrogen peroxide will remain in solution. For example, if concentrated sulphuric acid be allowed to react with barium peroxide, ozonized oxygen is evolved; if the acid is of moderate concentration, ordinary oxygen gas is evolved: $2BaO_2+2H_2SO_4=2BaSO_4+2H_2O+O_2$; while if dilute acid be used, hydrogen peroxide is formed: $BaO_2+H_2SO_4=BaSO_4+H_2O_2$. Barium peroxide is the usual starting point for the preparation of hydrogen peroxide; for example, in one process:

> Gradually add barium peroxide to ice-cold water through which a stream of carbon dioxide is passing. The insoluble barium carbonate is precipitated, and a dilute aqueous solution of hydrogen peroxide remains: $BaO_2+CO_2+H_2O=BaCO_3+H_2O_2$. If an excess of carbon dioxide be used, the yield of hydrogen peroxide is low and an insoluble barium percarbonate, $BaCO_4$, is precipitated.[18]

In the modifications of this process, the barium peroxide is mixed with a little ice-cold water and gradually added to ice-cold dilute hydrochloric,[19] sulphuric,[20] hydrofluosilicic acid,[21] hydrofluoric,[22] or phosphoric acid.[23] A barium salt—chloride, sulphate, fluosilicate, or phosphate—and hydrogen peroxide are formed. In the first case, the barium chloride is soluble. It can be removed by adding just sufficient silver sulphate to precipitate insoluble barium sulphate and silver chloride: $BaCl_2+Ag_2SO_4=BaSO_4+2AgCl$. This method is mainly of historical interest, because L. J. Thénard employed a similar process when he discovered hydrogen peroxide in 1818. The process with sulphuric acid, as employed by R. Wolffenstein, is as follows:

> Gradually add barium peroxide, suspended in a little water, to a mixture of equal volumes of water and sulphuric acid (cooled by a freezing mixture of ice and salt) until the solution is just barely acid. If too much barium peroxide has been added, a little more sulphuric acid is needed. Keep the solution in a freezing mixture for about a day. Filter off the insoluble matter, and evaporate the liquid on a water-bath, at about 70°, in a smooth platinum or porcelain basin until signs of effervescence appear. This will occur when the solution contains about 45 per cent. of hydrogen peroxide. Cool the solution quickly. Concentrated solutions soon decompose if they are not kept cold.

By treating a cold aqueous solution of sodium peroxide with dilute and cold hydrochloric acid, a solution of hydrogen peroxide in sodium chloride is obtained: $Na_2O_2+2HCl=2NaCl+H_2O_2$—hydrofluoric acid has been recommended in place of hydrochloric acid; and by treating potassium peroxide with tartaric acid in the cold, an aqueous solution of hydrogen peroxide contaminated with a little potassium tartrate is obtained. Most of the potassium tartrate separates from the cold solution. Hydrofluosilicic acid and potassium peroxide has been recommended.[24]

A. von Baeyer and V. Villiger, G. Adolph and A. Pietzsch, and L. Löwenstein found that if persulphates [25] be treated with dilute acids hydrogen peroxide is obtained; R. Wolffenstein and E. Merck used percarbonates; and F. Jaubert found that if a mixture of a perborate with an equivalent amount of a dry solid organic or inorganic acid, or an acid salt be moistened with water, hydrogen peroxide is formed. Hydrogen peroxide is prepared commercially from potassium persulphate or persulphuric acid.

The concentration of solutions of hydrogen peroxide.—The concentration of solutions of hydrogen peroxide has been effected in many ways. A 3 per cent. solution of hydrogen peroxide, which is free from alkaline compounds, from traces of salts of the heavy metals, and from suspended solids, can be concentrated on the water-bath at 75° to a 50·7 per cent. solution with a loss of about 36 per cent., and to a 66·6 per cent. solution with a loss of about 72 per cent. Further concentration by evaporation is impracticable because of the decomposition. The solution can also be further concentrated by evaporation over concentrated sulphuric acid **in vacuo,** or rather under reduced pressure until one volume of the liquid gives 475 volumes of oxygen gas.

By agitating the liquid with 10 to 12 times its volume of ether, decanting off the ethereal liquid, and removing the ether by evaporation on a water-bath, a 73·8 per cent. solution can be obtained from a 48 per cent. aqueous solution.[26] A. Houzeau concentrated dilute solutions by freezing out the water; and by this means M. Hanriot obtained a residual liquid such that one volume of liquid gave 70 volumes of oxygen.

The fractional distillation of hydrogen peroxide.—A solution of hydrogen peroxide decomposes rapidly when heated to 100°—even if the solution be dilute—hence, for a long time, the concentration of an aqueous solution of hydrogen peroxide by fractional distillation was thought to be impracticable. M. Hanriot (1885) concentrated the liquid by distillation under reduced pressure, and obtained a liquid of such a concentration that one volume furnished 267 volumes of oxygen. In 1894, R. Wolffenstein discovered that anhydrous hydrogen peroxide can be readily distilled under reduced pressure without undue decomposition; and it also can be distilled at temperatures below 85° in a very rapid stream of an inert gas. W. Spring observed a violent explosion in concentrating hydrogen peroxide by vacuum distillation.

The aqueous solution, containing about 45 per cent. of hydrogen peroxide, can be distilled under reduced pressure in the following manner. Fit up the apparatus indicated in Fig. 13. Transfer the solution to a round-bottomed, thick-walled litre flask *A*, fitted with a receiver *B*, and a thermometer *T* passing through a one-hole rubber stopper. The receiver *B* is placed over a funnel so that cold water can be sprayed on the receiver, and run off to the sink through rubber tubing attached to the stem of the funnel. The side neck of the receiver is connected, by pressure tubing, with a manometer; which in turn is connected with a 3-way stop-cock *E*, a water trap *G*, and a filter pump *D*. The flask *A* is heated by an oil bath *F*, and Bunsen's burner. When the manometer shows a pressure of about 15 mm. and the thermometer a temperature between 35° and 40°, a dilute aqueous solution of hydrogen peroxide in water distils into the receiver. The temperature rises gradually to about 70°, when a very concentrated solution of hydrogen peroxide remains in the distilling flask *A*. Further concentration is best effected by placing a beaker containing some of the hydrogen peroxide solution in a mixture of solid carbon dioxide and ether. The whole mass freezes. Drop a little of the frozen solid into a portion of the concentrated hydrogen peroxide solution. At between −8° to −10° small needle-shaped crystals separate. Drain away the mother liquid from the crystals; melt the crystals and cool the mass, so that another crop of crystals is obtained. Repeat the operations. The solution remaining in the distilling flask will serve for most experiments where concentrated solutions of hydrogen peroxide are required. If desired, it can be concentrated a little more by evaporation over sulphuric acid under reduced pressure.

Concentrated hydrogen peroxide begins to attack the glass distilling flask at about 80°. R. Wolffenstein, by fractional distillation, obtained a solution of 90 per cent. hydrogen peroxide at 81°–85° at 68 mm. pressure; and by repeatedly redistilling the product he got a liquid containing 99 per cent. of hydrogen peroxide and boiling at 84°–85° C. at 68 mm. pressure.

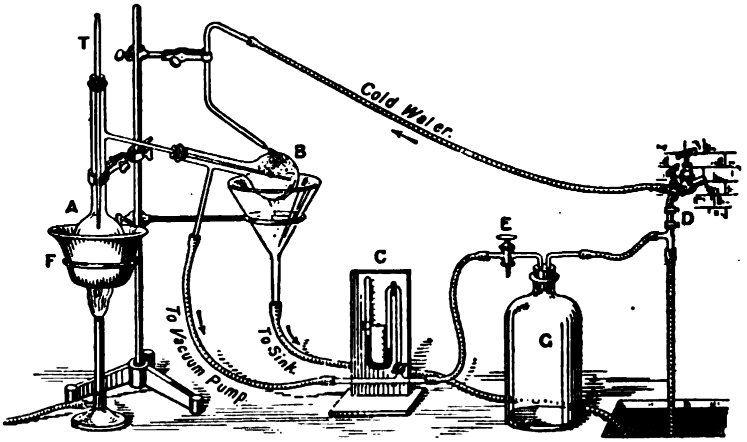


FIG. 13.—Distillation of Hydrogen Peroxide under Reduced Pressure.

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§ 9. The Physical Properties of Hydrogen Peroxide

Hydrogen peroxide is a viscid transparent liquid which does not wet solids so easily as water. In thick layers, it has a blue **colour**; and a metre long column has the same tint as a 1·8 metre long column of water. There is always a greenish tinge along with the blue, and W. Spring[1] attributes this to the presence of minute bubbles of oxygen. The **specific gravity** is 1·453, according to L. J. Thénard; 1·4996, according to W. Spring; and, according to J. W. Brühl,[2] 1·4584 at 0°, 1·4375 at 2°, and 1·4378 at 20°, referred to water at 4°. J. W. Brühl says that the specific gravity is *das scharfste Kriterium* of the purity and dryness since the smallest amount of water reduces the specific gravity in a marked degree, thus, the presence of 0·52 per cent. of water lowers the value of this constant to 1·4094 (0°); and a 45·9 per cent. solution, according to H. T. Calvert, has a specific gravity 1·144. I. Traube has investigated the molecular volume of hydrogen peroxide. The liquid has no smell; the vapour has a smell recalling that of nitric acid. Dilute solutions have a bitter metallic taste. When a drop of the liquid peroxide comes in contact with the skin, it forms a white blister. According to W. Spring, the **surface tension** of the liquid of specific gravity 1·4996 is 3·5374 (10°), when water at the same temperature has the value 7·750.

According to J. L. Thénard, the liquid does not freeze at 30°, but it freezes in a mixture of ether and solid carbon dioxide, and if a trace of the solid is put into the liquid cooled to —8° to —10°, transparent needle-like prisms are formed; the recrystallized peroxide has the **melting point** —2°; hydrogen peroxide evaporates slowly at ordinary temperatures and pressures, and he has studied the volatility of aqueous solutions of hydrogen peroxide at different temperatures. The **boiling point** of the anhydrous liquid at different pressures is

	21	29	33	38	44	47	68 mm.
Boiling point . .	62·8°	69·7°	73·7°	76·7°	79·7°	80·2°	84·85°

H. C. Jones, J. Barnes, and E. P. Hyde[3] have measured the lowering of the freezing points of solutions of various acids and salts in hydrogen peroxide and found this solvent to have a greater ionizing power than water, *vide infra*. The **specific heat** of hydrogen peroxide calculated[4] by W. Spring from the specific heat of the 34·25 per cent. solution is 0·6208—this number is to be regarded as an upper limit since other numbers are obtained with more dilute solutions.

M. Berthelot, J. Thomsen, and R. de Forcrand[5] have published thermochemical data for this compound, from which it follows that the **heat of formation** $H_2O_{liq.}+O_{gas}=H_2O_{2liq.}-22{\cdot}16$ Cals.; and $H_{2gas}+O_{2gas}=H_2O_{2liq.}+46{\cdot}84$ Cals. R. de Forcrand found that freshly distilled solutions of hydrogen peroxide with the composition and formula indicated below have the heats of solution:

Per cent. H_2O_2	35·31	42·66	55·16	65·38	85·93
$H_2O_2+nH_2O$, when $n=$.	3·46	2·53	1·54	1·00	0·3
Heats of solution . . .	0·071	0·093	0·099	0·310	0·403 Cal.

By extrapolation the **heat of solution** of the anhydrous peroxide: $H_2O_{2liq.}+Aq.=H_2O_{2solution}+0{\cdot}46$ Cal. The solution is distinctly acid; the **heat of neutralization** is 2·70 Cals.

The oxidation potential of the oxygen electrode is diminished by the addition of hydrogen peroxide. Attempts to measure the electrode potential by W. Nernst, F. Haber and S. Grinberg give material for calculating a value for the free energy of hydrogen peroxide, but, as with ozone, G. N. Lewis and M. Randall believe that there is no satisfactory evidence that the electromotive force is due to a single definite reversible reaction, and they calculated a value for the free energy from the dissociation pressure of barium dioxide and the equilibrium between hydrated barium dioxide and water. The **free energy** of the reaction $H_{2aq.}+O_{2aq.}=H_2O_{2aq.}$ at 298° K. is —30,970 cals. for the formation of the HO_2' ion on the assumption that hydrogen peroxide in solution is an acid which ionizes $H_2O_2=H^{\cdot}+HO_2'$; G. N. Lewis and M. Randall give $\frac{1}{2}H_2+O_2=HO_2'$; for the free energy of the reaction $H_2O_{2aq.}=H_2O_{liq.}+\frac{1}{2}O_2$, which measures the tendency of aqueous hydrogen peroxide to decompose, they give at 298° K. —25,650 cals. W. Nernst from e.m.f. measurements obtained —17,100 cals., a difference of 8500 cals. For the **heat of vaporization** $H_2O_{2liq.}=H_2O_{2gas}$, calculated from J. W. Brühl's and R. Wolffenstein's measurements of the vapour pressure of pure hydrogen peroxide, G. N. Lewis and M. Randall find 12,300 cals. per gram-molecule, or the free energy at 298° K. is 3500 cals. The same calculation makes the vapour pressure of hydrogen peroxide at 25° to be 2·1 mm.; the boiling point, 144°; and Trouton's constant, 29·5. This high value shows that hydrogen peroxide is a very abnormal liquid. If F. M. Raoult's laws of ideal solutions were followed by aqueous hydrogen peroxide, the vapour pressure of hydrogen peroxide would be $2{\cdot}1/56{\cdot}5=0{\cdot}037$ mm., but W. Nernst's distillation experiments give about one-fourth or one-fifth the value corresponding with F. M. Raoult's law. If this value be approximately 0·01 mm., the free energy of the reaction $H_2O_{2aq.}=H_2O_{2gas}$ at 298° K. is $RT\log(760/0{\cdot}01)=6700$ cals.; for $H_2+O_2=H_2O_{2liq.}$ at 298° K., —27,770 cals.; and for $H_2+O_2=H_2O_{2gas}$, at 298° K., —24,270 cals. From the heat of vaporization, and J. Thomsen's and R. de Forcrand's thermochemical data, the heat of the reaction at 291° K. is —32,600 cals.

G. N. Lewis and M. Randall assume that the thermal capacity of hydrogen peroxide may, as a first approximation, be taken as being the same as that of the tetratomic gas NH_3, and accordingly $C_p=7{\cdot}5+0{\cdot}0042T$; this in conjunction with $C_p=6{\cdot}5+0{\cdot}0009T$ for hydrogen, and $C_p=6{\cdot}5+0{\cdot}0010T$ for oxygen, gives the free energy of hydrogen peroxide, $H_2+O_2=H_2O_{2gas}$ as $-31{,}100+5{\cdot}5T\log T-0{\cdot}00115T^2-8{\cdot}08T$, when the integration constant is evaluated from the free energy at 291° K. From this equation it would appear to be impossible to obtain spontaneously appreciable amounts of hydrogen peroxide from the two elemental constituents at a temperature below 1000°. The free energy of the reaction $H_2O_{gas}+\frac{1}{2}O_2=H_2O_{2gas}$ was also found to be $26{,}310+4{\cdot}56T\log T-0{\cdot}0028T^2+0{\cdot}00000027T^3-11{\cdot}80T$. From this equation, the pressure of hydrogen peroxide in equilibrium with water vapour at atmospheric pressure is 10^{-7} atm. at 2000° K., and 3×10^{-6} atm. at 3000° K. The experiment of M. Traube in which a considerable yield of H_2O_2 is obtained by the rapid cooling of an oxyhydrogen flame cannot, therefore, be explained by assuming that H_2O_2 is largely present in the gases in the hottest portion of the oxyhydrogen flame. It must be explained rather by assuming that in the colder parts of the flame, probably between 500° and 1000° C., hydrogen and oxygen combine directly to form hydrogen peroxide.

Thermochemistry of hydrogen peroxide.—While the formation of a gram-molecule of liquid water from hydrogen and oxygen is attended by the *evolution* of 68·4 Cals., the oxidation of water to hydrogen peroxide in aqueous solution would be attended by an *absorption* of 23·1 Cals., and consequently, it is not to be expected that this compound will be formed during the combustion of hydrogen in oxygen—except possibly by arresting the reaction under special conditions on the assumption that hydrogen and oxygen first formed hydrogen peroxide as a transient intermediate product, before forming water. To prepare hydrogen peroxide an indirect process is employed. Oxygen unites with barium oxide with the evolution of 5·9 Cals. per molecule of barium peroxide, BaO_2, and this compound in turn is decomposed by hydrochloric acid with the evolution of 11·0 Cals. Again, in the remarkable reaction whereby hydrogen peroxide reacts with silver oxide forming water, silver, and oxygen, $H_2O_2+Ag_2O \rightarrow 2Ag+H_2O+O_2$, one school of chemists says that the attraction of oxygen atoms for one another in the two different compounds upsets the unstable silver oxide and hydrogen peroxide; but since the heat of formation of silver oxide is 3·5 Cals., and of hydrogen peroxide, 11·2 Cals., the reaction will evolve 7·7 Cals., an amount sufficient to account for the reaction apart from any alleged molecular attraction. Still further, the powerful oxidizing effects produced by hydrogen peroxide have been attributed to the effects of nascent oxygen in the atomic condition. There is no particular need for this assumption because, when hydrogen peroxide decomposes into water and oxygen: $2H_2O_2=2H_2O+O_2$ $+44·8$ Cals., the heat evolved by the reaction, if confined to the products of the reaction, would suffice to raise the temperature nearly 1000°, and this amply suffices to explain the marked oxidizing properties of hydrogen peroxide over those of oxygen. The superior oxidizing properties of ozone can be explained in a similar manner.

The **index of refraction**[6] (20·4°) is 1·40379 for the Li-line; 1·40421 for the H_α-line; 1·40624 for the Na-line; 1·41100 for the H_β-line; and 1·41494 for the H_γ-line. According to J. W. Brühl, the specific refraction by Lorentz and Lorenz's formula is 0·1708 for the H_α-line and 0·1742 for the H_γ-line; the specific dispersion is therefore 0·0039. According to P. Drude and H. T. Calvert, the **dielectric constant** of the anhydrous peroxide is 92·8 when the value for water is 81. This high value for the dielectric constant indicates that hydrogen peroxide is a very abnormal liquid. J. Dewar and J. A. Fleming investigated the effect of temperature on the dielectric constant. H. T. Calvert observed that hydrogen peroxide did not present the so-called anomalous electrical absorption.

L. J. Thénard found that when hydrogen peroxide is electrolyzed, it decomposes like water with hydrogen at the negative and oxygen at the positive pole, but the proportion of oxygen is much greater than with water. M. Berthelot, E. Schöne, M. Hanriot, and S. Tanatar found that with feeble currents and concentrated solutions, the hydrogen peroxide is reduced by the hydrogen at the cathode, and no gas is there given off, while oxygen is given off at the anode: $2H_2O_2=2H_2O+O_2$. The specific **electrical conductivity** of a 4·5 per cent. solution is $2·89\times10^8$. H. C. Jones, J. Barnes, and E. P. Hyde[7] could not determine the electrical conductivity of aqueous solutions because they could find no satisfactory material for the electrodes which would resist chemical action. H. C. Jones and his co-workers found that the *salts*, potassium chloride, sodium nitrate, potassium nitrate, etc., lower the freezing point of solutions of hydrogen peroxide less than they do water, possibly because of the formation of compounds analogous with $KF.H_2O_2$, $Na_2SO_4.9H_2O.H_2O_2$, etc., isolated by S. Tanatar; while *acids*, like sulphuric, oxalic, or acetic acid, lower the freezing point of solutions of hydrogen peroxide more than they do water, presumably because hydrogen peroxide has a stronger ionizing power than water. The action of *bases* on hydrogen peroxide, studied by G. Bredig and H. T. Calvert, is analogous with the action of an acid on a base, for peroxides are formed: $2NaOH+3H_2O_2=Na_2O_4+4H_2O$, and it therefore follows that hydrogen peroxide has acid properties; indeed, G. Carrara and A. Bringhenti believe that it is a monobasic acid which ionizes in solution $H_2O_2 \rightleftharpoons H^{\cdot}+HO_2'$.

Solubility.—Hydrogen peroxide dissolves in *water* in all proportions. According to J. W. Brühl, it is insoluble in *petroleum ether*,[8] and exerts no chemical action on that menstruum. When aqueous solutions are shaken out repeatedly with ether much of the hydrogen peroxide can be extracted. An ethereal solution of hydrogen peroxide is more stable than the aqueous solution. The strength of aqueous solutions is represented commercially by the number of volumes of oxygen which 100 c.c. of the solution will furnish on decomposition. Thus 100 c.c. of a real 10-*volume solution* should give 10 times its own volume of oxygen when decomposed; as a matter of fact, a 3 per cent. solution of hydrogen peroxide by weight is very nearly a 10-volume solution; a 5 per cent. hydrogen peroxide solution is nearly 20-volume strength, and so on. The most concentrated solution on the market is called *perhydrol*, and it contains about 30 per cent. of hydrogen peroxide corresponding with a concentration of 100 volumes. There is some ambiguity in this mode of expressing the concentration of the solutions, because if the solution be decomposed by potassium permanganate, $2KMnO_4+5H_2O_2+3H_2SO_4=5O_2+2MnSO_4+K_2SO_4+8H_2O$, half the oxygen comes from the permanganate, and in that sense, a 10-volume solution would furnish but five volumes of oxygen derived from the peroxide, and five from the permanganate. In addition to perhydrol, there is also on the market a 3 per cent. solution intended for general purposes, and a purer 3 per cent. solution for medicinal purposes. Besides, there is the so-called *solid hydrogen peroxide*—known in commerce as *hyperol*—a white crystalline product containing equimolecular parts of urea and hydrogen peroxide, which is made[9] by dissolving urea in perhydrol; it furnishes a solution of hydrogen peroxide when treated with citric or other acids.

The **coefficient of distribution** between water and *ether* at 17·5° is, according to K. Osikoff and S. Popoff,

Volume of ether : volume of water	0·5	1	2	5	7	9	10
Con. in ether · Conc. in water .	0·0575	0·0596	0·050	0·060	0·074	0·070	0·072

The presence of sodium chloride has no influence on the coefficient, but sodium and potassium carbonates lower the solubility of the peroxide in ether.[10] Hydrogen peroxide is soluble in many organic solvents.[11] The partition coefficient (concentration in solvent: concentration in water) for *ethyl acetate* is 1:215; *nitrobenzene*, 1:200; *acetophenone*, 7:4; *amyl acetate*, 1:8; *ethyl isovalerianate*, 1:40; *isoamyl propionate*, 1:12; *chloroform*, 1:600; *benzene*, 1:200; *isobutyl alcohol*, 1:3; *propyl formate*, 1:8; *isobutyl butyrate*, 1:50; *propyl butyrate*, 1:30; *phenol* (25°), 1:45; *aniline* (25°), 1:4; and *quinoline* (25°), 1:0·276. Quinoline is thus a very good solvent for hydrogen peroxide, and when equal volumes of quinoline and an aqueous solution are agitated together, the quinoline layer contains more than half the peroxide.

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§ 10. Quantitative Application of the Law of Mass Action

> Chemical phenomena must be treated as if they were problems in mechanics.—L. MEYER (1868).

I. Kant[1] has said that in every department of physical science there is only so much science as there is mathematics; and as our knowledge of natural phenomena grows more clear and precise, so does it become more and more possible to employ mathematical methods. Owing to the absence of all mathematical treatment in chemical phenomena in his time, I. Kant denied to chemistry the name of science.

The most simple type of chemical reaction is one in which individual molecules are involved in the change; more complex reactions are concerned with the mutual action of two or more molecules. For example, in the decomposition of nickel carbonyl, $Ni(CO)_4 \rightarrow Ni + 4CO$, the individual molecules of nickel carbonyl are independently concerned in the change—this type of reaction is called a *unimolecular reaction*; with a reaction of the type, $H_2O + COCl_2 \rightarrow 2HCl + CO_2$, the mutual action of two molecules is necessary for the reaction, and this is accordingly called a *bimolecular reaction*; and in the formation of ozone, $3O_2 \rightarrow 2O_3$, the mutual action of three molecules of oxygen is necessary and this is accordingly called a *termolecular reaction*. The back reaction, in the preceding bimolecular reaction, is $CO_2 + 2HCl \rightarrow COCl_2 + H_2O$, which is a termolecular reaction. The terms uni-, bi-, ter-, and multi-molecular, or what is equivalent, mono-, di-, tri-, poly-molecular reaction, were introduced by J. H. van't Hoff[2] to indicate the number of molecules concerned in a reaction. Reactions involving more than two molecules are not very common. This is easily understood if we assume that bimolecular reactions are caused by the collision of two molecules, termolecular reactions by the simultaneous collision of three molecules, etc. The probability of a simultaneous collision between three molecules is very much less than between two molecules, and the greater the number of molecules taking part in a given transformation, the more likely is the reaction to proceed by some other path than by the simultaneous collision of a large number of reacting molecules.

The decomposition of hydrogen peroxide in light.—A solution of hydrogen peroxide decomposes when it is exposed in a quartz vessel to the rays of light from a mercury lamp. The decomposition ceases when the light is extinguished. If the amounts of hydrogen peroxide in the solution exposed for various periods of time be determined, the rate of decomposition can be calculated. It is found that if a represents the initial concentration of the solution expressed in gram-molecules per litre, and x the amount decomposed at the time t, the solution will then contain $a-x$ gram-molecules of the compound in question. Let L. Wilhelmy's hypothesis, *op. cit.*, be now tested. The velocity of the reaction at any time t must be equal to $k(a-x)$. If the symbol dx be employed to denote the amount of peroxide decomposed in the minute interval of time dt, the velocity of the reaction, the amount of substance decomposed in unit time, at the moment t, will be represented by

$$\frac{dx}{dt}=k(a-x)\,;\quad \therefore\ \frac{1}{t}\log\frac{a}{a-x}=k \quad . \quad . \quad . \quad (1)$$

The passage from the equation on the left to that on the right involves a very simple mathematical operation. The expression $a\div t(a-x)$ measured at different intervals of time must be a constant, k, if the reaction progresses so that only *one molecule* of hydrogen peroxide is concerned in the process $H_2O_2 \rightarrow H_2O+O$. Selecting a few measurements by J. H. Mathews and H. A. Curtis (1914),[3] we get

Time (t)	0	100	160	220	310	432
H_2O_2 per cent. (x) . . .	1·58	1·06	0·83	0·63	0·44	0·26
k	0·0040	0·0041	0·0042	0·0041	—	0·0042

The values of k are computed by the substitution of $a=1{\cdot}58$, and the corresponding values of x and t in the second of the above equations. The constancy of the different values of k is quite consistent with the hypothesis. However, suppose that the decomposition were to be represented by the usual equation, $2H_2O_2 \rightarrow 2H_2O+O_2$, implying that *two molecules* of hydrogen peroxide mutually react producing water and oxygen molecules. Then the velocity of the reaction must be represented by

$$\frac{dx}{dt}=k_1(a-x)(a-x)\,;\quad \therefore\ \frac{1}{t}\cdot\frac{x}{a(a-x)}=k_1 \quad . \quad . \quad . \quad (2)$$

With the same data as before, the values of k_1 are no longer even approximately constant. Hence, it is inferred that the decomposition of hydrogen peroxide in light is a unimolecular reaction, $H_2O_2 \rightarrow H_2O+O$, and not really a bimolecular reaction, $2H_2O_2 \rightarrow 2H_2O+O_2$, even though the last-named equation is conventionally used to represent the process in order that attention may be focussed on the initial and end products of the reaction. The unimolecular reaction is slow enough to be readily measured. The atoms of oxygen from two different molecules of hydrogen peroxide unite to form molecular oxygen, $O+O=O_2$, far too quickly to influence the measurement of the unimolecular change. This may be illustrated[4] by the following analogy :

> The time occupied in the transmission of a telegraphic message depends both on the rate of transmission along the conducting wire, and on the rate of progress of the messenger who delivers the telegram ; but it is obviously this last slower rate that is of really practical importance in determining the time of transmission.

Hence the following rule : *If a chemical reaction takes place in two stages, one of which is considerably faster than the other, the observed order of the whole reaction will be determined by the order of slower change.*

The decomposition of hydrogen peroxide in contact with platinum.—It has been found by G. Bredig and M. von Berneck (1900)[5] that while the catalytic decomposition of dilute solutions of hydrogen peroxide—say below $\frac{1}{50}$th gram-molecule per litre—by colloidal platinum is undoubtedly unimolecular, $H_2O_2 \rightarrow H_2O+O$, more concentrated solutions—say above the ½ gram-molecule per litre—decompose bimolecularly, $2H_2O_2 \rightarrow 2H_2O+O_2$; and that with intermediate concentrations, both types of reaction prevail. For instance, with a concentration of 0·0034 gram-molecule of hydrogen peroxide per litre, G. Dyer and A. B. Dale (1913)[6] find the following values of the constant k :

Unimolecular reaction . .	0·014	0·016	0·015	0·013	0·015	0·015
Bimolecular reaction . .	0·0036	0·0047	0·0048	0·0052	0·0073	0·0090

The constancy of the values of k in the first case is satisfactory, but not in the second case. Hence it is inferred that the decomposition of hydrogen peroxide by colloidal platinum is a uni- not a bi-molecular reaction. Again, with a concentration of 0·145 gram-molecules of hydrogen peroxide per litre, the values of the constant k are :

Unimolecular reaction . .	0·0075	0·0068	0·0062	0·0057	0·0051	0·0054
Bimolecular reaction . .	0·0015	0·0015	0·0015	0·0015	0·0014	0·0016

Here the fluctuations in the value of the so-called constant show that the decomposition of the hydrogen peroxide is undoubtedly a bi- and not a uni-molecular process. The decomposition of hydrogen peroxide by heat similarly follows the bimolecular law. To summarize, the decomposition of hydrogen peroxide in light, and when stimulated by colloidal platinum in dilute solutions, is a unimolecular process ; and when decomposed by heat, or by colloidal platinum in concentrated solutions, it is a bimolecular process. It has also been found that the velocity of the photochemical decomposition of hydrogen peroxide is proportional to the radiant energy absorbed. The energy absorbed during the decomposition of a gram-molecule of hydrogen peroxide is nearly equal to that given out by the decomposition of the substance in darkness.

The decomposition of steam by red-hot iron.—Let the method just developed be applied to the reaction of steam on red-hot iron previously described ; and let C_0, C_1, C_2, C_3 respectively denote the concentrations of the iron, steam, hydrogen, and iron oxide at any time t.

$$\underset{C_0}{3\mathrm{Fe}}+\underset{C_1}{4\mathrm{H_2O}}=\underset{C_2}{4\mathrm{H_2}}+\underset{C_3}{\mathrm{Fe_3O_4}}$$

From Guldberg and Waage's law, the velocity of the decomposition of steam will be proportional to the product of the concentrations of each of the reacting molecules. There are presumably three molecules of iron and four of steam. Hence, the velocity of the decomposition of steam$=kC_0{}^3C_1{}^4$; and, similarly, the velocity of the oxidation of hydrogen$=k'C_2{}^4C_3$. The condition of equilibrium when these two velocities are equal must therefore be $kC_0{}^3C_1{}^4=k'C_2{}^4C_3$. The condition of equilibrium, however, is independent of the concentrations of the two solids ; and hence, $kC_0{}^3$ must be a constant number, say k_1 ; and likewise, $k'C_3$ must be another constant number, say k_2. The condition of equilibrium can accordingly be written $k_1C_1{}^4=k_2C_2{}^4$. The concentrations of the two gases, hydrogen and steam, must be proportional to their partial pressures p_1 and p_2 respectively. Accordingly, the preceding equation can be written :

$$\frac{p_1}{p_2}=\text{Constant}$$

since the fourth root of a constant is itself constant. In an experiment by G. Preuner (1904),[7] at 200°, when the partial pressure of steam p_1 was 4·6 mm. of mercury, that of hydrogen was 95·9. Hence, the value of the constant is nearly 0·048. In another experiment at the same temperature, the partial pressure of hydrogen p_1 was 195·3, then that of steam p_2 must have been $0·048\times195·3=9·3$—the observed value was 9·7. The value of the constant at 440° was 0·176 ; at 900°, 0·69 ; at 1025°, 0·78 ; and at 1150°, 0·86, showing that the ratio of steam : hydrogen approaches unity with a rise of temperature.

Examples.—(1) If p_1 denotes the partial pressure of steam, p_2 that of hydrogen, and p_3 that of oxygen, show that if k is a constant, then, for the reaction $2H_2O\rightleftharpoons2H_2+O_2$, $p_2{}^2p_3=kp_1{}^2$.

(2) When barium peroxide is heated, it decomposes : $2BaO_2\rightleftharpoons2BaO+O_2$. Show that for any given temperature, $p=$constant, where p denotes the partial pressure of oxygen.

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§ 11. The Chemical Properties of Hydrogen Peroxide

Solutions of hydrogen peroxide are not very stable, and readily decompose into oxygen and water. Similar remarks apply to the anhydrous peroxide. If the liquids are free from other substances they are moderately stable at ordinary temperatures. J. W. Brühl[1] found that after anhydrous peroxide had been kept 50 days protected from atmospheric dust, it had lost only one-half per cent. of peroxide by decomposition. According to R. Wolffenstein, aqueous solutions keep very well if they are free from alkaline substances, salts of the heavy metals, and from particles of alumina and silica. R. Böttger, M. Berthelot, and P. Sabatier found that the presence of acids increases the stability of aqueous solutions. A 3 per cent. solution suffered no appreciable change after it had been kept for a year. The fact was well known to L. J. Thénard, who considered that the acid combines chemically with hydrogen peroxide. He said:

> With phosphoric, sulphuric, hydrochloric, hydrofluoric, nitric, oxalic, citric, and acetic acids hydrogen peroxide forms compounds in which it is less easily decomposable than when alone. In these compounds, the acid was at first regarded as existing in a higher state of oxidation. The comparatively weak carbonic and boracic acids do not give stability to peroxide of hydrogen. . . . The evolution of oxygen gas from these mixtures takes place less easily and more slowly than from the pure peroxide of hydrogen; but when the acid is neutralized by an alkali, the former facility of decomposition is restored. The greater the quantity of acid mixed with the peroxide, the more does the affinity of the acid for that compound interfere with its decomposition by elevation of temperature, or by contact with most of the bodies mentioned below. If any of the acids just enumerated be added to hydrogen peroxide which has begun to evolve gas, the escape of gas ceases; it recommences at a higher temperature, but the whole of the oxygen is not driven off, even by half an hour's boiling. It is remarkable that although gold decomposes the pure peroxide much more rapidly than bismuth does, yet the quantity of acid required to stop the action of the gold is smaller than that which must be added to prevent the action of the bismuth. Hydrogen peroxide brought into a state of effervescence by gold, palladium, or rhodium, is restored to tranquillity by the addition of a single drop of dilute sulphuric acid.

L. J. Thénard also knew that alkaline solutions do not keep very well. G. Lemoine attributes the retarding effects of acids to their affinity for water which counteracts the catalytic action of the water; he attributes the accelerating effects of the caustic alkalies to the cyclic formation and decomposition of alkali peroxides. Hydrogen peroxide solutions corrode glass vessels faster than water, and the liquid becomes alkaline. Hydrogen peroxide is for preference kept in paraffin or paraffin-lined glass bottles, or in quartz-glass vessels. The rate of decomposition of solutions of hydrogen peroxide prepared with ordinary tap-water is said by W. Clayton to be fifty times the rate with highly purified water.

A little platinum black dropped into the solution may cause an explosion; in any case, it causes rapid decomposition. Similar remarks apply to finely divided gold, silver, and similar metals, as well as to powdered manganese dioxide. The action appears to be catalytic since the manganese dioxide, etc., remains at the end of the action unchanged in composition.[2]

J. L. Thénard's classical observations on the action of various substances on *eau oxygénée* are worth quoting:

> Substances which induce the evolution of oxygen without themselves undergoing any alteration:—A violent action occurs with charcoal (forming carbon dioxide), silver, gold, platinum, palladium, rhodium, iridium, and osmium. The action is the more vigorous

the finer the state of subdivision of the metal. A moderate action occurs with mercury, lead filings, powdered bismuth, and powdered manganese. The action is slight with copper, nickel, cobalt, and cadmium. A violent reaction occurs with manganese dioxide, manganese and cobalt sesquioxides, and lead monoxide. The reaction is moderate with ferric, potassium, sodium, magnesium, and nickel hydroxides. The reaction is mild with ferric, nickel, copper, bismuth and magnesium oxides; and feeble with the magnetic oxide of iron, and with uranium, titanium, cerium, and zinc oxides, and the hydrated dioxides of calcium, strontium, and barium. The reaction is very feeble with sodium carbonate, potassium hydrogen carbonate, manganous, zinc, ferrous, and copper sulphates; with potassium, sodium, barium, calcium, antimony, ammonium, and manganous chlorides; and with manganous, copper, mercurous, and silver nitrates. The fibrin of blood acts violently.

Substances which induce the evolution of oxygen but at the same time give up their own oxygen by reduction:—The oxides of platinum, gold, silver, and mercury are reduced to the metallic state; lead dioxide and red lead are reduced to lead monoxide. The action is in all cases violent.

Substances which allow some of the oxygen of the peroxide to escape as a gas and themselves absorb the remainder of the gas to form oxides:—Examples are—selenium forms selenic acid; arsenic or arsenious oxide forms arsenic acid; molybdenum, molybdic acid; tungsten, tungstic acid; and chromium, chromic acid. The metals potassium and sodium are violently oxidized; zinc forms zinc oxide; barium hydroxide forms barium dioxide; copper oxide forms a yellow peroxide; manganic oxide forms manganese dioxide; cobalt and iron monoxides form sesquioxides. The sulphides of arsenic, molybdenum, antimony, lead, iron, and copper are vigorously oxidized to sulphates; bismuth and stannic sulphides are slowly converted into sulphates; mercury and silver sulphides are not oxidized; and barium iodide probably forms the iodate.

The following oxides take the whole of the oxygen they require from hydrogen peroxide without liberating any gas—sulphur dioxide forms the trioxide; hydrosulphuric acid gives water, sulphur, and a little sulphuric acid; hydriodic acid forms iodine and water; the peroxides are precipitated from lime, strontia, or baryta water; and stannous oxide forms stannic oxide.

No action was observed with antimony; tellurium; tin; iron; alumina; silica; tungstic acid; chromium sesquioxide; antimonious and antimonic oxides; stannic oxide; sodium phosphate; potassium, sodium, calcium, barium, or strontium sulphate; alum; turbite; potassium chlorate; potassium, sodium, barium, strontium, or lead nitrate; zinc, stannic, or mercuric chloride; white of egg—liquid or coagulated; glue; and urea.

Hydrogen peroxide is not decomposed perceptibly faster with organic substances like potassium oxalate or acetate, alcohol, camphor, olive oil, sandarac, woody fibre, starch, gum, sugar, mannite, and indigo than when it is alone, but in some cases, the gas evolved is mixed with carbon dioxide—*e.g.* with starch or sugar.

J. H. Walton and D. O. Jones[3] found that the metal salts which catalytically decompose hydrogen peroxide in aqueous solutions, act similarly if amyl alcohol, amyl acetate, isobutyl alcohol, or quinoline be substituted for water. The reaction with manganese acetate in a solution of quinoline with 2 per cent. of water is bimolecular, and unimolecular if the quinoline be saturated with water. A small trace of some of the extremely finely divided metals—colloidal platinum, colloidal gold, etc.—can accelerate the decomposition of an indefinitely large amount of the peroxide. The action, though different, has been compared with that of yeast on a solution of sugar, and these colloidal metal solutions have been styled **inorganic ferments.** According to G. Bredig, a gram-atom of *colloidal platinum* diluted to approximately 70 million litres, can distinctly accelerate the decomposition of more than a million times this amount of hydrogen peroxide. The reaction in neutral and acid solutions is unimolecular, and is irreversible and complete, $H_2O_2=H_2O+O$, not $2H_2O_2=2H_2O+O_2$; with organic ferments, the reactions are not usually complete. Under similar circumstances, in alkaline solutions, one gram-atom of colloidal manganese diluted to 10,000,000 litres; colloidal cobalt or copper to one million litres; and colloidal lead to 100,000 litres, can act in a similar way; since their action is more or less retarded or paralyzed by traces of certain other substances, so that the inorganic ferments are said to be **poisoned** by these agents.[4] The catalysis of hydrogen peroxide by colloidal platinum, and the poisoning of the catalyst has been studied by G. Bredig and his co-workers, J. H. Kastle and A. S. Loevenhart, E. H. Neilson and O. H. Brown, etc. The following act as poisons in retarding the activity of colloidal platinum: arsine, phosphine, phosphorus, carbon disulphide, mercuric chloride, sulphide, or cyanide; hydrocyanic acid; cyanogen iodide; bromine; iodine; hydrogen sulphide; sodium thiosulphate, nitrate, and sulphite; carbon monoxide; aniline; hydroxylamine; hydrochloric acid; oxalic acid; arsenious acid; phosphorous acid; nitrous acid; hydrofluoric acid; amyl nitrite; pyrogallol; nitrobenzene; and ammonium chloride and fluoride. The decomposition is accelerated by hydrazine, dilute nitric acid, and formic acid; and it is not affected by potassium chlorate, ethyl alcohol, amyl alcohol, ether, glycerol, turpentine, and chloroform. G. Phragmén studied the effect of sodium phosphate and of the hydroxide on the decomposition of hydrogen peroxide.

G. Bredig and W. Reinders investigated the influence of *colloidal gold* on the decomposition of hydrogen peroxide in alkaline solutions, and the poisoning of the catalytic agent by potassium chloride, sodium phosphate, potassium cyanide, sodium sulphide, thiosulphate, and sulphite. Mercuric chloride stimulates the activity of the catalyst probably because that salt is reduced to colloidal mercury, which itself acts catalytically. In feebly alkaline solutions, the effect of 0·0003 mgrm. of colloidal gold is perceptible per c.c. of solution. G. Bredig and his co-workers have investigated the action of *colloidal palladium* under similar conditions. The catalytic agent is activated by hydrogen. Hydrogen cyanide, hydrogen sulphide, arsine, iodine, and mercuric chloride act as poisons; while carbon monoxide acts first as a positive and then as a negative catalyst. G. A. Brossa investigated the catalytic action of *colloidal iridium;* F. Ageno, *colloidal boron;* and G. Bredig and A. Marck, *colloidal manganese dioxide.* C. Doelter investigated the effect of a number of *minerals;* G. Lemoine, the effect of *wood charcoal;* and E. B. Spaer, the effect of *pressure* on the decomposition of hydrogen peroxide.

The decomposition of hydrogen peroxide by *blood, hæmoglobin, animal* or *plant extracts*, etc., has been studied by A. Béchamp, G. Senter, etc.[5] F. L. Usher and J. H. Priestley, A. Heffter, J. Dewitz, K. Togami, and E. J. Lesser[6] have studied the catalysis of *enzymes;* A. Bach, by yeast *catalase;* H. van Laer, by *diastase;* A. Renard, by *milk;* and J. J. Ford, by *starch.* In a general way, the agents which retard the activity of colloidal platinum also retard the activity of protoplasmic catalysts, but not all those which retard the activity of the latter interfere with the activity of the former.

Charcoal or magnesium mixed with a trace of manganese dioxide ignites immediately in contact with hydrogen peroxide. With finely powdered iron or lead, hydrogen peroxide remains quiescent, but if a trace of manganese dioxide be present, the iron burns. A few drops of liquid hydrogen peroxide on a piece of cotton wool will make the cotton inflame, although the peroxide can be filtered through gun-cotton. Similar results are obtained with aqueous solutions of hydrogen peroxide, but the action is much less vigorous. Rough surfaces have a disturbing effect on the stability of hydrogen peroxide—a concentrated solution is decomposed when poured on a ground-glass surface. W. Clayton (1916) considers that the chief factor in the decomposition of aqueous solutions of hydrogen peroxide is colloidal organic matter; he doubts if the nature of the surface of the vessel is really so active as is generally supposed; and he further attributes the observed effects to variations in the amount of colloidal organic matter which is present. The presence of small quantities of some substances[7]—*e.g.* alcohol, glycerol, ether, naphthalene, sodium pyrophosphate, oxalic acid, pyrogallol, acetanilide (1 : 2000); magnesium silicate; etc.—act as preservatives and make the solutions more stable, and these agents have been called **anticatalysts** or **negative catalysts.** The use of many of these preservatives has been patented. The use of sodium or calcium chloride as a preservative is preferred to sulphuric or phosphoric acid for medicinal hydrogen peroxide.[8] Light is a factor in the decomposition of hydrogen peroxide; an eight per cent. solution was decomposed completely after ten months' exposure, while a similar solution in darkness was but little affected.[9] H. Thiele found that exposure to ultraviolet light from a mercury lamp hastened the decomposition.[10] H. A. Curtis also showed that the oxidizing power of hydrogen peroxide, as manifested in bleaching dyes, is hastened in a similar manner. The effect cannot be duplicated by substituting oxygen for hydrogen peroxide so that the result is not due to the formation of ozone. The presence of radium bromide increases the speed of decomposition of the peroxide.[11] The compound is also decomposed when heated.

The chemical reactions with hydrogen peroxide fall into five types:

(1) The hydrogen peroxide is decomposed and the second compound is *reduced*. With permanganates, for example, both substances are simultaneously reduced, and the resulting oxygen comes from both the permanganate and the peroxide.

(2) The hydrogen peroxide is decomposed, and the second compound is *oxidized* by the oxygen derived from the peroxide, as was the case with ozone. Sulphur dioxide, for instance, changes into sulphuric acid. There are numerous other similar oxidations.

(3) Certain acids form special addition products with the hydrogen peroxide, thus sulphuric acid gives persulphuric acid; molybdic acid, permolybdic acid; chromic acid, perchromic acid; etc.

(4) Certain bases may react by double decomposition whereby the hydrogen or part of the hydrogen of the peroxide is replaced by a metal. In this case, the hydrogen peroxide has the character of an acid.

(5) Hydrogen peroxide unites with many organic and inorganic salts much in the way of water of crystallization, and it is then called hydrogen peroxide of crystallization,[12] *e.g.* $NH_4CrO_5.H_2O_2$; $(NH_4)_2SO_4.H_2O_2$.

H. A. Curtis has shown that the oxidizing power of hydrogen peroxide, as manifested in the bleaching of dyes, is increased by exposing the reaction mixture to light of short wave-lengths. This effect cannot be duplicated by substituting oxygen for hydrogen peroxide in the reaction mixture, indicating that the result is not due to formation of ozone.

Concentrated solutions of hydrogen peroxide in **water** form [13] a crystalline **monohydrate,** $H_2O_2.H_2O$, and **dihydrate,** $H_2O_2.2H_2O$. For the action of ozone on hydrogen peroxide, *vide* ozone.

The halogens, **chlorine, bromine,** and iodine, act slightly on hydrogen peroxide solutions producing the haloid acids and oxygen,[14] *e.g.* E. Schöne gives with chlorine, $H_2O.O+OH_2+Cl_2=2HCl+O_2+H_2O$; or $H_2O_2+Cl_2=2HCl+O_2$. C. F. Schönbein found that bromine gives oxygen, and hydrogen bromide. **Iodine,** in the presence of alkali carbonates, is transformed into hydrogen iodide. E. Lenssen found that **hydrogen chloride** gives oxygen and the free halogen or chloric acid and water; **hydrogen bromide** or iodide gives oxygen the free halogen. The affinity of the halogen acids for hydrogen peroxide varies as the affinity of the halogen for oxygen.[15] The reaction depends on the order of mixing. If **hydriodic acid** be added to the peroxide the reaction is more energetic than if the peroxide is added to the acid; the reverse obtains with the other haloid acids. It is probable the peroxide first liberates the haloid acids from the haloid salts and then decomposes the acid. According to J. Brode,[16] ferrous or cupric sulphate and molybdenum or tungsten trioxide accelerate the decomposition of hydriodic acid catalytically. The presence of acids affects the reaction with the different catalytic agents in a different way. Copper sulphate alone is not very active, but it stimulates the catalytic effects of ferrous sulphate. Molybdenum and tungsten trioxides act more vigorously than ferrous sulphate. **Hypochlorous acid** is reduced by hydrogen peroxide, $H_2O_2+HOCl=H_2O+HCl+O_2$; chloride of lime reacts similarly, the reaction is quantitative; one molecule of oxygen is obtained for each molecule of hydrogen peroxide employed. Hence, the reaction can be employed for the quantitative determination of either hydrogen peroxide or chloride of lime.[17] Hydrogen peroxide has no action on the alkali **chlorates** or **perchlorates** or perchloric acid; the periodates and periodic acid are reduced to iodates or iodic acid respectively. The **iodates** decompose hydrogen peroxide catalytically without themselves being affected by this agent. **Bromic acid** is reduced to bromine and hydrobromic acid with the liberation of oxygen. According to S. Tanatar,[18] **potassium fluoride** forms monoclinic prisms, KF,H_2O_2. According to C. F. Schönbein, **potassium iodide** in alkaline solution forms free iodine and potassium hydroxide, $2KI+H_2O_2=2KOH+I_2$; so also, in *acid solutions*, or in the presence of ferrous sulphate. In the decomposition of iodides by hydrogen peroxide in acid solution, the liberated iodine may oxidize to iodic acid if the iodine be kept in solution by the addition of, say, hydriodic acid. The reaction takes place only in the presence of hydrochloric or hydrobromic acid. V. Auger (1911) represents the course of the reaction by the equations: $2HCl+H_2O_2=2H_2O+Cl_2$; $I_2+3Cl_2=2ICl_3$; $5ICl_3+9H_2O\rightleftharpoons3HIO_3+I_2+15HCl$. According to G. Meissner,[19] in *neutral solutions*, potassium iodide is not decomposed, but the peroxide is decomposed catalytically. E. Schöne represents the reaction by a set of quite imaginary equations: With a feebly acid solution, iodine is liberated, the liquid becomes alkaline, and oxygen is evolved. The alkaline reaction disappears in a few days and the coloration by the free iodine decreases. E. Péchard assumes that an iodate and a periodate are formed as intermediate products, but **periodates** are at once reduced to iodates by hydrogen peroxide; and iodates and perchlorates have no action on hydrogen peroxide. More probably, a hypoiodite is the intermediate product: $H_2O_2+KI=H_2O+KIO$; $KIO+H_2O_2=KI+H_2O+O_2$. The corresponding **alkali chlorides** and **alkali bromides** are very slowly attacked in a similar manner.

According to V. Auger, the **sodium periodate**, $Na_2H_3IO_6$, is very slowly decomposed by hydrogen peroxide forming sodium iodate, and liberating more oxygen than corresponds with the equation because of the catalytic decomposition of the peroxide. S. Tanatar found acid or alkaline solutions of periodic acid are reduced to iodic acid in acid or alkaline solutions, while iodic acid is stable; but V. Auger found that the results with **periodic acid** vary according to the conditions with dilute solutions, the acid is quickly and completely reduced to iodic acid, with the separation of very little iodine. In concentrated solutions the reaction is incomplete and much iodine is formed. Cold solutions of hydrogen peroxide decompose solutions with less than 0·6 per cent. of **iodic acid** and iodine is set free; if over 0·8 per cent. of iodic acid is present the solution remains colourless, owing to the fact that the reaction $I_2+5H_2O_2=2HIO_3+4H_2O$ proceeds faster than $2HIO_3+5H_2O_2=I_2+6H_2O+5O_2$. According to S. Tanatar, hydrogen peroxide has no action on acid or alkaline solutions of **perchloric acid** or **chloric acid**; and **bromic acid** is reduced to hydrogen bromide with a little bromine, and the hydrogen bromide is oxidized by the peroxide.

According to M. Kleinstück, **silver chloride** suspended in a solution of potassium hydroxide is quickly reduced by hydrogen peroxide: $2AgCl+H_2O_2+2KOH=2Ag+O_2+2KCl+2H_2O$. A. P. H. Trivelli has studied the action of hydrogen peroxide on silver subbromide. H. T. Calvert[20] found that hydrogen peroxide acts in darkness on a photographic plate as if it had been exposed to light, and it is thought that the activity of certain metals and organic compounds in darkness on photographic plates, observed by W. J. Russell, is due to the formation of hydrogen peroxide by the action of moisture on these substances. L. Graetz found that the effect produced by hydrogen peroxide is not prevented by shielding the plate with paper, ebonite, or metal foil. O. Dony-Henault investigated the hypothesis that a kind of radioactivity is induced during the decomposition of hydrogen peroxide into water and oxygen. The activity is lessened by lowering the temperature; it is not accelerated by platinum foil, although this metal accelerates the decomposition of the peroxide; additions of sulphuric acid, alcohol, or dilute alkalies decrease the effect. J. Precht and C. Otsuki do not believe that the photographic activity of hydrogen peroxide is a radiation phenomenon at all; rather it is a consequence of the direct reducing action of the vapour of hydrogen peroxide on the gelatinized silver bromide of the plate. M. Padoa found that if a substance capable of decomposing hydrogen peroxide, *e.g.* platinum black, or manganese dioxide—be inserted between the peroxide and the photographic plate, no action occurs.

Hydrogen peroxide oxidizes **selenium** with the formation of selenic acid. Colloidal **tellurium** is attacked by dilute solutions of the peroxide, while the crystalline element reacts but slowly with 60 per cent. peroxide at 100°.[21] According to T. Fairley, the oxidizing power of hydrogen peroxide is singularly dormant in the case of pure **hydrogen sulphide,** for if alkaline or other salts be absent, the two substances may remain in contact a considerable time with no more decomposition than would have occurred with a solution of hydrogen peroxide alone. Hydrogen sulphide, however, is very slowly oxidized with the deposition of sulphur and the formation of sulphuric acid; but the decomposition is very swift with **hydrogen selenide.**[22] **Sulphurous acid** is oxidized to sulphuric acid, but according to L. Marino, selenious acid is not oxidized; the **sulphides, hyposulphites,** and **tetrathionates** are also oxidized to sulphates. A. Gutbier found that **tellurium** and **tellurium dioxide,** in alkaline solutions, are oxidized [23] to telluric acid, H_2TeO_4. Concentrated **sulphuric acid** forms Caro's acid, $HO.OSO_3H$; and when the latter is treated with water, it forms hydrogen peroxide and sulphuric acid.[24] Hydrogen peroxide transforms **nitrous acid** quantitatively into nitric acid; [25] **nitric oxide,** NO, furnishes a product which blues starch and potassium iodide paper very quickly, and hence, said C. F. Schönbein, the product cannot be nitric acid; and it is thought to be a compound of the two components. **Ammonia** is quickly oxidized to the nitrite and nitrate. If hydrogen peroxide be added to a large excess of ammonia dissolved in ether, and the solution cooled to —48°, a crystalline deposit of $(NH_4)_2O_2.H_2O$ is formed; the crystals rapidly decompose at ordinary temperatures.[26] Hydroxylamine hydrochloride at 50° forms some nitric acid, and gives off a mixture of nitrogen and oxygen.[27] **Hydroxylamine sulphate,** $(NH_2OH)_2H_2SO_4$, is quantitatively oxidized by hydrogen peroxide at 40°: $(NH_2OH)_2.H_2SO_4+6H_2O_2=H_2SO_4+2HNO_3+8H_2O$; in alkaline solutions, nitrous and nitric oxides, nitrous and nitric acid are formed.[28] According to T. Weyl, hydrogen peroxide solutions—6 to 30 per cent.—at 60°, convert yellow **phosphorus** into phosphine, phosphorous and phosphoric acids. The peroxide acts more vigorously on Schenck's phosphorus. The reaction has been represented [29] by the equations: $3H_2O_2+2P=2P(OH)_3$, followed by $4P(OH)_3=PH_3+3PO(OH)_3$.

Arsenic furnishes arsenic acid without giving off oxygen. F. Raschig found that **antimony sulphide** dissolves in an ammoniacal solution of hydrogen peroxide forming ammonium antimoniate and ammonium sulphate.[30] With **bismuth nitrate** in a warm, slightly alkaline solution, K. Hasebrock reported that hydrogen peroxide gives yellowish-brown bismuthic anhydride; bismuthous hydroxide gives the same product.[31] K. Hasebrock found that the reaction is quantitative.

Some **metals** which appear to be either insoluble or but sparingly soluble in acids often dissolve in the cold dilute acid if hydrogen peroxide be present.[32] With hydrochloric acid, the action is due to the generation of free chlorine, and accordingly all the metals, except those which form insoluble chlorides, are dissolved. Thus, T. Fairley found that a mixed solution of ferric chloride and hydrogen peroxide dissolves **gold,** and adds that the dissolution is accelerated by heat, and is sometimes followed by a reprecipitation of the gold. With dilute sulphuric acid, **copper,** silver, mercury, **nickel,** and **bismuth** are soluble in the presence of hydrogen peroxide, while **tin, lead,** gold, **platinum,** and **antimony** are not attacked. A mixture of glacial acetic acid with hydrogen peroxide dissolves copper, silver, lead, mercury, and bismuth in the cold, but has no action on tin, nickel, gold, and platinum. T. Fairley says that gold dissolves readily in a mixed solution of potassium cyanide and hydrogen peroxide, but only at the surface of a solution of the potassium cyanide alone. The presence of hydrogen peroxide also hinders the precipitation of gold by ferrous sulphate or oxalic acid. C. Weltzien found **magnesium** slowly reacts with hydrogen peroxide, forming an alkaline liquid, which on evaporation gives a white mass soluble in water, and which is probably magnesium hydroxide;

likewise also with **aluminium.** H. B. Baker and L. H. Parker found the reaction with sodium amalgam is faster with a solution of hydrogen peroxide than with water. There is probably a peroxidation as indicated below. According to S. Droste, a 3 per cent. solution of hydrogen peroxide slowly dissolves aluminium; 250 c.c. dissolved 0·2 grm. of the metal in 45 days, forming white insoluble aluminium hydroxide, $Al(OH)_3.H_2O$; the soluble or colloidal hydroxide does not appear to be formed. T. Okaya has studied the rhythmic decomposition of hydrogen peroxide by **mercury** (*q.v.*).

Powdered **silver** is a powerful catalytic agent in the decomposition of hydrogen peroxide. L. J. Thénard found that in the presence of nitric acid silver oxide is partly reduced and partly dissolved. According to M. Berthelot, there is a cyclic series of reactions in which the metal is alternately peroxidized and reduced.[33] Silver, Ag_2O, is reduced to metallic silver by a reaction which B. C. Brodie symbolizes: $H_2O_2+Ag_2O \rightarrow 2Ag+H_2O+O_2$, so that half the oxygen is derived from the silver oxide and half from the hydrogen peroxide. M. Berthelot has shown that metallic silver is not exclusively formed, since some of the reduced silver is peroxidized. W. Manchot, and A. von Baeyer and V. Villiger have studied the action of hydrogen peroxide on silver. The finely divided silver, formed during the reaction between silver oxide and hydrogen peroxide, acts catalytically on the latter, so that a mixture of an excess of hydrogen peroxide on metallic silver always gives off more oxygen than is represented by the above equation, and there is no need for assuming the formation of a silver peroxide. The catalytic action of finely divided silver, gold, platinum is most vigorous in alkaline solutions, weakest in acid solutions; and intermediate in neutral solutions. T. Fairley assumes that unstable oxides are formed in alkaline solutions, and more stable salts are formed in acid solutions. Hence, most metals dissolve in dilute acids in the presence of hydrogen peroxide. According to E. Mulder, the action of hydrogen peroxide on silver oxide, dioxide, carbonate, nitrate, and peroxynitrate, is catalytic. **Gold oxide** is similarly reduced: $Au_2O_3+3H_2O_2 \rightarrow 2Au+3H_2O+3O_2$. Curiously enough, in these reactions the reducing agent is itself reduced; usually the reducing agent is oxidized during the reduction.

A series of peroxides are formed with solutions of the hydroxides or salts of the alkalies, alkaline earths, or metals. These reactions show that hydrogen peroxide behaves like a monobasic or a dibasic acid. V. Macri noted that when ammonia is added to hydrogen peroxide in the presence of calcium chloride, calcium dioxide, CaO_2, is precipitated. Hydrogen peroxide is decomposed catalytically by **carbon;** there is no appreciable oxidation; a mixture of carbon, magnesium, and manganese dioxide takes fire in hydrogen peroxide. O. Masson[34] found that **potassium cyanide** at ordinary temperatures gives potassium cyanate, potassium carbonate, and ammonium carbonate. No oxygen is given off so long as any potassium cyanide remains unoxidized. With **titanium** salts[35] hydrogen peroxide gives an orange-yellow coloration supposed to be due to the formation of pertitanic anhydride, TiO_3, by a reaction symbolized: $TiO_2+H_2O_2=H_2O+TiO_3$. In alkaline solutions, salts of the type $Na_2O.TiO_3.3H_2O$ are formed. The particular tint depends upon the amount of titanium present, and hence the reaction is used for the determination of the amount of titanium in various materials. The tint of a solution containing an unknown amount of titanium is compared with that of similar solutions containing a known quantity of titanium; and the amount in the unknown solution determined by simple rule of three. The reaction is also used as a test for hydrogen peroxide. It is said that one part of titanium in 1800 parts of water gives a deep yellow coloration, and one part in 180,000 a light yellow coloration. **Cerium** and **vanadium** salts give a brick-red coloration; **molybdenum** salts, the intense yellow of permolybdic acid—$H_2Mo_2O_8$; **uranium** salts, a bluish coloration due to the formation of peruranic acid, $UO_4(H_2O_2)_2$; in alkaline solutions yellow peruranates are formed. With **tungsten** salts, pertungstates are obtained in a similar way. J. R. Cain and J. C. Hostetter find that **vanadic acid** is reduced by hydrogen peroxide. **Zirconia** and **cerium oxide** give peroxides analogous to pertitanic oxide; and **thorium oxide** [36] gives a peroxide Th_2O_7. **Lead monoxide** is converted into the puce-coloured dioxide, PbO_2, by an alkaline solution of peroxide, and the **lead dioxide** is then decomposed forming the monoxide.[37] Lead dioxide, obtained when red lead is digested with dilute nitric acid, dissolves very slowly, but if a few drops of hydrogen peroxide be added, all the lead dioxide dissolves in a few moments. The lead dioxide is reduced to lead monoxide by the hydrogen peroxide, $PbO_2+H_2O_2=PbO+H_2O+O_2$, and the product dissolves immediately in the dilute acid. This method is generally employed to hasten the solution of red lead in dilute acid prior to analysis. **Thallium oxides** behave similarly. C. F. Schönbein found that thallium is oxidized to $TlO(OH)$; with an excess of hydrogen peroxide, the oxidation products are oxygen, water, and thallous hydroxide. The latter is not affected by hydrogen peroxide. **Mercuric oxide** is reduced to mercurous oxide in alkaline solutions. G. Bredig and A. Antropoff [38] obtained an explosive peroxidized compound, HgO_2, by the action of hydrogen peroxide on mercuric oxide; copper sulphide forms the sulphate. The precipitation of oxides by hydrogen peroxide from alkaline or ammoniacal solutions of copper, silver, mercury, and bismuth salts, with the evolution of oxygen, is the basis of several processes for the separation of a number of metals from one another by W. R. E. Hodgkinson and A. H. Coote, etc. C. F. Schönbein found **cupric hydroxide** changes from blue to green when treated with hydrogen peroxide, and forms an unstable peroxide, H_2CuO_3; [39] on the contrary, in alkaline solutions, **cupric salts** are reduced to cuprous salts.[40] **Stannous salts** are oxidized to stannic salts without loss of oxygen. In neutral or acid solutions **ferrous salts** are oxidized to ferric salts; and in alkaline solutions ferric hydroxide and alkaline ferrates are reduced to ferrous salts. Ferric salts are not affected. H. Colin and A. Sénéchal have studied the action of ferric chloride on hydrogen peroxide. Alkaline solutions of **potassium ferricyanide** were reported by E. Lenssen to be reduced to the ferrocyanide, $2K_3FeCy_6+2KOH+H_2O_2=2K_4FeCy_6+2H_2O+O_2$, and ferrocyanides to be oxidized to ferricyanides. C. Weltzien said the opposite is true. J. Quincke recommends a process based on the reduction of ferricyanide to ferrocyanide for the volumetric determination of hydrogen peroxide, or of potassium ferricyanide. In neutral or acid solutions, the reaction is reversed, and **potassium ferrocyanide** is oxidized to the ferricyanide. M. Prud'homme [41] assumes that when solutions of potassium ferricyanide and hydroxide are boiled, equilibrium is attained in the reversible reaction, $2K_3FeCy_6+2KOH=2K_4FeCy_6+H_2O_2$, because (i) potassium ferricyanide and hydroxide are formed when a solution of hydrogen peroxide is added to one of the ferrocyanide; (ii) the addition of an excess of hydrogen peroxide to a solution of potassium ferricyanide and sodium hydroxide forms the ferrocyanide with the evolution of oxygen; and (iii) indigotin is bleached more rapidly by hydrogen peroxide in the presence of alkali hydroxide than in acid solutions. E. S. Barralet, C. F. Schönbein, E. Schöne, and W. Wobbe have examined the sensitiveness of the reaction as a test for hydrogen peroxide. According to T. Bayley, in alkaline solutions, **cobaltous hydroxide** forms a black peroxide; **nickel hydroxide** is not changed, but the sesquioxide forms nickelous hydroxide, with the evolution of oxygen. G. Watson has studied the action of hydrogen peroxide on ammoniacal solutions of nickel sulphate. **Iron sulphide** forms the sulphate; **molybdenum sulphide** forms sulphuric and molybdic acids; brown **lead sulphide** forms the white sulphate; **bismuth sulphide** and **tin sulphide** are only attacked slightly; **mercury and silver sulphides** are still less attacked. Metallic **iron** is but slightly attacked,[42] **tungsten** and **molybdenum** respectively form tungsten and molybdenum trioxides. According to V. Macri, hydrogen peroxide prevents the precipitation of ammonium phosphomolybdate when solutions of ammonium molybdate and phosphoric acid are mixed. B. Kuriloff and W. Städel found that **zinc oxide** is but slightly attacked; **zinc hydroxide** is peroxidized.[43] Similarly with **magnesium hydroxide** and with **cadmium hydroxide.** The **oxides of yttrium, didymium, lanthanum, and samarium** furnish oxides approximating R_4O_9. With alkaline solutions, hydrogen peroxide transforms the **chromic oxides**[44] into chromates; with neutral or acid solutions of chromic acid, H_2CrO_4, hydrogen peroxide forms a blue solution which immediately begins to decompose with the evolution of oxygen. The solutions of both hydrogen peroxide and of chromic acid are comparatively stable in the cold; when mixed they simultaneously decompose—half the oxygen comes from the peroxide and half from the chromic acid. It is therefore inferred that an unstable compound of both is formed—possibly $3H_2O_2.2CrO_3$—which breaks up with the evolution of oxygen leaving behind chromic sesquioxide, Cr_2O_3, which immediately dissolves in the acid solution. The transient intermediate compound has been isolated by operating at a low temperature. The blue-coloured peroxide, whatever it be, is much more soluble and stable in ethereal than in aqueous solutions, so that if a solution of chromic acid and hydrogen peroxide in a test-tube be shaken with ether, a blue ethereal solution of the peroxide will float on the surface of the aqueous layer. The compound decomposes when the ether is evaporated. This reaction is used for the detection of chromates. Add hydrogen peroxide to the neutral or alkaline solutions containing a chromate, and then acidify with dilute sulphuric acid. The presence of a chromate is indicated by a blue coloration. If but small quantities of chromate be present, shake up the solution with 2 or 3 c.c. of ether. The separation of a blue ethereal layer indicates chromic acid. The necessary modification of the process for the detection of hydrogen peroxide will be obvious. It is said that this method will indicate one part of hydrogen peroxide in 80,000 parts of water. If chromic acid be added to the solution of hydrogen peroxide mixed with hydrogen sulphide, V. Macri found that the latter makes no difference to the reaction.

The action of hydrogen peroxide on manganese compounds.—Hydrogen peroxide transforms manganous hydroxide in neutral or alkaline solutions into the dioxide which catalytically decomposes the hydrogen peroxide; if the solution is acid, manganese dioxide is reduced to manganous oxide: $MnO_2+H_2O_2+2HCl=MnCl_2+O_2+2H_2O$. The reducing action of the hydrogen peroxide is only apparent. According to B. C. Brodie (1872),[45] the oxides of silver, manganese, etc., have an atom of oxygen which is readily disengaged from its combination. Similarly, hydrogen peroxide readily parts with its odd atom of oxygen. Consequently, the atom of oxygen in hydrogen peroxide is supposed to *oxidize* the odd oxygen atom in the metallic peroxide. According to C. Weltzien, a *neutral solution* of potassium permanganate is reduced to potassium hydroxide and hydrated manganese dioxide, which catalytically decomposes the peroxide. In the presence of sulphuric or nitric acid, the peroxide reduces the permanganate to a manganous salt: $5H_2O_2+2KMnO_4+3H_2SO_4=2MnSO_4+K_2SO_4+8H_2O+5O_2$, so that the solution of potassium permanganate, acidified with sulphuric acid, is rapidly reduced and decolorized by hydrogen peroxide. The reaction is quantitative and is used in the volumetric determination of hydrogen peroxide.

According to C. F. Schönbein, the presence of a millionth part of hydrogen peroxide in a solution can be detected by its decolorizing action. Consequently, if an acidified solution, containing a known amount of potassium permanganate, be run from a burette into a known volume of a solution of hydrogen peroxide until the pink colour of the permanganate is no longer discharged, it follows, from the equation, that every two molecules of $KMnO_4$ correspond with five molecules of H_2O_2; or 2×158 (the approximate molecular weight of $KMnO_4$) grams of potassium permanganate correspond with 5×34 (the approximate molecular weight of H_2O_2) grams of hydrogen peroxide; otherwise expressed, *one gram of potassium permanganate represents* 0·5382 *gram of hydrogen peroxide.*

EXAMPLE.—45 c.c. of a standard solution of potassium permanganate containing 20 grams of $KMnO_4$ per litre were decolorized by 25 c.c. of a solution of hydrogen peroxide. What amount of H_2O_2 is present in a litre of the hydrogen peroxide? Here 1000 c.c. of the standard solution contain 20 grams of $KMnO_4$; hence, 1 c.c. contains 0·02 gram; or 45 c.c. contain 0·9 gram; but from the equation, one gram of $KMnO_4$ represents 0·5382 gram of H_2O_2; hence, 25 c.c. of hydrogen peroxide has 0·5382 × 0·9 = 0·4844 gram of H_2O_2. Hence, a litre will have 19·4 grams of H_2O_2.

Less permanganate is required for titrating a mixture of hydrogen peroxide and sulphuric acid than if a mixture of permanganate and sulphuric acid is used for titrating hydrogen peroxide alone. According to T. M. Lowry and J. H. West, this is due to the formation of persulphuric acid when sulphuric and hydrogen peroxide are mixed together, and the slowness of the reaction between persulphuric acid and potassium permanganate.

Higher hydrogen peroxides.—M. Berthelot (1880)[46] noticed that when potassium permanganate is titrated with hydrogen peroxide at a low temperature, say 12°, the permanganate is decolorized without liberating oxygen, and hence he concluded that this is due to the formation of a compound H_2O_3, or, as A. Bach suggests, H_2O_4, which is stable only at low temperatures. For instance, with hydrogen peroxide, H_2O_2, one gram-molecule of oxygen is liberated for every molecule of the peroxide decomposed: $2KMnO_4+5H_2O_2+3H_2SO_4=K_2SO_4+2MnSO_4+8H_2O+5O_2$; with hydrogen tetroxide, if it exists, and if it reacts in an analogous manner, each molecule requires just as much potassium permanganate as hydrogen peroxide, but twice as much oxygen would be liberated: $2KMnO_4+5H_2O_4+3H_2SO_4=K_2SO_4+2MnSO_4+8H_2O+10O_2$. Similar remarks would apply to Berthelot's hypothetical H_2O_3. According to A. Bach (1897),[47] also, the oxidation products of nascent hydrogen from palladium hydride oxidize indigo solutions more rapidly than hydrogen peroxide, and he therefore inferred that a higher peroxide than H_2O_2 is formed during the slow oxidation of hydrogen. Again, there is nothing to show that the rubidium and potassium tetroxides have the respective formulæ: Rb_2O_4 and K_2O_4; analysis alone gives a percentage composition corresponding with RO_2 and KO_2; but, just as sodium peroxide is represented by the formula Na_2O_2 on account of its relation to hydrogen peroxide, known to have a molecular formula H_2O_2, so the peroxides of rubidium and potassium are assumed to be derivatives of a hypothetical hydrogen peroxide, H_2O_4.

A. Bach (1900) sought for the supposed higher hydrogen peroxides (1) in the oxidation products of nascent hydrogen; (2) in the product derived from the action of dilute acids on sodium peroxide, Na_2O_2; and (3) on potassium tetroxide, K_2O_4; and (4) in the oxidation product of Caro's acid on potassium permanganate. It was found that the corresponding amounts of oxygen obtained from each of these products by the permanganate titration is:

Hydrogen peroxide.	(1) Oxidation products of nascent hydrogen.	(2) Sodium peroxide.	(3) Potassium tetroxide.	(4) Caro's acid.
1	1·07	1·17	1·28	1·65

These results might be caused by the presence of hydrogen trioxide, H_2O_3, or hydrogen tetroxide, H_2O_4. A. M. Clover (1903) failed to verify A. Bach's conclusion. During the permanganate titration of A. Bach, the reaction, $2KMnO_4+3H_2SO_4+5H_2O_2=K_2SO_4+2MnSO_4+8H_2O+5O_2$ occurs, and the hydrogen in the solution can be estimated from (1) the amount of standard permanganate used in the titration, or (2) from the volume of oxygen evolved. Bach found from 25 to 34 per cent. more oxygen was evolved than corresponded with the permanganate required for the titration, and he concluded that a higher peroxide than H_2O_2 must have been present in the solution. H. E. Armstrong (1900) and W. Ramsay (1901)[48] tried to explain Bach's results by assuming that hydrogen peroxide was consumed in a secondary reaction—namely, the formation of persulphuric acid, or Caro's acid, by the interaction of hydrogen peroxide with the sulphuric acid in the solution; but A. von Baeyer and V. Villiger (1900) showed that neither Caro's acid nor persulphuric acid rapidly affected potassium permanganate, so that titration with permanganate does not give the strength of a solution of hydrogen peroxide in sulphuric acid; more peroxide is present than is represented by the amount of permanganate consumed. This criticism cannot be valid because in his permanganate titrations,

A. Bach does not appear to have used sufficient acid, and some manganese dioxide was in consequence precipitated ; this acted catalytically, decomposed the hydrogen peroxide remaining in the solution with the evolution of oxygen ; hence, more oxygen gas was formed than corresponded with the hydrogen peroxide actually decomposed by the permanganate. This conclusion is confirmed (i) by the results obtained when sufficient acid is present to keep the manganese oxide in solution, and (ii) solutions of sodium peroxide also give an excess of oxygen if an insufficient amount of acid is present during the titration. At present, therefore, the evidence in support of the higher hydrogen peroxides is not satisfactory.

According to M. Kleinstück,[49] **carbonyl chloride** and **phenyl carbonate** react with alkaline hydrogen peroxide, and so does a saturated solution of potassium hydrogen carbonate in a pressure bottle at 100°. The distillate obtained by passing steam into the product reduces ammoniacal silver oxide, and is therefore said to contain formaldehyde, H.COH. M. Kleinstück therefore suggests that possibly the assimilation of **carbon dioxide** by plants proceeds : $2H_2CO_3+2H_2O_2=2H.COH+2H_2O+3O_2$. Hydrogen peroxide oxidizes many organic compounds particularly in the presence of an inorganic salt as catalytic agent—*e.g.* it converts **sugars** into ozones, and **benzene** into phenol in the presence of ferrous sulphate ; many organic **alkaloids** are converted into new crystalline bases which are often coloured ; thus **quinine** turns lemon-yellow ; **nicotine,** blood-red ; etc. With **potassium cyanide** it forms potassium cyanate, $KCy+H_2O_2=KCyO+H_2O$, and according to H. Cook, ammonia and potassium formate are simultaneously produced. The **monohydric alcohols** are not attacked, but the **polyhydric alcohols**—glycol, glycerol, mannite, etc.—are oxidized to the corresponding aldehydes, particularly in presence of ferrous sulphate. **Oxalic acid** is converted into carbon dioxide ; **tannin, gallic acid,** and **pyrogallol** are not browned by hydrogen peroxide ; **indigo** solution is slowly bleached, and more rapidly if ferrous sulphate is present. Tincture of **guaiacum** is turned blue. **White of egg** in a solution of lactic acid, and the **serum** of blood, become insoluble at 40°. **Fibrin** and **blood** act catalytically on the decomposition of hydrogen peroxide.

The uses of hydrogen peroxide.—Hydrogen peroxide bleaches many organic colouring agents—*e.g.* litmus and indigo solutions. Dilute solutions of hydrogen peroxide are used for bleaching silk, feathers, straw, hair, ivory, teeth, etc., where more violent bleaching agents—*e.g.* chlorine—would injure the material. Instead of hydrogen peroxide an acidified solution of sodium peroxide is sometimes employed. The actions are similar. Since the products of the decomposition of hydrogen peroxide—water and oxygen—are harmless, it is also used medicinally as an antiseptic, etc. Numerous mixtures of hydrogen peroxide with disinfectants have been registered, and they are sold under various trade names—*e.g. perhydrol, dioxogen, hydrozone, glycozone, pyrozone, peroxal,* etc. M. Pettenkofer's proposal is to use hydrogen peroxide for cleaning oil paintings which have been darkened by the action of hydrogen sulphide—sometimes present in the air of towns—upon the lead compounds in the paint. The brownish-black coloured lead sulphide is transformed into white lead sulphate. According to reports, the treatment is sometimes satisfactory and sometimes it spoils the picture. Ethereal solutions of hydrogen peroxide are used in photography for intensifying negatives. Hydrogen peroxide is also used in analytical work for the oxidation of sulphites to sulphates ; arsenites to arsenates ; chromic salts to chromates ; ferrous to ferric salts ; nitrites to nitrates ; etc.

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§ 12 The Qualitative and Quantitative Determination of Ozone and Hydrogen Peroxide

The detection of ozone and hydrogen peroxide is complicated by the fact that while many reagents produce marked colorations with these two substances, yet other substances like nitrogen peroxide, chlorine, and bromine give similar colorations, so that the results with this group of reagents are merely characteristic of an oxidizing gas.

In 1842, C. F. Schönbein [1] used test papers soaked in a solution of starch and potassium iodide ; these are coloured blue by ozone. The iodine must be free from iodate or a blue colour will be obtained by the carbon dioxide which decomposes the iodate.[2] Even in the absence of iodates, the blue coloration is produced by other oxidizing agents—chlorine, nitrous acid, vapours of ethereal oils, hydrogen peroxide, etc.[3] Ozone with potassium iodide gives potassium hydroxide and iodine, and it is the latter which gives the blue coloration with starch. Attention has been directed to mixing reagents with the potassium iodide which are sensitive to the alkali instead of the iodine. Thus, A. Houzeau (1868) [4] made test papers by soaking them in a mixture of potassium iodide and wine-red litmus. These papers are coloured blue by ozone, ammonia, etc. A. R. Leeds recommended phenolphthaleïn in place of litmus ; C. Arnold and C. Mentzel tried rosolic acid, and also fluoresceïn. The former gives a red colour with ozone, the latter, with black paper, gives a green fluorescence. Neither chlorine nor nitrogen oxide gives the red with rosolic acid. While it is possible to prepare an ozone paper in this way which is not affected by chlorine or nitrogen oxide, hydrogen peroxide gives the same reactions as ozone.[5] This remark also applies to the substitution of cadmium or zinc iodide in place of potassium iodide. Nevertheless, the methods in use for the determination of ozone and hydrogen peroxide are based on the action of these agents upon a neutral solution of potassium iodide. The results are satisfactory provided other oxidizing agents are absent.

In the quantitative determination of ozone, a known volume of air is drawn through such a neutral solution of potassium iodide, when the ozone liberates iodine : $O_3+2KI+H_2O=O_2+I_2+2KOH$. The liberated iodine is determined by acidifying the solution, and titrating with standard sodium thiosulphate, $Na_2S_2O_3.5H_2O$. The reaction is symbolized : $I_2+2Na_2S_2O_3=2NaI+Na_2S_4O_6$; and accordingly, every gram-molecule of sodium thiosulphate corresponds with a gram-atom of iodine, which in turn corresponds with half a gram-molecule of ozone.

EXAMPLE.—Assuming that $\frac{1}{10}N$ sodium thiosulphate solution contains the $\frac{1}{20}$th gram-molecule of the crystallized salt, $Na_2S_2O_3.5H_2O$, per litre, the above equations show that

1000 c.c. of this solution must be equivalent to $\frac{1}{40}$th of a gram-molecule of ozone, that is, 1·2 grms. of ozone. If therefore the ozone in 100 c.c. of air, at n.p.t., ultimately required 4·9 c.c. of $\frac{1}{10}N$ sodium thiosulphate, there were present 4·9 × 0·0012=0·0059 grm. of ozone. A gram of ozone at n.p.t. occupies about 466·7 c.c. Hence 100 c.c. of ozonized air contained 466·7 × 0·0059=2·7 c.c., *i.e.* the air contained 2·2 per cent. of ozone.

The old method of estimating ozone in, say, the atmosphere was to expose ozone test papers for a definite time to the air and compare the resulting tint with a standard scale of colours obtained with air containing known quantities of ozone. Since other oxidizing substances, likely to be present in air, produce similar reactions, it is a moot question whether the large number of ozone determinations which have been made really represent ozone, hydrogen peroxide, nitrogen oxides, or chlorine. The blackening of the silver foil by ozone, as already indicated, is not a sufficiently delicate test. The tests dependent on the reduction of various metal salts—gold, thallium, lead, manganese, and palladium—do not distinguish between ozone, hydrogen peroxide, or other oxidizing or reducing agents.

Numerous organic substances have been proposed at various times for the detection of ozone and of hydrogen peroxide. For instance, tincture of guaiacum was recommended for hydrogen peroxide by C. F. Schönbein.[6] The reagent is more sensitive if a little malt extract, or diastase, be used in conjunction with the tincture.[7] C. F. Schönbein claimed that one part of hydrogen peroxide in two million parts of atmospheric air can be detected by the blue colour which is obtained, and according to E. Schöne, the reagent can be made over 20 times more delicate than this. If the diastase be not used, the coloration is produced by many other oxidizing agents—nitrous acid, ozone, chlorine, etc.—but with diastase, E. Schöne claims that the mixture forms *ein sehr charakterisches und empfindliches Reagens auf Wasserstoffperoxyd.* The bleaching of blue indigo solution, used as a test for ozone by C. F. Schönbein, is not characteristic. C. Wurster[8] recommended dimethyl- or tetramethyl-*p*-phenylenediamine, particularly the latter, as a distinctive reagent for ozone, and test papers prepared with this reagent have been called *tetra-paper*, or *tetra-base-paper.* The claims, however, are not justified since hydrogen peroxide, chlorine, nitrous acid, etc., also colour the reagent. Many other reagents have been proposed[9]—for example, a naphthylamine or azoamidonaphthylaminebenzolsulphonic acid by L. I. de N. Ilosva; and the aniline dye, ursol *D*, by G. V. Chlopin. According to G. Erlwein and T. Weyl (1898) a freshly prepared solution of from 0·1 to 0·2 grm. of metaphenylenediamine hydrochloride in 90 c.c. of water containing 100 c.c. of a 5 per cent. solution of sodium hydroxide develops a yellowish-brown or red in a few seconds, if but 0·00008 grm. of ozone be present; oxygen alone acts very slowly, while nitrous acid and hydrogen peroxide give no coloration. According to C. Arnold and C. Mentzel (1902), however, all oxidizing gases give yellow colours with this reagent.

In their investigation, *Ueber alte und neue Reaktionen des Ozons*, C. Arnold and C. Mentzel propose the use of test papers soaked in an alcoholic solution of tetramethyl di-para-diamidodiphenylmethane, a name abbreviated to *tetramethyl base*. This substance is not to be confounded with the tetra-base of C. Wurster. Paper soaked in this reagent is called *tetramethyl base test paper.* The colour is not affected by hydrogen peroxide but is turned pale violet with ozone; blue, with chlorine and bromine; and from straw yellow to pale dirty brown with nitrous acid. According to F. Fischer and H. Marx, the tetramethyl base test papers should be used moist. If dry test papers are used, the results are misleading—*e.g.* ozone gives a yellow colour. C. Arnold and C. Mentzel also found that a saturated alcoholic solution of benzidine furnishes a reagent which is coloured brown by ozone; blue by bromine, chlorine, and nitrous acid; while hydrogen peroxide, hydrogen sulphide, ammonia, ammonium sulphide, and hydrocyanic acid give no result. If copper sulphate be present hydrogen peroxide and hydrocyanic acid give a blue coloration. According to K. V. Charitschkoff (1909), the pink-coloured paper obtained by soaking filter paper in a benzene solution of cobalt naphthalate is coloured olive-green by hydrogen peroxide (0·03 per cent.), but not by ozone.

The two most characteristic reactions for hydrogen peroxide are the chromic acid-ether test which C. F. Schönbein found sensitive enough to detect one part of the peroxide in 20,000 parts of liquid; and the yellow coloration of a solution of titanic sulphate which E. Schöne found to be sensitive to one part of hydrogen peroxide in 1,000,000; L. I. de N. Ilosva gives a sensitiveness of 1 : 90,000. *The most characteristic and reliable test for hydrogen peroxide is titanium sulphate; and guaiacum tincture with malt extract is the most sensitive.* E. H. Kaiser and L. McMaster (1908)[10] report that a brown solution containing a mixture of ferric chloride and potassium ferricyanide is coloured blue or green by hydrogen peroxide according to the amount of the peroxide present. Ozone and nitrogen peroxide do not reduce the ferricyanide to ferrocyanide—nitrogen peroxide alone produces a blue coloration with ferric chloride. This test is not so characteristic since sulphur dioxide, etc., reduce the ferricyanide. According to C. F. Schönbein, it is sensitive enough to show the presence of one part of hydrogen peroxide in four million parts of solution.

The reactions of the more interesting distinguishing tests with ozone, hydrogen peroxide, chlorine and nitrogen peroxide are summarized in Table III.

TABLE III.—DISTINGUISHING TESTS FOR HYDROGEN PEROXIDE, AND OZONE.

Reagent.	Ozone.	Hydrogen peroxide.	Chlorine.	Nitrogen peroxide.
KI and starch	Blue	Blue	Blue	Blue
Indigo solution	Bleached	Bleached	Bleached	Bleached
Litmus solution	Bleached	Bleached	Bleached	Bleached
Clean silver foil	Blackened	Nil	White film	No change
Mercury bead	Tail on glass	Nil	White	No change
CrO_3 and ether	Nil	Blue	Nil	Nil
Titanic acid	Nil	Yellow	Nil	Nil
Tetramethyl base	Violet	Nil	Blue	Yellow to brown
$KMnO_4$ solution	Unchanged	Decolorized	Decolorized	Decolorized

C. Engler and W. Wild (1896)[11] state that if a mixture of ozone and hydrogen peroxide be passed through a concentrated solution of chromic acid, the hydrogen peroxide is alone decomposed, the ozone is not affected. H. McLeod used a mixture of sodium bicarbonate, potassium dichromate, and sulphuric acid for arresting hydrogen peroxide, but not ozone. According to E. H. Kaiser and L. McMaster, nitric oxide is also arrested at the same time; and they find that if a mixture of ozone, hydrogen peroxide, chlorine, and nitrous oxide be passed through a solution of potassium permanganate, ozone alone escapes unchanged, and it will react with starch and potassium iodide in the usual way.

The general methods employed for the quantitative determination of hydrogen peroxide in solutions are: (1) *Gasometric*, from the volume of gas given off when the solutions are decomposed; (2) *Iodometric*, the amount of iodine liberated from solutions of potassium iodide; and (3) *Oxidation*, the mutual decomposition of hydrogen peroxide and potassium permanganate, in the presence of sulphuric acid.

The general methods available for the quantitative determination of ozone are: (1) *Gravimetric*, by precipitation of thallic oxide from solutions of thallous salts; and (2) *Iodometric*, from the amount of iodine liberated from solutions of potassium iodide.

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§ 13. The Composition and Constitution of Hydrogen Peroxide

> Rational chemical formulæ are a kind of contracted equation ; a compound may have several rational formulæ and that one is best which expresses the greatest number of reactions.—C. GERHARDT (1856).

In spite of the fact that the composition and molecular weight of hydrogen peroxide have been determined ; in spite of the simplicity of the resulting formula, H_2O_2 ; and in spite of the many ingenious (sometimes far-fetched) arguments which have been deduced from experiments made to determine the relative disposition of its component atoms, the constitution of this compound has not been yet established by unequivocal experiments.

The empirical formula.—L. J. Thénard (1818) introduced a weighed amount of the peroxide in a small vial into a graduated cylinder over mercury. The vial was broken and its contents decomposed either by introducing manganese dioxide, or by heat; 17 parts of hydrogen peroxide by weight gave nearly 8 parts by weight of oxygen, and $17-8=9$ parts by weight of water. Otherwise expressed, 34 parts of hydrogen peroxide give 18 parts of water and 16 parts of oxygen. Hence, the peroxide contains hydrogen and oxygen in the proportion of 2 atoms of oxygen. The simplest formula for hydrogen peroxide is therefore HO. There is here nothing to show whether HO or some multiple of HO, say, H_nO_n, is the proper formula for the compound, since the latter has the same percentage composition as the former.

The molecular formula of hydrogen peroxide.—The instability of hydrogen peroxide prevents a determination of its vapour density being made in the regular manner. The molecular weight has been determined by the freezing-point method.[1] The result is nearly 34. This agrees with the formula H_2O_2—the generally accepted value.

The constitutional or graphic formula of hydrogen peroxide.—The evidence for the constitution of hydrogen peroxide deduced from its reactions, or from the reactions of the analogous peroxides, is somewhat ambiguous because different lines of argument lead to different conclusions in spite of very positive assertions in favour of particular formulæ. One group of evidence favours the formula HO.OH with both oxygen atoms bivalent; another group favours HO : OH with both oxygen atoms quadrivalent; and still a third group favours $H_2 : O : O$ with one oxygen atom bi- and the other quadri-valent. The two formulæ HO.OH and HO ⁝ OH are similar in type, and with our present knowledge, it does not matter very much which be favoured; the evidence for HO : OH against HO.OH is mainly physical, and special weight was given to the former by J. W. Brühl (1895). M. Traube (1893) has also argued for a similar constitution. A. Bach (1900), following C. T. Kingzett (1882), favours $H_2{=}O{=}O$; and a similar type of formula has been advocated in order to emphasize the analogy between hydrogen peroxide —assumed to be $H_2{=}O{=}O$—and ozone—assumed to be $O{=}O{=}O$. When two lines of arguments lead to two independent formulæ, each of which seems highly probable if the other be ignored, some one is almost sure to suggest that both formulæ are right, and that one formula represents the equilibrium state under one set of conditions, and likewise also for the other formula under another set of conditions. There is thus a labile intra-molecular change from one form to the other: $H_2{=}O{=}O \rightleftharpoons HO \vdots OH$. This type of chemical change has been called *tautomerism*. O. Mumm (1907)[2] has assumed that hydrogen peroxide is an illustration of the phenomenon; and E. Bose suggested in 1901, that hydrogen peroxide can exist in two different forms in one of which it acts as an oxidizing agent, and in the other as a reducing agent. Otherwise expressed, an acid solution favours the $H_2{=}O{=}O$ formula, and an alkaline solution the $HO{=}OH$ formula.

1. *Evidence for HO—OH or H.O.O.H.*—L. Carius (1863) noticed that ethylene, C_2H_4, unites directly with hydrogen peroxide to form *sehr klein Mengen* of ethylene glycol, $C_2H_4(OH)_2$, presumably by the equation:

$$\begin{array}{l}H_2{=}C\\ H_2{=}\overset{|}{C}\end{array}+\begin{array}{l}OH\\ OH\end{array}\rightarrow\begin{array}{l}H_2{=}C{-}OH\\ H_2{=}\overset{|}{C}{-}OH\end{array}$$

This does not conclusively prove that the constitutional formula is HO.OH since the glycols are similarly formed by oxidizing one of the olefine series (of which ethylene is a member) with potassium permanganate. Similarly, the formation of hydroxides by the action of hydrogen peroxide on metals like zinc:

$$Zn+H_2O_2=Zn{<}\begin{smallmatrix}OH\\ OH\end{smallmatrix}$$

and on sulphur dioxide forming $SO_2(OH)_2$. Here the hydrogen peroxide enters into union as $2OH'$. The inference that hydrogen peroxide is accordingly constituted HO.OH is inclusive, because the hydroxides are formed by other oxidizing agents not containing hydroxyl groups.

The hydrogen of hydrogen peroxide can be indirectly replaced by the ethyl (C_2H_5) or benzoyl (C_6H_5CO) radicle, to form the corresponding peroxides—*viz.* ethyl peroxide, $(C_2H_5)_2O_2$, and benzoyl peroxide, $(C_6H_5CO)_2O_2$. It has been argued that if ethyl peroxide has the formula $(C_2H_5)_2 : O : O$, it should furnish ethyl oxide (ether), $(C_2H_5)_2O$, when exposed to the reducing action of nascent hydrogen: $(C_2H_5)_2O_2+2H \rightarrow (C_2H_5)_2O+H_2O$; and if benzoyl peroxide be constituted $(C_6H_5CO)_2 : O : O$, it should furnish benzoic anhydride, $(C_6H_5CO)_2O$, under similar conditions. As a matter of fact, A. von Baeyer and V. Villiger (1900) obtained neither ethyl oxide nor benzoic anhydride when the respective peroxides were treated with platinum and hydrogen in the cold; the actual products were respectively ethyl alcohol, C_2H_5OH, and benzoic acid, $C_6H_5.CO.OH$. Hence, it is argued that the reactions are of the type $(C_2H_5)_2O_2+2H=2C_2H_5OH$, unless a tautomeric alteration in the relations of the oxygen atoms in the molecule occurs during the reduction, and it followed that the constitution of ethyl peroxide is $C_2H_5.O.O.C_2H_5$, and of benzoyl peroxide, $C_6H_5CO.O.O.COC_6H_5$; and by analogy it is argued that hydrogen peroxide is probably constituted HO.OH, and not $H_2 : O : O$.

The view that hydrogen peroxide contains two hydroxyl groups is further supported by the fact, emphasized by M. Traube (1893), that hydrogen peroxide is formed in many reactions involving the reduction of oxygen $H.H+O : O \rightarrow HO : OH$, and not by the oxidation of water $H_2 : O+O \rightarrow H_2 : O : O$ as might be expected if

$H_2 : O : O$ represented the formula of this compound. In M. Traube's experiment, when the electrodes, during the electrolysis of acidulated water, were separated by a porous cell, no hydrogen peroxide could be detected in the electrolyte; but when air was bubbled about the cathode, the hydrogen appears to unite with molecular oxygen to form hydrogen peroxide. Consequently, he considers that hydrogen peroxide cannot be regarded as oxidized water since it is never formed as a product of oxidation, but is always formed by the reduction of molecular oxygen. He considers the peroxide to be formed by the coupling together of molecular oxygen and molecular hydrogen, and the oxygen which is given off in reactions with hydrogen peroxide is not formed from atomic oxygen, but the oxygen atoms, already paired in the hydrogen peroxide molecule, are liberated. With silver oxide, for example, the reaction is not altogether catalytic, for part at least of the silver oxide is reduced by the hydrogen of the peroxide—*vide* silver oxide.

$$Ag_2\boxed{O+H_2}O_2 \rightarrow 2Ag+H_2O+O_2 ; \text{ not } Ag_2\boxed{O+O\begin{matrix}OH\\H\end{matrix}} \rightarrow 2Ag+O_2+\begin{matrix}OH\\H\end{matrix}$$

Most of the reactions of hydrogen peroxide are similar reduction processes, while if hydrogen peroxide were built of two hydroxyl groups, it would rather act as an oxidizing agent. In all its decompositions, said M. Traube, hydrogen peroxide gives off molecular oxygen. M. Traube rather favoured the formula H.O : O.H, oxygen tervalent, but this is usually altered to H.O.O.H, oxygen bivalent, or to H.O ⋮ O.H, oxygen quadrivalent.

W. Spring (1895) considers the fact that hydrogen peroxide viewed in thick layers is rather more deeply coloured than water agrees with the view that it contains molecular oxygen, and he tries to give this rather feeble argument more weight by pointing out that ammonium iodide, NH_4I, is colourless while the tri-iodide, $NH_4I.I_2$, is green, and the pentaiodide, $NH_4I.I_4$, is violet. W. Spring also considers that the specific heat determinations of the elements H_2 and O_2 show that only part of their available free energy is used in forming hydrogen peroxide, and hence, the molecule has probably a more complex linking than is shown by the simple formula $H.H+O : O{=}HO.OH$.

J. W. Brühl (1896) determined the index of refraction and specific gravity of hydrogen peroxide purified by R. Wolffenstein's process, and found the molecular refraction R for the spectrum lines H_α and H_γ to be $R_\alpha=5{\cdot}791$ and $R_\gamma=5{\cdot}817$; hence the molecular dispersion $R_\gamma-R_\alpha=0{\cdot}136$. If corresponding constants for water and for hydrogen atom be subtracted, a value for hydroxyl OH is obtained:

	R_α	R_γ	$R_\gamma-R_\alpha$
HOH	3·69	3·71	0·09
H	1·10	1·05	0·04
HO	2·59	2·66	0·05

Doubling the value for OH to get the value for HO.OH, there follows the calculated values: $R_\alpha=5{\cdot}18$, $R_\gamma=5{\cdot}32$, and $R_\gamma-R_\alpha=0{\cdot}10$. The actual spectrometric constants are therefore larger than those calculated for the compound HO.OH, and since the additive rule here employed has been applied to a large number of compounds, the difference is explained by assuming that *the two oxygen atoms of hydrogen peroxide are joined by multiple bonds.* Again, the sum of the optical constant of an atom of oxygen, such as occurs in the molecule of water, is less than the observed constant for an equivalent of molecular oxygen, and the dispersion, $R_\gamma-R_\alpha$, of molecular oxygen is double that for the equivalent oxygen in water:

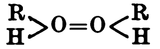
		R_α	R_γ	$R_\gamma-R_\alpha$
2O in water		2·968	3·212	0·036
Molecular oxygen	liquid	3·958	3·964	0·069
	gaseous	—	4·09	—

Again, fewer bonds are supposed to be concerned in uniting the atoms of molecular oxygen than is the case with the oxygen atoms in the molecule of hydrogen peroxide, because the optical constants calculated for hydrogen peroxide are rather less than for molecular oxygen :

	R_α	R_γ	$R_\gamma - R_\alpha$
Oxygen in water	2·968	3·212	0·036
Oxygen in hydrogen peroxide .	3·591	3·717	0·055
Oxygen molecule { liquid .	3·958	3·964	0·069
Oxygen molecule { gaseous .	—	4·09	—

M. Traube assumed oxygen to be tervalent in hydrogen peroxide, HO : OH, but there is no satisfactory evidence to warrant this assumption. The oxygen group of elements are bi- or quadri-valent, and there is much circumstantial evidence which warrants the assumption of quadrivalent oxygen. The multiple-bonded oxygen in hydrogen peroxide is therefore based on a quadrivalent oxygen, and the formula is written HO : OH, or HO≡OH.

J. W. Brühl [3] assumes that the oxygen in water has two latent valencies, $H\cdot\dot{O}\cdot H$, which are the cause of the tendency of water to form associated molecules. Indeed, E. Beckmann [4] found that all associated liquids are of the water type. Thus, the alcohols and the fatty acids are usually associated,[5] and J. T. Hewitt and T. F. Winmill attribute the association of phenols, R.OH, in the liquid condition to the coupling of the molecules in virtue of the residual valencies of the contained oxygen.



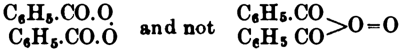
$$\begin{matrix}R\\H\end{matrix}\!>\!O=O\!<\!\begin{matrix}R\\H\end{matrix}$$

J. W. Brühl explains the cause of the great ionizing power of water as follows: Since hydrogen peroxide has even more unsaturated valencies than water, he inferred that hydrogen peroxide must possess a great power of ionization—three-quarters perhaps even greater than that of water. The ionizing power is not easily determined because of the great tendency of hydrogen peroxide to decomposition. Owing to the parallelism between dielectric constants and ionizing power, it also follows that the dielectric constant of hydrogen peroxide will be high. This has been demonstrated by H. T. Calvert,[6] who found the dielectric constant to be 92·8 (18°), when the value for water is 81 (18°). Again, according to P. Drude,[7] all hydroxyl compounds, with the exception of water, show an anomalous electrical absorption in that they are poor conductors of electricity and yet they absorb electromagnetic waves of short wave-length (70 cm.)—normally, substances which conduct electricity moderately well are non-absorbent. H. T. Calvert also found that hydrogen peroxide does not show this phenomenon of anomalous absorption. Hence, this compound is not to be regarded as a di-hydroxyl HO.OH, but, preferably, as a compound H.O$\vdots$O.H, "analogous with acetylene, and like acetylene it is formed endothermally, and is explosive."

2. *Evidence for* $H_2=O=O$.—A. Bach's formula $H_2=O=O$ is regarded by some as "undoubtedly representing the structure of the molecule correctly." The central quadrivalent oxygen is considered to be so heavily loaded with atoms that it readily parts with the two hydrogen atoms in the presence of oxidizing substances, or gives up the extra oxygen in contact with reducing agents. In the former case, it acts as a reducing agent, and in the latter, as an oxidizing agent. On this assumption, the reactions of ozone with hydrogen and barium peroxides are represented :

$$H_2=O=O+O=O=O \rightarrow H_2O+2O_2 ; \quad Ba=O=O+O=O=O \rightarrow BaO+2O_2$$

R. Willstätter and E. Hauenstein [8] have shown that the reduction of ethyl and benzoyl peroxides by platinum and hydrogen in the cold furnishes ethyl alcohol and benzoic acid respectively. It is therefore argued that the formula of benzoyl peroxide must be



$$\begin{matrix}C_6H_5.CO.O\\C_6H_5.CO.\dot{O}\end{matrix} \quad \text{and not} \quad \begin{matrix}C_6H_5.CO\\C_6H_5\,CO\end{matrix}\!>\!O=O$$

since the latter would give rise to benzoic anhydride, not the acid. A. Rius y Miró claims that this argument is weakened by the fact that the water formed in the reaction might hydrolyze any aldehyde formed; but the same result is obtained by reducing the peroxide in a boiling solution by means of yellow phosphorus. In addition, potassium orthophosphate is the sole product of the reduction of potassium perphosphate by potassium iodide in acetic acid solution, or by ferrous or cobalt hydroxides in alkaline solution. It is also shown that sulphuric acid cannot be oxidized to persulphuric acid by permanganic acid, plumbic salts, or nickel peroxide. The majority of oxidations due to hydrogen peroxide are really hydroxylations, but, although this is contrary to the asymmetrical formula, the case of potassium permanganate shows it does not necessarily lead to the symmetrical formula. This formula does not explain the reducing properties of hydrogen peroxide, attributed to weakly bound hydrogen atoms. A. Rius y Miró accordingly suggests the formula $\mathrm{H}<^{\mathrm{O}}_{\mathrm{O}}>\mathrm{H}$ for hydrogen peroxide, and proposes to call peroxides of the type RO_2R, *anhydrohydroperoxides*, to distinguish them from A. Baeyer's hydroperoxides.

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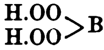
§ 14. Peroxides and Peracids

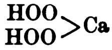
Hydrogen peroxide has several properties in common with the acids. For example, purified hydrogen peroxide—perhydrol—reddens blue litmus before bleaching the colour; its acidity can be partly neutralized by the addition of alkaline solutions; it can be more readily extracted from its ethereal solution by alkaline lye than by water; and hydrogen peroxide displaces the acid radicle from sodium halides, silicate, borate, metaphosphate, and sulphide, and from potassium ferro- and ferri-cyanides.[1] In 1895, W. Spring pointed out that hydrogen peroxide behaves like a mono- and a di-basic acid in that it contains two hydrogen atoms which can be replaced singly or in pairs by equivalent radicles. The substitution products can be regarded as salts. The mono-substituted products are of the type ROOH, where R denotes a monad radicle—elementary or compound—and the di-substituted products are of the type ROOR, where the two R's may be the same or different. A. von Baeyer and V. Villiger[2] called the former **hydroperoxides**—*e.g.* ethyl hydroperoxide, $C_2H_5.OOH$, the latter **peroxides**—*e.g.* diethyl peroxide, $C_2H_5.OO.C_2H_5$. The peroxides can thus be regarded as salts of the acid, hydrogen peroxide, formed by the action of this compound on, say, the hydroxide of the alkalies or alkaline earths. Thus, by the action of sodium ethoxide, $C_2H_5.ONa$, on hydrogen peroxide in alcohol solution, R. Wolffenstein[3] prepared sodium hydroperoxide: $C_2H_5ONa + HOOH \rightarrow C_2H_5OH + NaOOH$, and according to electrical conductivity methods.

it is inferred that the salt is really NaOOH, and not $NaOONa.H_2O_2$. J. Tafel called the salt NaOOH, *sodyl hydroxide*. E. Schöne[4] prepared



$$\begin{matrix}H.OO \\ H.OO\end{matrix}\!>\!Ba$$

Barium hydroperoxide



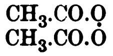
$$\begin{matrix}HOO \\ HOO\end{matrix}\!>\!Ca$$

Calcium hydroperoxide

by the action of an excess of hydrogen peroxide on the hydroxides of the alkaline earths. If potassium or sodium carbonate be added to hydrogen peroxide, the corresponding alkaline peroxide is formed and carbon dioxide is evolved, *e.g.* $H_2O_2 + Na_2CO_3 \rightarrow Na_2O_2 + CO_2 + H_2O$; on the contrary, if the hydrogen peroxide be added to a solution of the carbonate oxygen is evolved: $2H_2O_2 + Na_2CO_3 \rightarrow Na_2CO_3 + 2H_2O + O_2$. The sodium carbonate in the latter case merely acts as a catalytic agent. It is not at all uncommon to find reactions progressing differently according to the way the substances are mixed together. The peroxides, in some cases, can also be precipitated from solutions of the corresponding salts by the addition of hydrogen peroxide. For instance, with lead acetate, PbA_2, lead peroxide is formed: $PbA_2 + H_2O_2 \rightarrow PbO_2 + 2HA$. An *excess* of hydrogen peroxide with lead peroxide furnished lead monoxide: $PbO_2 + H_2O_2 = PbO + H_2O + O_2$. Hydrated peroxides of the alkaline earths of the type $BaO_2.8H_2O$ are precipitated from solutions of the hydrated oxides by hydrogen peroxide; and conversely, when these peroxides are dissolved in dilute acids, the corresponding amount of hydrogen peroxide is set free. In both cases, hydrogen peroxide behaves like an acid, and the peroxides can accordingly be regarded as salts of hydrogen peroxide just as the nitrates are salts of hydrogen nitrate—to wit, nitric acid. It can be added that for similar reasons water liberates hydrogen peroxide from its assumed salts—the peroxides—and hence also water has been called an acid—water acid.

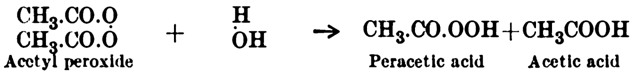
The organic radicles can also displace the hydrogen from hydrogen peroxide to form corresponding hydroperoxides and peroxides. The relations of the alcohols to the ethers and of the acids—*e.g.* acetic acid, CH_3COOH—to the acid anhydrides—*e.g.* acetic anhydride $(CH_3CO)_2O$—are analogous to the relations between the hydroperoxides and the peroxides—*e.g.*

$$CH_2.CO.OOH$$



$$\begin{matrix}CH_3.CO.O \\ | \\ CH_3.CO.O\end{matrix}$$

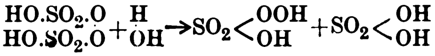
The action of water on the acid anhydrides—*e.g.* $(CH_3.CO)_2O + HOH \rightarrow 2CH_3.COOH$—recalls the action of water on the peroxides. For instance, with acetyl peroxide, peracetic and acetic acids are formed:



$$\begin{matrix}CH_3.CO.O \\ | \\ CH_3.CO.O\end{matrix} + \begin{matrix}H \\ | \\ OH\end{matrix} \rightarrow CH_3.CO.OOH + CH_3COOH$$

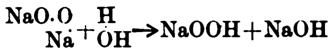
Acetyl peroxide Peracetic acid Acetic acid

with persulphuric acid, monopersulphuric acid or Caro's acid and sulphuric acid are formed:



$$\begin{matrix}HO.SO_2.O \\ | \\ HO.SO_2.O\end{matrix} + \begin{matrix}H \\ | \\ OH\end{matrix} \rightarrow SO_2\!<\!\begin{matrix}OOH \\ OH\end{matrix} + SO_2\!<\!\begin{matrix}OH \\ OH\end{matrix}$$

and with sodium peroxide, sodium hydroperoxide and hydroxide are formed:



$$\begin{matrix}NaO.O \\ | \\ Na\end{matrix} + \begin{matrix}H \\ | \\ OH\end{matrix} \rightarrow NaOOH + NaOH$$

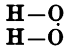
The formation of the organic acids by the action of water on the acid chlorides is analogous with the formation of the peracids by the action of hydrogen peroxide on the acid chlorides: thus, $CH_3CO.Cl + HOOH \rightarrow CH_3CO.OOH + HCl$; or $HO.SO_2.Cl + HOOH \rightarrow HO.SO_2.OOH + HCl$. Similarly, just as the acid anhydride is formed by the action of an acid hydrate and acid chloride: $CH_3CO.OH + ClCO.CH_3 \rightarrow CH_3CO.O.CO.CH_3 + HCl$, so does hydrogen peroxide, and its acid chloride—*viz.*

hypochlorous acid, HOCl—form the corresponding acid anhydride, H.OO.OH, which, being unstable, decomposes into water and oxygen:

$$HOO\,H+Cl\,OH \rightarrow HOO.OH+HCl \rightarrow HCl+H_2O+O_2$$

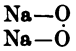
D. I. Mendeléeff (1881)[5] subdivided the oxides of the type RO_2 into two classes—the superoxides and the polyoxides—depending upon the valency of the element united to the oxygen atoms: the one class was considered to be constituted on the hydrogen peroxide type, the other on the condensed water type.

Superoxides, peroxides, or true peroxides.—Those oxides in which the oxygen atom or atoms, over and above those required to form the basic oxide, are *singly linked* to the metal and to the other oxygen atoms, so as to form a chain. The valency of the metal is the *same* in the peroxide as in the basic oxide; *e.g.*



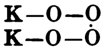
$$\begin{matrix}H-O\\ \vert \\ H-O\end{matrix}$$

Hydrogen peroxide.



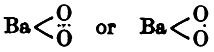
$$\begin{matrix}Na-O\\ \vert \\ Na-O\end{matrix}$$

Sodium peroxide.



$$\begin{matrix}K-O-O\\ \vert \\ K-O-O\end{matrix}$$

Potassium tetroxide.

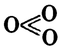


$$Ba{<}\begin{matrix}O\\ \vert \\ O\end{matrix} \text{ or } Ba{<}\begin{matrix}O\\O\end{matrix}$$

Barium peroxide.

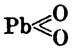
The superoxides have also been called **peroxidates** or **peroxites** and regarded as salts of hydrogen peroxide, for they are supposed to be constituted like this compound. These oxides were Schönbein's antozonides—a term now obsolete.

Polyoxides, dioxides, or pseudo-peroxides.—Those peroxides in which the oxygen atom or atoms, over and above those required to form the basic oxide, are *doubly linked* to the metal so that the valency of the metal in the dioxide is *greater* than the valency of the metal in the basic oxide; *e.g.*



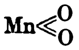
$$O{\leqslant}\begin{matrix}O\\O\end{matrix}$$

Ozone.



$$Pb{\leqslant}\begin{matrix}O\\O\end{matrix}$$

Lead dioxide.



$$Mn{\leqslant}\begin{matrix}O\\O\end{matrix}$$

Manganese dioxide.

These oxides possess feeble basic or feeble acidic properties—possibly both. They are supposed to be constituted on the double water type with a quadrivalent element taking the place of the four hydrogen atoms in two molecules of water. These oxides were Schönbein's *ozonides*—a term now applied to quite different compounds.

The peroxides which yield hydrogen peroxide when treated with water or a dilute acid are probably constituted like hydrogen peroxide. Thus, sodium peroxide with hydrochloric acid gives hydrogen peroxide; and potassium tetroxide, which gives oxygen and hydrogen peroxide, is probably constituted on the same plan. The polyoxides or dioxides are not usually attacked by dilute acids. Both types with concentrated sulphuric acid evolve oxygen. The mechanism of the reaction is probably different in the two cases. With the super- or per-oxides, hydrogen peroxide is probably formed as an intermediate product: $BaO_2+H_2SO_4=BaSO_4+H_2O_2$; followed by $2H_2O_2=2H_2O+O_2$. With manganese dioxide: $2MnO_2+2H_2SO_4=2MnSO_4+2H_2O+O_2$. Similarly with hydrochloric acid, both give chlorine, but with the peroxides hydrogen peroxide is first formed, and this reacts with the excess of acid forming chlorine: $2HCl+H_2O_2=2H_2O+Cl_2$; with the di- or poly-oxides, on the other hand, an intermediate perchloride can often be detected—with manganese dioxide, probably $MnCl_3$; and with lead dioxide, $PbCl_4$ is formed.

The differences in the behaviour of the true and false peroxides—typified by BaO_2 and PbO_2—has prompted many hypotheses. B. C. Brodie and C. F. Schönbein have assumed that the normal oxygen molecule contains a negatively and a positively charged oxygen atom, that substances undergoing oxidation have a preference for oxygen carrying one kind of charge while the oppositely charged oxygen is consumed in a secondary reaction. The positively charged oxygen was called *antozone*, and the corresponding oxides—PbO_2, $KMnO_4$, etc.—were called *ozonides*; the negatively charged oxygen atom formed *antozonides*—*e.g.* Na_2O_2, BaO_2, H_2O_2, etc. For instance, $H_2O+O=$hydrogen peroxide; and $MnO+O=$manganese dioxide. The union of antozone O^+ with ozone O^- gives ordinary oxygen, and such a reaction was supposed to occur when hydrogen peroxide (an antozonide) reacts with, say, lead peroxide (an ozonide). No direct experimental evidence can be quoted demonstrating the existence of Schönbein's antozone.

S. Tanatar[6] has suggested that the differences between the true and false peroxides are due to differences in the thermal values of the reactions which occur when the oxides are treated with acids. The formation of hydrogen peroxide from water requires 23 Cals., and if the thermal value of the reaction between the metal of the peroxide and the radicle of the acid is less than this value, no hydrogen peroxide can be produced. The strong acids—*e.g.* hydrochloric acid—give hydrogen peroxide with barium peroxide, while the weaker acids—*e.g.* phenol—give oxygen but no hydrogen peroxide. Hence, the distinction between a true or false peroxide is arbitrarily determined by the strength of the acid used in making the test. S. Tanatar further states that appreciable amounts of hydrogen peroxide are formed when nickel dioxide is treated with sulphuric acid, because (i) the solution liberates iodine from potassium iodide; and (ii) decolorizes a solution of potassium permanganate; but C. Tubandt and W. Riedel[7] could not get the confirmatory tests with chromic and titanic acids, and it is hence inferred that the liberation of iodine is due to the formation of traces of a persulphuric acid; and that the bleaching of the permanganate is not real, but rather a masking of the pink colour of the permanganate by the green colour of the nickel solution. The formation of hydrogen peroxide occurs not only when hydrocyanic acid acts on nickel peroxide, but also when nickel hydroxide is used; the peroxide is presumably formed by the autooxidation of the complex nickel cyanides which are formed. G. Pellini and D. Meneghini[8] have shown that there are possibly two nickel peroxides, one of which gives hydrogen peroxide when treated with acids, and the other does not. According to S. Tanatar, the former may really be a compound of hydrogen peroxide and nickel monoxide, and not a dioxide at all.

Attempts have been made to show that two of the best-known dioxides, PbO_2 and MnO_2, are differently constituted because lead dioxide when decomposed by sulphurous acid, H_2SO_3, furnishes lead sulphate, $PbSO_4$, while manganese dioxide furnishes manganous dithionate, MnS_2O_6. It is more probable that the action in both cases is similar, manganese dioxide forming the normal sulphite, $Mn(SO_3)_2$; and lead dioxide, the basic sulphate, $PbO.SO_3$. Both salts then undergo internal rearrangement, the former producing a dithionate, and the latter a normal sulphate.

There is a distinction between the peracids analogous to that occurring between the peroxides. The true peracids are either formed by the action of hydrogen peroxide on ordinary acids or their derivatives, or else they furnish hydrogen peroxide when hydrolyzed with dilute sulphuric acid—with concentrated sulphuric acid they behave like the peroxides and give ozonized oxygen. The prefix *per* is applied to many acids—perchloric acid, permanganic acid, etc.—to denote that they contain relatively more oxygen than the acid indicated when the prefix is deleted. These acids do not give hydrogen peroxide by hydrolysis, moreover they are not formed by the action of hydrogen peroxide. In many cases, it is not clear whether the so-called peracid is an additive compound of the acid with hydrogen peroxide of crystallization, analogous to water of crystallization, or whether it is a real peracid in which the acid radicle has united with the hydrogen peroxide.

The elements which form peracids belong to the 3rd, 4th, 5th, and 6th groups of Mendeléeff's periodic system, although O. Carrasco (1911) claims to have prepared a perzincic acid. If the claim be established, zinc in the second group will have to be included in the list of elements forming true peracids. T. S. Price[9] represents the elements forming peracids in black type as illustrated in Table IV.

TABLE IV.—ELEMENTS IN THE PERIODIC SYSTEM FORMING PERACIDS.

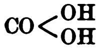
Group III.		Group IV.		Group V.		Group VI.	
B		**C**		**N**		O	
Al		Si		**P**		**S**	
Sc		**Ti**		**V**		**Cr**	
	Ga		Ge		As		**Se**
Y		**Zr**		**Cb**		**Mo**	
	In		**Sn**		Sb		Te
(**La**)		Ce		—		—	
—		—		—		—	
Yb		—		**Ta**		**W**	
	Tl		Pb		Bi	—	
—		Th		—		**U**	

T. S. Price also shows that, omitting the first two rows, the elements which form peracids are mainly confined to the members of the even series, and that the stability of the peracids increases with increasing atomic weight of the element in agreement with the rule that with the elements of the even series the higher the atomic weight the greater their basicity—for instance, in the 6th group, peruranic acid is the most stable peracid of the family, and can be prepared at ordinary temperatures; while permolybdic acid can be obtained only at temperatures approaching —10°. Pertungstic acid is more stable than permolybdic acid.

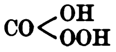
The peracids can be regarded as derivatives of hydrogen peroxide in which one of the hydrogen atoms is replaced by an acid radicle. Otherwise expressed, the peracids can be regarded as acids in which one or more hydroxyl groups are replaced by the monad radicle O.O.H.

Ordinary acids.		Peracids.	
Metaboric acid . . .	HO.BO	Perboric acid . . .	HOO.BO
Acetic acid . . .	$CH_3CO.OH$	Peracetic acid. . .	$CH_3.CO.OOH$

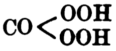
The diabasic acids form two series of peracids according as one or both the hydroxyl groups are replaced by the HOO- radicle.


$\mathrm{CO}<\begin{matrix}\mathrm{OH}\\\mathrm{OH}\end{matrix}$

Carbonic acid.

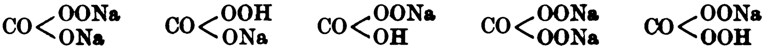

$\mathrm{CO}<\begin{matrix}\mathrm{OH}\\\mathrm{OOH}\end{matrix}$

Monopercarbonic acid.


$\mathrm{CO}<\begin{matrix}\mathrm{OOH}\\\mathrm{OOH}\end{matrix}$

Dipercarbonic acid.

Similarly with the acids of higher basicity. The peracids form **persalts**. There are theoretically two acid persalts and one normal persalt of the monoperacids, and one each of the diperacids. For example,


$\mathrm{CO}<\begin{matrix}\mathrm{OONa}\\\mathrm{ONa}\end{matrix} \quad \mathrm{CO}<\begin{matrix}\mathrm{OOH}\\\mathrm{ONa}\end{matrix} \quad \mathrm{CO}<\begin{matrix}\mathrm{OONa}\\\mathrm{OH}\end{matrix} \quad \mathrm{CO}<\begin{matrix}\mathrm{OONa}\\\mathrm{OONa}\end{matrix} \quad \mathrm{CO}<\begin{matrix}\mathrm{OONa}\\\mathrm{OOH}\end{matrix}$

Salts of the percarbonic acids.

There is also a series of acid derivatives of hydrogen peroxide in which the acid characteristics belong rather to the acid radicle itself than to the presence of the HOO-group. They are generally prepared by electrolysis, and they can be regarded as derivatives of hydrogen peroxide in which both the hydrogen atoms are replaced by acid radicles. They are rather acid peroxides than true peracids, although they are commonly called peracids. For example

Hydrogen peroxide.	Persulphuric acid.	Percarbonic acid.
$\begin{matrix}\mathrm{HO}\\\mathrm{HO}\end{matrix}$	$\begin{matrix}\mathrm{HO.SO_2.O}\\\mathrm{HO.SO_2.O}\end{matrix}$	$\begin{matrix}\mathrm{HO.CO.O}\\\mathrm{HO.CO.O}\end{matrix}$

The salts of these acid peroxides do not give the characteristic reactions of hydrogen peroxide. For instance, the persulphates do not give the blue coloration by the chromic acid and ether test; potassium permanganate in acid solution is not decolorized; iodine is not separated from potassium iodide; etc. These salts, however, may be hydrolyzed into hydroperoxides in aqueous solutions and they may then show the characteristic reactions of hydrogen peroxide. In this series of persalts, the free acids corresponding with the persulphates have alone been isolated. It will be observed that further complications are theoretically possible, for these peroxide acids may form true peracids by the replacement of one or both the hydroxyl radicles by HOO-radicles. Thus,

$$\begin{array}{ccc} \mathrm{HO.CO.\underset{\cdot}{O}} & \mathrm{HOO.CO.\underset{\cdot}{O}} & \mathrm{HOO.CO.\underset{\cdot}{O}} \\ \mathrm{HO.CO.\dot{O}} & \mathrm{HO.CO.\dot{O}} & \mathrm{HOO.CO.\dot{O}} \end{array}$$

Peracids of the acid peroxides.

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CHAPTER XV

ELECTROLYSIS AND THE IONIC HYPOTHESIS

§ 1. The Products of Electrolysis

> The electricity which decomposes, and that which is evolved by the decomposition of a certain quantity of matter are (qualitatively and quantitatively) the same.—M. FARADAY.

ONE or both of the products of electrolysis may be an insoluble solid, a soluble liquid, a gas, etc. When an insoluble solid is formed it may stick to the electrode, or fall to the bottom of the electrolytic cell ; if a gas, not too soluble in the electrolyte, be formed, it can be collected in a suitable receiver. Substances are not always visible when in solution. The soluble matter can often be isolated more or less completely by surrounding the proper electrode with a porous pot which retards the diffusion and mixing of the products separated at the two electrodes. This is done, for example, in the industrial preparation of chlorine.

The electrolysis of a solution of copper sulphate furnishes the products : copper, sulphuric acid, and oxygen. This is more than was present in the copper sulphate used at the start. It is therefore assumed, as a trial hypothesis, that Cu and SO_4 ions are produced at the electrodes during the passage of the current ; that the Cu-cation carries a positive charge of electricity, and the SO_4-anion a negative charge. Consequently, the Cu-ion will be found at the negative electrode, and the SO_4-ion at the positive electrode. The ions are de-electrified at the electrodes—the Cu-ion at the cathode, and the SO_4-ion at the anode. The de-electrified copper ions are deposited as metallic copper about the cathode ; and the de-electrified SO_4-ion, at the anode, reacts at once with the solvent (water), producing sulphuric acid and oxygen: $2SO_4+2H_2O=2H_2SO_4+O_2$. When an aqueous solution of potassium nitrate is electrolyzed, potassium hydroxide and gaseous hydrogen are formed at the cathode ; and nitric acid and oxygen at the anode. It is assumed that the potassium nitrate is first decomposed into two electrified K^+ and NO_3^- ions at the electrodes ; and that the K^+-ion, when de-electrified, reacts with water at the cathode, producing potassium hydroxide and hydrogen ; and the NO_3^- ion, when de-electrified at the anode, reacts with water, giving nitric acid and oxygen: $4NO_3^-+2H_2O=4HNO_3+O_2$. Again, if a solution of copper sulphate be electrolyzed with copper electrodes, metallic copper is deposited at the cathode, and the sulphuric acid produced at the anode attacks and dissolves the copper cathode forming copper sulphate. This explains how the total concentration of a solution of copper sulphate does not alter if it be electrolyzed in a cell with a copper anode. Similar remarks apply to the electrolysis of solutions of silver nitrate with a silver anode, Fig. 1 ; of ferrous ammonium sulphate with an iron anode ; of nickel ammonium sulphate with a nickel anode ; etc.

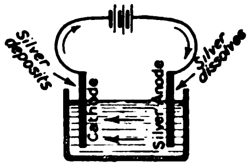

FIG. 1. — Electrolysis of Silver Nitrate.

Electroplating.—If a plate of silver be used as the anode during the electrolysis of silver nitrate, metallic silver will be dissolved by the nitric acid as fast as the acid is formed.

Thus, the concentration of the silver nitrate in the solution will remain unchanged and metallic silver will be transported from anode to cathode. This is the principle of the method of electroplating. In the case of *silver-plating* a firmer and more uniform deposit of silver is obtained by using a solution of silver cyanide in potassium cyanide as the electrolyte in place of a solution of silver nitrate. The article to be plated, say a brass spoon, is attached to a wire and dipped in the solution of silver salt, and this is made the cathode. A bar or sheet of silver is made the anode. A rather weak electric current is sent through the electrolyte. The electrolyte is decomposed, and silver (cation) is deposited on the article to be plated (cathode); the anion collecting at the anode dissolves the silver anode, and thus keeps the strength of the electrolyte unchanged. What is dissolved at the anode is deposited at the cathode. Salts of other metals—nickel, iron, gold, platinum, etc.—can be used as electrolytes in a similar manner, and accordingly articles can be nickel-plated, gold-plated, etc. The plated articles may be afterwards burnished.

Units.—We first inquire if there is any relation between the quantity of electricity passing through an electrolytic cell and the amount of decomposition. In order to fix a standard of measurement, let the quantity of electricity required to deposit 0·001118 gram of silver be called a **coulomb.** This is the so-called **unit quantity of electricity.** Hence 108 grams of silver, that is, a chemical equivalent of silver, will be deposited by 96,540 coulombs of electricity. This amount of electricity is often called a **farad.**

The so-called "hydraulic analogy" of an electric current might here be cited. The quantity of water flowing through a pipe can be expressed in gallons or cubic feet per second; in a similar way, **quantity of electricity** may be expressed in terms of coulombs per second. An electric current carrying one coulomb per second is called an **ampère.** This is the so-called **unit current of electricity.** A coulomb by the same analogy would correspond with, say, a gallon or cubic foot of water; and an ampère with a gallon or a cubic foot of water *per second*. For example, if 20 coulombs of electricity pass through a current in 20 seconds, the current is $60 \div 20 = 3$ ampères, or 3 coulombs per second. The total quantity of water delivered by a pipe is determined by the "head" or pressure of water, so that in order to pass a certain number of gallons per second through a given pipe, a certain pressure must be applied to overcome the frictional resistance of the pipe. In the same way, a certain electromotive force—electrical pressure—is required on account of the **resistance** offered by the wire to the flow of electricity. Just as water pressure is measured in pounds per square inch, or in feet "difference of level" or "head," so the unit of electrical pressure, the **volt**, is the difference of potential needed to produce a current of one ampère in a conductor whose resistance is equivalent to that of a uniform column of 14·45 grams of mercury, 106·3 cm. long. The resistance of such a column is called an **ohm.** Hence a volt is the electric pressure required to produce a current of one ampère in a conductor of one ohm resistance. The terms **voltage, electrical pressure,** and **electromotive force** are generally applied synonymously to an electric current, or, if the current be not directly under consideration, the term **difference of potential** is used. It is, of course, needless to dwell on the fact that the analogy used above in comparing an electric current with a moving fluid is merely a convenience. It is probable that electricity is not a fluid, and the analogy must not be carried much further.

§ 2. Faraday's Laws of Definite Electrolytic Action

Nature presents us with a single quantity of electricity. For each chemical bond which is ruptured within an electrolyte, a certain quantity of electricity traverses the electrolyte, which is there in all cases.—G. J. Stoney (1881).

M. Faraday (1834) [1] found that the amount of chemical work done by an electric current is directly proportional to the quantity of electricity which passes through the electrolyte. If one farad leads to the separation of 108 grams of silver, two farads will lead to the separation of 216 grams of silver, and so on. Similar results are obtained with other electrolytes. Hence, said Faraday, "**the chemical decomposing action of a current is constant for a given quantity of electricity;**" or, "the quantity of chemical decomposition is exactly proportionate to the quantity of electricity which has passed through the electrolyte;" if w denotes the number of grams of an element set free by the decomposition of a compound by the passage of a quantity of electricity C, then w is proportional to C; and consequently, "the products of decomposition . . . afford a very excellent and valuable measure of the electricity concerned in their evolution." The increase in the weight of, say, the negative electrode during the electrolysis of silver nitrate or copper sulphate owing to the deposition of metallic silver or copper respectively, is a measure of the quantity of electricity which has passed through the system. A cell specially designed for such measurements is called a **silver voltameter** or a **copper voltameter** respectively.

Provided there are no disturbing secondary actions, the amount of electro-decomposition is not affected by the strength (or intensity) of the current, the time the current is passing, the concentration of the solution, the nature of the dissolved substance, nor by the temperature. The same quantity of electricity will always liberate the same quantity of the elements stated. The accuracy of the law is said to have been established for "currents so small that a century would be required for the separation of a milligram of hydrogen," and in large electrochemical works, the law is continually being verified by the passage of millions of coulombs. In every case, the law describes the phenomena exactly. **The quantity of an element liberated by the passage of one farad of electricity is called the electrochemical equivalent of the element.**

Again, let a current be *simultaneously* passed through six cells containing respectively dilute sulphuric acid, aqueous solutions of silver nitrate, cuprous chloride and hydrochloric acid, cupric sulphate, gold chloride, and stannic chloride. The experiment is conducted by arranging the electrolytic cells as illustrated in the plan, Fig. 2. After about half an hour's electrolysis the amounts of the different elements collected at the cathode can be weighed or measured. The results will be very nearly:

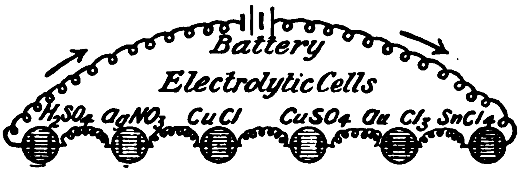

FIG. 2.—Experiment illustrating Faraday's Laws.

	Dilute H_2SO_4		$AgNO_3$	CuCl	$CuSO_4$	$AuCl_3$	$SnCl_4$
	Cathode. Hydrogen.	Anode. Oxygen.	Silver.	Copper.	Copper.	Gold.	Tin.
Amount found .	0·0266	0·2126	2·9370	1·6900	0·8440	1·7476	0·7554 gram
If H = 1 . .	1	8	108	63·5	31·8	65·7	29·8
Atomic weight .	1·01	16	107·9	63·6	63·6	197·2	119
Valency . .	1	2	1	1	2	3	4

Accordingly, chemically equivalent quantities of the different elements (that is, atomic weight ÷ valency) are liberated by the passage of the same quantity of electricity. Consequently, **the electrochemical equivalent of an element is numerically the same as the chemical equivalent.** The equivalent weights of bodies are those quantities of them which are decomposed by equal quantities of electricity. Hence, it is inferred that electricity determines the combining forces because it determines the combining weights.

At first sight, this result appears to contradict the principle of excluded perpetual motion, because, if the current from a $Zn|H_2SO_4|Pt$ battery be sent through an indefinite number of electrolytic cells containing dilute sulphuric acid, the same amount of hydrogen would be liberated in each, and sufficient hydrogen could be collected to furnish, on combustion, enough heat to evaporate the solution of zinc sulphate in the battery to dryness, to transform the zinc sulphate to metallic zinc and sulphuric acid, and so reconstruct the battery; and have some hydrogen remaining in excess. The experiment fails. The current will not traverse an indefinitely large number of cells. W. H. Wollaston[2] showed in 1801 that in dealing with electrical energy we are concerned with two different factors, and that "quantity of electricity" is only one of these factors. Faraday's law describes the influence of "quantity of electricity" upon electrolysis. It says nothing about the electrical **pressure**—the electromotive force, described, say, in volts—required to drive a given **quantity** of electricity through the system. Hence, Faraday's work may be summarized: **The same quantity of electricity passing through one or more electrolytes connected up in series, will liberate in each cell chemically equivalent amounts of the products of electrolysis, provided the electromotive force permits the necessary current to be maintained.** It might here be added that, for reasons which will be discussed later, a certain specific electrical pressure or voltage—called the **decomposition voltage**—is required to electrolyze a given solution; thus, hydrochloric acid requires about 1¼ volts, and fused sodium chloride about 4 volts.

Nomenclature.—Let each positive charge of electricity be represented by a small dot, and each negative charge by a small dash at the upper right-hand corner of the chemical symbol for an element, then, a silver ion will be written $Ag^{\cdot}$; a zinc ion by $Zn^{\cdot\cdot}$; a nitrate ion, NO_3'; and a sulphate ion by SO_4''. In the electrolysis of aqueous solutions of salts, etc., the separation of an ion at one electrode is always attended by the separation of a chemically equivalent ion or ions at the other electrode. For instance, with zinc chloride, for every $Zn^{\cdot\cdot}$ which is de-electrified at the cathode, two Cl' ions will be de-electrified at the anode. In order to designate positive ions J. Walker (1901)[3] appends *ion* to the stem with a prefix mono-, di-, tri-, . . . to indicate the number of charges carried by the ion. Thus $H^{\cdot}$ is called *hydrion*; $Na^{\cdot}$, *sodion*; $Fe^{\cdot\cdot}$, *diferrion*; $Fe^{\cdot\cdot\cdot}$, *triferrion*; etc. For negative ions, the termination of -ate becomes *-anion*; -ite, becomes *-osion*; and -ide, becomes *-idion*. Thus OH' is hydroxidion; Cl', *chloridion*; ClO_3', *chloranion*; OCl', *hypochlorosion*; SO_3'', *sulphosion*; SO_4'', *sulphanion*; etc. To this, A. Smith (1901) adds the term *ionogen* for "bodies which are capable of undergoing ionization," reserving the term *electrolyte* for the solution as a whole than for the substance dissolved.

We have just seen that the electrochemical and chemical equivalents are numerically the same, and therefore the electrochemical equivalent of an element is obtained by dividing the atomic weight by the valency. The same quantity of electricity—positive or negative—must therefore be carried by each univalent atom, and accompany it in all its movements in the electrolytic fluid. This quantity has been called the **unit charge of the ion.** At first sight this deduction appears to be rather startling, for it seems to imply either that the electric charges are divisible or that the so-called bivalent atoms are composed of two sub-atoms, the tervalent atoms, of three sub-atoms; etc. The former hypothesis is generally accepted. Accordingly, a univalent atom is supposed to carry one charge of electricity (96,540 coulombs); a bivalent atom two charges, and an n-valent atom, n charges. According to this view, valency represents the number of charges of electricity which are associated with the respective ions, **and chemically equivalent quantities of matter have the same capacity for electricity.** That is, "the chemical equivalent is the electrical unit of matter," or, as M. Faraday expressed it:

> The equivalent weights of bodies are simply those quantities which contain equal quantities of electricity, or have naturally equal electric powers; it being electricity which determines the equivalent number because it determines the combining force. Or, if we adopt the atomic theory or phraseology, then the atoms of bodies which are equivalent to each other in their ordinary chemical action have equal quantities of electricity naturally associated with them.

So close is the relation between the chemical and electrochemical equivalents that R. Luther (1905) proposed to define the combining weight of a univalent element as the quantity corresponding with 10,000 electromagnetic units, which, in turn, is very nearly 100,000 coulombs. Hence this means little more than multiplying the numbers at present in use by 3·46 per cent.

Quantity of electrolytic work done by a current.—M. Faraday has shown that the amount of chemical decomposition in a given time depends upon the amount of current employed; and that the one magnitude can be computed when the other is known. To find the relation between the chemical equivalent of an element and quantity of electricity. Let ϵ denote the chemical equivalent of a substance, then the weight w of an element liberated by constant quantity of electricity is proportional to ϵ, but, w is also proportional to the quantity of electricity C; and therefore $w=k\epsilon C$, where k is a constant sometimes called *Faraday's constant.* If suitable units be chosen, $w=\epsilon C$. Consequently, **the electrochemical equivalent of an element is the amount in grams liberated by one coulomb.** Careful measurements have shown that 0·001118 grm. of silver will be deposited by one coulomb. Since the chemical equivalent of silver is very nearly 107·88, hydrogen unity, 0·001118 grm. is 107·88 times greater than the amount of hydrogen which will be separated by a coulomb; accordingly, 0·00001036 grm. or $1{\cdot}036\times10^{-5}$ grm. *of hydrogen will be separated by the passage of one coulomb of electricity.* The electrochemical equivalent of univalent copper is $63{\cdot}5\times1{\cdot}036\times10^{-5}$; of bivalent copper, $\frac{1}{2}$ of $63{\cdot}5\times1{\cdot}036\times10^{-5}$; of ferrous iron, $\frac{1}{2}$ of $56\times1{\cdot}036\times10^{-5}$; of ferric iron, $\frac{1}{3}$ of $56\times1{\cdot}036\times10^{-5}$; and generally, if ϵ denotes the chemical equivalent of an element—that is, atomic weight $\div$valency—the electrochemical equivalent is $1{\cdot}036\times10^{-5}\epsilon$. Again, if a coulomb of electricity liberates $1{\cdot}036\times10^{-5}$ grms. of hydrogen per second, a ampères will liberate $1{\cdot}036\times10^{-5}a\epsilon$ grms. per second, and generally, *the number of grams of an element whose chemical equivalent is liberated by the passage of a ampères of electricity flowing for t seconds is* $1{\cdot}036\times10^{-5}\epsilon at$. If ϵ denotes the electrochemical equivalent of an element, such that $\epsilon=1{\cdot}036\times10^{-5}e$, the number of grams of an element whose electrochemical equivalent is ϵ liberated by the passage of a ampères flowing for t seconds is ϵat. It also follows that $1{\cdot}036\times10^{-5}A/n$ grms. of an n-valent element of atomic weight A, will be deposited per coulomb. By Avogadro's rule, a gram-molecule of a gas—of molecular weight M and N-atoms per molecule—occupies $22{\cdot}4\times10^3$ c.c. Hence $(22{\cdot}4\times1{\cdot}036\times10^{-2})/Nn$ c.c. of the gas are given off per coulomb. For a univalent gas with two atoms per molecule, $N=1$, $n=2$, and therefore 0·116 c.c. are obtained per coulomb at n.p.t., or 8·6193 coulombs are required per c.c. of gas. This corresponds with 0·4176 litre per ampère hour, or 2·3943 ampères are needed per litre of gas; or with 14·750 c. ft. are liberated per 100 amp. hours, or 67·798 amps. are needed per cubic foot of gas.

EXAMPLES.—(1) An electric current is passed simultaneously through the following solutions: Hydrochloric acid, ferrous sulphate, ferric sulphate, and silver potassium cyanide. If 5·2 litres of hydrogen at n.p.t. were evolved from the hydrochloric acid, how much metal would be deposited in the case of the iron and silver salts? Here 5·2 litres of hydrogen weigh 0·4664 grm. The chemical equivalent—that is, one gram—of hydrogen is equivalent to $\frac{1}{2}$ of $56=28$ grms. of ferrous iron; to 18·67 grms. of ferric iron; and to 108 grms. of silver. Hence, $0{\cdot}4664\times28=13$ grms. of iron will be deposited from the ferrous sulphate; 8·7 grms. from the ferric sulphate; and 50·1 grms. from the silver solution.

(2) A current of 0·04 amp. was passed through a solution of copper sulphate for $1\frac{1}{2}$ hrs. Hence, how much copper was deposited when the electrochemical equivalent of copper is 0·000329 grm.? There are 5400 seconds in $1\frac{1}{2}$ hrs., hence $0{\cdot}000329\times0{\cdot}04\times5400$ grms. of copper were deposited.

(3) A current of $2\frac{1}{2}$ amps. was obtained from a voltaic cell for $2\frac{1}{4}$ hrs. How much zinc was dissolved, given the electrochemical equivalent of zinc is 0·000337? Ansr. 6·8 grams.

(4) What are the electrochemical equivalents ϵ of hydrogen, of copper (cupric), and of zinc? Hydrogen, $1{\cdot}036\times10^{-5}\times1=0{\cdot}00001036$; copper, $\frac{1}{2}$ of $63{\cdot}5\times1{\cdot}036\times10^{-5}=0{\cdot}000329$; zinc, $\frac{1}{2}$ of $65\times1{\cdot}036\times10^{-5}=0{\cdot}000337$.

(5) In C. Höpfner's method (1900),[4] a solution of ferric and sodium chlorides is used as electrolyte and the copper passes into solution as cuprous chloride. Compare the quantity of electrical energy required to precipitate copper from Höpfner's solution, and from a solution containing copper sulphate. Here bivalent copper requires $2\times96{,}540$ coulombs for precipitating 63·57 grms., while univalent copper requires but 96,540 coulombs for precipitating the same weight of copper. Hence the precipitation of a given weight of copper from cuprous chloride requires but half the electrical energy as that required when cupric sulphate is used.

H. von Helmholtz (1881)[5] has emphasized the fact that the evidence indicates that electricity associates with the atoms of matter in multiples of one fundamental quantity, but never in fractions of it; these fractions may not be impossible, but they have not yet been found. Hence the evidence for the atomic nature of electricity is much the same as for the atomic nature of matter. The charge on a monad atom is therefore a natural unit of electricity. To illustrate the prodigious electrical capacity of the molecules, H. von Helmholtz estimates that if the opposite electricities were extracted from a milligram of water, and given to two spheres a mile apart, these two spheres would attract each other with a force of ten tons.

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§ 3. The Velocity of Electrolytic Conduction

> The conduction of electricity through electrolytes is utterly indistinguishable from metallic conduction except for the action at the electrodes which is not part of true conduction at all.—J. T. SPRAGUE (1892)

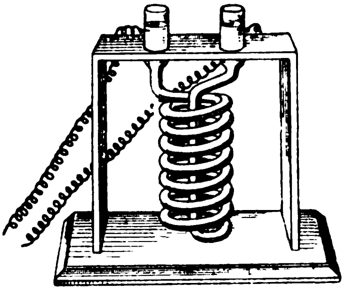

FIG. 3. — Velocity of Electrolytic Conduction.

An electric current travels through an electrolytic solution as quickly as if the same current were sent through a copper wire of the same resistance, and the products of electrolysis appear simultaneously at both electrodes, however far apart the electrodes be placed. N. M. Hopkins (1905)[1] passed a current through a tube 1500 cm. long, and through another tube 10 cm. long, and measured the time required for the current to pass by means of a chronograph sensitive to nearly 10,000 cm. per second. The tubes were filled with dilute sulphuric acid and fitted with electrodes—the anode of copper and the cathode of platinum. As soon as the current passed, bubbles of hydrogen appeared at the cathode simultaneously with the blue colour of copper sulphate at the anode. The electrolyte 1500 cm. long conducted as quickly as the electrolyte 10 cm. long. The experiment can be illustrated by the apparatus sketched in Fig. 3, which almost explains itself. The long spiral tube contains the electrolyte as in Hopkins' experiment. As soon as the circuit is closed electrolysis begins. As A. E. Dolbear puts it:

> If the two terminals of an electric circuit were on opposite sides of the Atlantic ocean, and a current were sent through the circuit, hydrogen would appear on one side and oxygen on the other . . . and in amounts defined by Faraday's laws of electrolysis.

Returning to Fig. 3, the known rates of diffusion of molecules in solutions are altogether too slow to allow the SO_4 which attacked the copper, to have come from the same H_2SO_4 molecule as the hydrogen liberated at the cathode. Further, it is supposed that the electrical energy used in electrolysis is entirely expended in overcoming the resistance of the electrolyte, and no measurable quantity of work is needed for tearing apart the components of the decomposing molecule. Hence, it follows that (i) **the molecules of an electrolyte in solution must be in a condition to conduct the electric current immediately the necessary electrical stress is applied to overcome the resistance of the liquid**; and that (ii) there must be either an exchange of partners among all the molecules of the liquid which take part in conducting the current, or else anions and cations exist in the liquid in the free state.

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§ 4. The Effect of the Solvent

Those bodies only are electrolytes which are composed of a conductor and a non-conductor.—W. A. MILLER.

Does the salt alone, or the water alone conduct the current; or is the conduction of the current shared between the solvent and solute; or does neither the salt nor the water alone conduct the current, but is the current carried by a hydrate which conducts and is decomposed by the current as a whole? The more care taken in the purification of water, the less does it conduct electricity, and consequently, it is assumed that pure water is a non-conductor in spite of the fact that perfectly non-conducting water has not yet been made. Pure dry liquid hydrogen chloride, like water, appears to be a non-conductor. A mixture of water and hydrogen chloride is an electrolyte. Hence, it is inferred that **the electrolytic conductivity of a solution is a joint property of solvent and solute, and not a property of either constituent alone.** Solutions of dry hydrogen chloride in some solvents—*e.g.* dry benzene or chloroform—conduct electricity so feebly, if at all, that they are said to be non-conducting; and solutions of some substances in water conduct no better than water itself—*e.g.* solutions of sugar or alcohol in water. Hence, also, it follows: **the electrolytic conductivity of a solution depends upon some specific relation between the solvent and the solute.** The same conclusion can be deduced in the following manner: If the solute—say copper sulphate—alone conducts the current in a cell with platinum electrodes, then copper alone will be deposited at the cathode, and the SO_4 at the anode decomposes the water forming sulphuric acid and liberating oxygen; *i.e. all the free acid appears at the anode.* If the water alone conducts the current oxygen alone appears at the anode, and at the cathode, hydrogen decomposes the copper sulphate forming sulphuric acid and depositing copper; *i.e. all the free acid appears at the cathode.* If water conducts $1/x$th and the solute conducts $(1-x)/x$th of the current, then the ratio of the free acid formed at the anode, to the free acid formed at the cathode, will be as $(x-1):1$. So far as observation shows, some free acid is always formed at both electrodes, and hence the conduction of the current is probably shared by the solvent and solute. The facts observed also fit the assumption that a hydrate or hydroxylic compound exists in solution, and this conducts and is decomposed as a whole.

In a general way, aqueous solutions of acids, bases, and salts conduct electricity, and these substances are often called electrolytes, not because the salt conducts the current, but because their aqueous solutions conduct the current electrolytically. Some fused salts conduct electrolytically, *e.g.* with fused silver chloride and silver electrodes, silver is dissolved at the anode and deposited on the cathode, so that the total amount of silver chloride is maintained constant; with carbon electrodes, silver is deposited at the cathode, and chlorine evolved at the anode.

It is usually stated that an acid or alkali is added to water in order that the latter may be decomposed into its constituent elements by the electric current. The function of the acid (or, *mutatis mutandis*, of the alkali) has been a subject of some speculation. (i) It has been said that the mere presence of the acid simply makes the water a conductor and that the water alone is decomposed by the current: $2H_2O=2A_2{}^{+}+O_2{}^{-}$; it has also been said that the acid alone is decomposed by the current, and that the water is attacked by the products of the electrolysis and chemically decomposed. Symbolically, $2H_2SO_4=2H_2+2SO_4$ (electrolysis) followed by $2SO_4+2H_2O$

$=2H_2SO_4+O_2$ (chemical). As a matter of fact, it is very doubtful if pure anhydrous acid or pure water is a conductor. Hence, it is not more logical to say that the acid makes the water a conductor than that the water makes the acid a conductor. Each constituent loses its individuality when mixed together. At first sight, it seems as if **during the electrolysis of acidulated water, the mixture must be regarded as a unit which (1) conducts the current from one electrode to the other; and which (2) suffers decomposition by electrical influences at the surfaces of the electrodes.** Several working hypotheses can now be devised—*e.g.* with dilute sulphuric acid, it is plausible to assume that the electrolyte contains the complex $H_2SO_4.nH_2O$. During electrolysis, neither the water nor the acid is decomposed, but rather the complex: $2H_2SO_4.nH_2O=2nH_2^{+}+nO_2^{-}+2H_2SO_4$. The action of the current is to deprive the complex of both hydrogen and oxygen in the proportions $2H_2 : O_2$.

In a general way it may be said that (i) electrolytic conduction is accompanied by visible decomposition, or (ii) polarization phenomena (*q.v.*) may appear. (iii) An assembly of metals at a constant temperature can give no current, but if an electrolyte be introduced into the series a current can be obtained. (iv) According to the electromagnetic theory of light, if a conductor be transparent it will probably conduct electrolytically, *e.g.* fused salts, hot glass, etc.

§ 5. The Ionic Hypothesis

Let us learn to dream, then perhaps we shall find the truth.—A. Kekulé.

In framing hypotheses we must see that they agree with facts; in other respects, they may be as inconceivable (not self-contradictory) as any fairy tale.—M. M. P. Muir.

The main facts so far established by the preceding discussion of the phenomena attending electrolysis may now be summarized:

(1) Electrolytes in solution conduct electricity, and the process of electrical conduction is attended by a splitting of the molecules of the solute into anions and cations; the anions appear at the anode, and the cations at the cathode. The separation of a certain number of anions at the anode is simultaneously attended by the separation of a chemically or electrically equivalent number of cations at the cathode. During electrolysis, the anions and cations appear to be discharged electrically, because electrically neutral molecules appear as secondary products of the electrolysis.

(2) The anion which separates at the anode is not necessarily derived from the same molecule as the cation which appears at the cathode.

(3) Solvent and solute together make a conducting medium, since as a rule neither solvent nor solute alone shows any marked capacity for conducting electricity.

(4) No measurable time is needed to put an aqueous solution in a condition to conduct the current. Immediately the necessary difference of potential appears at the electrodes the process of electrolysis begins.

(5) Osmotic pressure and related phenomena show that electrolytes in dilute solution have what seems to be a molecular weight, which suggests that the ordinary chemical molecule of the electrolyte dissolved in certain solvents is dissociated into two parts.

It is generally agreed that during electrolytic conduction there is a convection of electricity by the atoms of matter, but there have been differences of opinion as to the mode of transit of the atoms through the liquid:

(1) **The molecular chain hypothesis of C. J. T. von Grotthus** was generally accepted in the first half of the nineteenth century. In his *Théorie de la décomposition des liquides par l'électricité galvanique*, he (1805)[1] assumed that the molecules of salt in solution are distributed throughout the solvent in an irregular manner without any signs of orientation, as represented diagrammatically at *A*, Fig. 4. The molecules, in the presence of a pair of oppositely charged electrodes

range themselves in "chains," like little magnets. The positively charged ions—cations—are directed towards the negatively charged cathode, and the negatively charged ions—anions—to the positively charged anode, *B*, Fig. 4. If the charges on the electrodes are great enough, the molecules in immediate contact with the electrodes will decompose, *C*, Fig. 4, and the charge on one of the ions will be neutralized by the charge on the electrodes. And the other ion will unite with the neighbouring molecule and liberate an ion with a similar charge. The free ion attacks the next molecule, and so the process is continued throughout the "chain."

To fix the idea, consider the end of the molecular chain at the cathode. There, a negatively charged ion is set free when a positively charged ion is neutralized at the cathode. This "negative" ion associates with the adjacent molecule of the chain; this molecule decomposes, forming a new molecule, liberating, at the same time, a negatively charged ion which associates with the next molecule of the chain, *D*, Fig. 4. This successive decomposition and recombination goes on throughout the chain of molecules from electrode to electrode. The new molecules so formed turn about, and are again ranged in a "chain" resembling *B*, as shown at *E*, Fig. 4. A cycle of changes of this nature is supposed to be going on all the time the current is passing through the electrolyte.

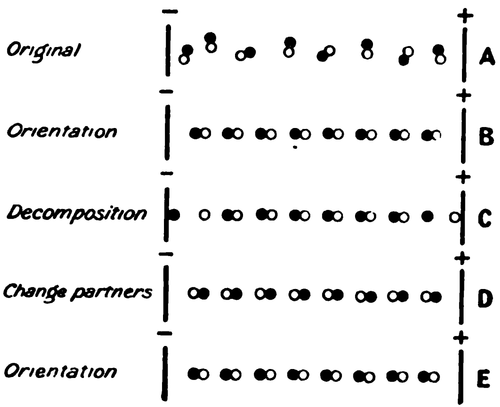


Fig. 4.—Diagrammatic Representation of C. J. T. von Grotthus' Chain Hypothesis.

C. J. T. von Grotthus' mechanical interpretation of the phenomenon is very ingenious, and it satisfactorily explained the facts known in his day, but later knowledge has shown that the hypothesis is not tenable in its original form. If the electricity be conducted by *Grotthus' chain*, no current can flow until the electromotive force driving the energy is equivalent to the energy represented by the heat of formation of the molecules undergoing decomposition *in the solution*. When a sufficient electromotive force is applied at the electrodes, the decompositions and recompositions of the molecules might proceed in the way described by Grotthus. No such critical electromotive force, however, has been found to be necessary for the passage of a current through electrolytic solutions. In H. von Helmholtz's air-free cell,[2] polarization is produced by an infinitesimal element, but no permanent leakage of electricity goes on through the cell until the applied current attains a certain voltage. The smallest electromotive force hitherto tried causes a current to flow when it is applied to copper electrodes immersed in a solution of copper sulphate. The total energy consumption is then nothing but that due to the "resistance" of the cell. Again, solutions of electrolytes, like metallic wires, conduct electricity in such a way that the rate at which electricity passes through the system is proportional to the electromotive force. This is true whatever be the magnitude of the force, and consequently, if a certain amount of electrical energy be expended in breaking up the molecules, this proportionality cannot obtain. Hence, very little electrical energy can be expended in breaking up the dissolved molecules into their respective ions, and it has therefore been urged that "the ions cannot be held together by a force of finite value." Consequently, in the homogeneous electrolyte without polarization no hypothesis which involves the tearing of the molecules asunder against the chemical binding forces can be admitted; there is no chemical cling of the atoms, but only a frictional rub. Otherwise, those electrolytes whose atoms or radicles are held together by the weakest attractions would most readily decompose electrolytically. This is by no means the case. For instance, mercuric chloride is much less stable than sodium chloride, and yet the latter is much more readily decomposed by an electric current.

G. F. Fitzgerald[3] has pointed out that the difficulty with Grotthus' hypothesis can be overcome if it be assumed that when the molecules are polarized, they draw one another apart at a rate proportional to the polarization. This at once makes the relation between electric force and decomposition a linear one, and so satisfies Ohm's law in the case of small currents. It also so far agrees with Clausius's hypothesis that it explains electrolysis and double decomposition as properties of the same kind. The molecules in a liquid will occasionally be arranged by accident in a proper polarized condition in a closed circuit for drawing one another apart; and if the circuit includes molecules of different kinds, there will result double decomposition. He added:

> The supposition that it is a particular arrangement that is required before exchanges take place, and that with this arrangement exchanges take place of their own accord, seems to explain electrolysis and double decomposition without supposing free atoms to exist within the liquid.

(2) **The electrostatic strain hypothesis of H. von Helmholtz.**—Here it is assumed[4] that each kind of matter has a specific attraction for electricity—some kinds for positive, other kinds for negative; that accordingly, work must be done to separate one atom from its electrical charge, or to remove electricity from an atom of high specific attraction and give it to another lower in the scale. Further, the chemical affinity is mainly due to the electrical attraction of oppositely charged atoms, and that when such atoms combine into a compound molecule, they do not discharge into each other, but retain their charge. During electrolysis, work is done, not in tearing the atoms asunder, but in tearing their electrical charges from them.

(3) **The ionization hypothesis of R. Clausius.**—As a trial hypothesis it may be assumed that the mere presence of the solvent leads to the fission of the molecules of the electrolyte into sub-molecules, each of which is charged with a definite amount of positive or negative electricity equivalent to 96,540 coulombs per chemical equivalent. The solution does not itself appear to be electrically charged, and hence it is assumed that equal quantities of positive and negative electricity are developed by the rupture of the molecules of the electrolyte during the process of solution. Solutions of electrolytes are supposed to normally contain a definite proportion of the sub-molecules charged with electricity. By a modification of M. Faraday's definitions the "sub-molecules" are called ions, and consequently: **ions are atoms or groups of atoms which carry a positive or negative charge of electricity, and they are formed by the dissociation of the electrolyte in the solution. Each molecule, on dissociation, furnishes two kinds of ions with equal and opposite charges of electricity.** Consonant with M. Faraday's work, it is further assumed that each monad ion carries a definite charge of electricity (96,540 coulombs); each dyad ion, two such charges; a triad ion, three such charges; etc.; but never a fraction of such a charge. To avoid confusing the phenomenon of dissociation, in which the products are not charged electrically, with the dissociation of a molecule into electrically charged ions, the term **ionization** is reserved for the latter phenomenon. The ionization of hydrochloric acid is represented in symbols: $HCl \rightleftharpoons H^{\cdot} + Cl'$; and of sodium chloride: $NaCl \rightleftharpoons Na^{\cdot} + Cl'$.

A. W. Williamson's theory of the continuous interchange of the atoms of the molecules of a compound was suggested in 1850, and it was followed in 1857 by R. Clausius' suggestion that the molecules of the solute are ionized when dissolved in the solvent, but R. Clausius appears to have assumed that *only an infinitesimally small fraction of the total number of dissolved molecules are so ionized.* As the ions are discharged at the electrodes during electrolysis, more molecules are ionized. The un-ionized molecules keep the electrolyte constantly supplied with a definite number of ions. The ions conduct the current; the "undissociated" molecules are inactive. Further, at any given temperature, there is a constant relation between the number of un-ionized molecules, and the number of ions. S. Arrhenius (1884), more bold or less cautious than R. Clausius, asserted that *a considerable fraction of the dissolved molecules are ionized, and that the number of ions increases more and more as the solution becomes more and more dilute.* W. Ostwald, J. H. van't Hoff, W. Nernst, and a large number of other workers have followed the logical consequences of Arrhenius' hypothesis in a great many directions; the results, on the whole, have been satisfactory, and the theory has thus stimulated the study of the properties of solutions in a remarkable manner. Some hold that the great cloud of subsidiary hypotheses which is needed to make the ionic theory presentable, serves also to obscure progress towards a more satisfactory view of the nature of solution. It is also maintained that the " principle of exhausting hypotheses " has not been followed, and that the favoured child—the ionic hypothesis—has grown into a tyrannical master; for instance, G. F. Fitzgerald (1896) has said that " the supposed advantage of the free ion theory is not only illusory but misleading." If this be a correct diagnosis of the ionic hypothesis we have some consolation in H. Davy's words: " The destruction of an error hardly ever takes place without the discovery of truth."

At first sight the ionic hypothesis appears so incredible and so opposed to the instinct, common sense, or prejudices of the chemist that it has been assailed by much wholesome criticism—particularly by H. E. Armstrong. For instance, it is asked:

1. *In view of the great chemical activity of metallic sodium in contact with water, is it profitable to postulate the existence of the element sodium in contact with water without chemical action?* This objection is said to " rest on a misunderstanding," because *electrically charged* ions of sodium in an aqueous solution of sodium chloride are very different from *neutral atoms* of metallic sodium. The ions of sodium carry large charges of electricity. It is urged that " chemists know practically nothing about the properties of atoms carrying large charges of electrical energy," and also that " the chemical activity of an atom of sodium charged with its 96,540 coulombs of electricity is much less than a neutral atom of sodium." In other words, the presence of the electrical charge on the sodium ion keeps the ordinary chemical activities of the atom in abeyance. This means that whenever a chemical difficulty arises in the application of the ionic hypothesis the assumption is made that " neutral atoms or atomic groups and ions are different substances," because the properties of a substance are determined as much by the energy it contains as by the kind of matter. In this way, the ions have been invested with such imaginary properties as may be needed to keep the ionic hypothesis consistent with facts.

2. *Compounds like mercuric chloride, very prone to thermal dissociation, are not readily ionized; while compounds like calcium chloride which resist thermal dissociation are readily ionized. Would not the ionic hypothesis predict the converse phenomena?* Mercuric chloride is very volatile and readily dissociates into its elements by heat; calcium chloride, on the contrary, does not readily volatilize or dissociate except at very high temperatures, yet it is said that the latter is readily ionized in solution while the former remains all but unchanged. Here again it is said that totally different phenomena are confused, and that the forces which produce ionization are quite different from those which produce thermal dissociation.

3. *Bodies carrying electrical charges of opposite sign are attracted and cling to one another; if therefore a mobile solution contains "free and independent" ions carrying enormous electrical charges of opposite sign, how can the charged ions remain more than momentarily free?* It is assumed that a certain proportion of the molecules of the solute are continually breaking down into free (charged) ions, and a certain proportion of the ions are continually recombining to form ordinary molecules, the result is, that the ratio between the number of free ions and paired ions (molecules) remains unchanged. This statement, of course, does not answer the perplexing question. Attempts have been made to refer the difficulty to the specific insulating

properties—the so-called dielectric constant—of the solvent. The action of the solvent has been compared with the function of the glass in a charged Leyden jar. This agrees with the non-conducting qualities of pure water, but experiments have shown that the relation between the insulating properties of a solvent and its ionizing properties is not an adequate and sufficient explanation of the observed facts. The two phenomena do not always vary concomitantly. A satisfactory answer to the question, therefore, has not yet been found.

4. *If an ionized salt, say, sodium chloride, is present in solution as a mixture of $Na^\cdot$ and Cl' ions, it might be thought possible to separate the two components by diffusion or by some other mechanical process.* When the molecules of certain gases—hydrogen, chlorine, etc.—exist free in a liquid, they will escape; but when, say, sodium chloride is ionized: $NaCl \rightleftharpoons Na^\cdot + Cl'$, it is said that the chlorine ions do not escape because of their electrical charge. S. Arrhenius also says that the great electrostatic attraction of the oppositely charged ions prevents any marked diffusion. W. Nernst, however, has shown that the concentration currents produced when, say, a solution of sodium chloride is carefully covered with a layer of water, leads to the conclusion that the greater mobility of the chlorine ions charges the upper layer negatively, and the lower layer positively, so that a current of electricity can be obtained by placing the two layers in electrical contact. R. C. Tolman (1911) whirled aqueous solutions of iodides—sodium iodide, potassium iodide, hydrogen iodide, etc.—in tubes in a powerful centrifugal machine, and found that the two ends of the tubes acquired charges of opposite sign. The extreme ends of the tubes acquired a negative charge presumably because of the accumulation there of the heavier positively charged iodine ions; and the opposite ends of the tubes acquired a positive charge presumably owing to the slight excess of positively charged sodium ions at that end. There is the possibility that the electrification of the tube was due to the friction against air.

5. *Salts which form solid compounds with two or more different amounts of water of crystallization have different solubilities in their different forms. Hence it is asked: Is it not more reasonable to assume that the molecules of the solute exist in solution as definite hydrates?* The ionic hypothesis answers: Only a definite fractional part of the salt is ionized, and this part is proportionally less, the more concentrated the solution. As a rule, in a saturated solution, only a small proportion of the solute is ionized. A similar observation applies to the existence of liquid crystals. This does not preclude the possibility that the un-ionized molecules and the ions are themselves hydrated.

6. *When a compound is formed from its elements with the loss of energy, the compound cannot be resolved into its elements unless energy be supplied. It is therefore pertinent to inquire: What is the source of the energy which leads to the fission of the molecule into ions carrying equal but opposite charges of electricity?* Here, again, it is necessary to reiterate that the ionic hypothesis refers not to the separation of a compound into its original constituents, but into charged ions; and it is interesting to observe that molecules of sodium chloride, etc., which appear to be very stable when dry, react with great facility when in solution. A little heat is supposed to be evolved during the ionization of many (not all) electrolytes, and the process of ionization is then presumably accompanied by an exothermal reaction which more than compensates for the energy needed for the fission of the molecule into oppositely charged ions.

There are also hypotheses which suppose ionization occurs by *collision.* G. T. Beilby (1905) considers that the ionization is essentially a mechanical operation, the result of the kinetic activity of the solute molecules, for in a dilute aqueous solution of, say, hydrogen chloride, each molecule of the solute is surrounded by and "at the mercy of" some millions of water molecules, all in a state of intense activity, and the rude mechanical jostling to which the molecule of hydrogen chloride is subjected will naturally tend to break it up into simpler portions mechanically more stable. J. Kendall[5] made a similar suggestion, but B. de Szyskowsky and J. Perrin regard this hypothesis as untenable—the latter says *la probabilité de rupture d'une molécule ne dépend pas des chocs qu'elle subit.*

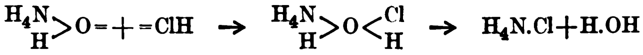
W. Nernst and J. J. Thomson have found that the ionizing power of a solvent is related with its specific inductive capacity or *dielectric constant* as indicated in the chapter on "Water." W. Nernst has pointed out that water has a higher specific inductive capacity than other liquids, and that liquids like methyl alcohol, formic acid, and others, which, as solvents, give solutions having electrolytic conductivity also have high specific inductive capacities. From this it is argued that the dissociating power of a solvent, or its power of producing ions, is greater the greater its specific inductive capacity. C. B. Thwing's numbers show that the dielectric constants, K, of the hydrocarbons and non-asssociated liquids approximate to $K=2{\cdot}6D$, where D is the specific gravity. Other liquids, particularly those which contain hydroxyl groups, have higher values than correspond with this rule, and H. Crompton has shown that if i be the association factor, C. B. Thwing's data can be represented by $K=2{\cdot}6Di^3$, or $i=\sqrt[3]{(K/2{\cdot}6D)}$, where the values of i so obtained run quite parallel with the values obtained by I. Traube, but are a little higher. R. Abegg also showed that the temperature coefficient of the dielectric constant is very small for non-associated liquids—there is only a slight change between 15° and $-80°$ for toluene and ether, but with other liquids there is a larger change as the temperature is lowered, probably due to increasing density and increasing association—with ethyl and amyl alcohol, and acetone, the change is quite marked. H. Crompton therefore argues that it is almost impossible to doubt that association plays an all-important part in determining the specific inductive capacity of a liquid, and that if there is any connection between specific inductive capacity and the power of ionization, it may be looked for rather in the fact that electrolytes are solutions of approximately non-associated salts in an associated solvent than in there being any peculiar ionizing power attaching to the solvent. According to P. Dutoit and E. A. Aston, and P. Walden, the association of the solvent may in turn be referred to the unsaturated character of the molecules of that menstruum. H. Crompton added: The supposed decrease in electrolytic dissociation with rising temperature is also accounted for, and means nothing more than the decrease in the association of the solvent. What has been termed the ionic fluidity of a given solution no doubt increases continually with rising temperature, and, therefore, up to a certain point, the conductivity increases. But the association of the solvent is also continually decreasing, and in the end this effect will become the more powerful, the conductivity, therefore, never rising above a certain maximum value. This explains the maximum in the molecular conductivity with rising temperature, first noticed by S. Arrhenius.

G. Ciamician (1890) attributed ionization to the *attraction between the solvent and the positive and negative parts of the salt.* The idea is supported by the fact that those solvents which ionize readily are the very ones which unite readily with the salts as water of crystallization, alcohol of crystallization, etc. Again, not a great many salts whose ions are univalent separate with water of crystallization while those with ions of higher valency nearly always do. This is taken to mean that possibly univalent ions are less hydrated than those of higher valency. This corresponds with experiments on the speeds at which ions move through the solvent—univalent ions generally travel faster than the bivalent ions, and the latter in turn go faster than tervalent ions. However, this evidence is inconclusive, since it does not follow that because such compounds separate from a solution therefore these compounds exist in solution. J. D. van der Waals (1891) expressed a similar idea and considered that the heat of hydration of the ions furnished the energy needed for the ionization of the salt. To this, D. Konovaloff (1893) adds, "only those solvents which react chemically with the solute furnish solutions which conduct electricity," and R. Abegg (1899) expressed it, "the degree of ionization depends upon the capacity of the ions to unite with the molecules of the solvent."

In the early days of the ionic hypothesis it was assumed that the solvent acts like a passive medium preventing the re-combination of the ions ; and it came as an antithesis to the so-called hydrate theory in which the solvent was regarded as intensely active, and formed complex molecular systems with the solute. The one hypothesis assumes that simplification (ionization) precedes chemical combination, the other assumes that complication (association) precedes chemical action. The accumulation of new facts rendered it necessary for the former to borrow from the latter, so that "the hydration of ions in aqueous solutions is admitted by almost all advocates of the ionic theory." It was A. Kekulé who, in his *Ueber die Constitution und die Metamorphosen der chemischen Verbindung* (1858), emphasized that molecular coalescence is a preliminary condition for many reactions ; the complex may then undergo a reversible change ; molecular re-arrangement ; or it may dissociate into more stable components. In the reaction between ammonia and hydrogen chloride water plays an essential part, here the molecular coupling is probably dependent on unsaturated valencies of water and ammonia ; it has been suggested that the water first reacts with the ammonia :

$$H_3N{=}+{=}OH_2 \rightarrow H_3N{=}OH_2 \rightarrow NH_4OH$$

and that the acid and base then react either through their ions or molecularly :



$$\substack{H_4N\\H}\!>\!O{=}+{=}ClH \rightarrow \substack{H_4N\\H}\!>\!O\!<\!\substack{Cl\\H} \rightarrow H_4N.Cl+H.OH$$

With water and calcium oxide $CaO{=}+{=}OH_2 \rightarrow CaO{=}OH_2 \rightarrow Ca(OH)_2$. The same view was emphasized by J. H. van't Hoff in 1878, and by H. E. Armstrong in 1891. The addition compound brings together elements, previously separate, into one common sphere of activity within which it is possible for them to interact. J. Kendall and J. E. Booge now consider ionization to be preceded by a combination between solvent and solute. Any unsaturated solvent possesses the power of forming complexes with itself by association and also with any unsaturated solute. It is assumed that the attractive forces holding together the radicles of the solute are now so diminished that ionization can take place. The union of the solute with molecules of the solvent thus promotes ionization, or the dissociation of the complex into radicles of opposite charge. They add :

> The mechanism of the electronic hypothesis of J. J. Thomson, G. N. Lewis, W. A. Noyes, etc., is based on the assumption that an unsaturated molecule contains electrons not rigidly fixed but free to move under the influence of an electric field—*e.g.* the oxygen atom in a water molecule has at least two electrical doublets $H^+ \rightarrow {}^-O^- \leftarrow {}^+H$, which can move into such a position or orbit as to exert a maximum attraction on the positive part of the doublet, thus producing an unequal distribution of the electrical charges. When two such molecules come into close proximity, this inequality will be greatly accentuated, and the mutual attraction may be sufficient to enable complex molecules to be formed by association. The associated molecule possesses a larger electrostatic moment, and the constraints on the electrons are accordingly weakened. The higher the degree of association, the larger the electrostatic moment, the weaker the constraints holding the charges, and the higher the dielectric constant. Such associated molecules may exert considerable attractive forces on the molecules of a solute especially when the latter also furnish strong fields of electric force. As a result, the complex may be much less stable than the simple component molecules, and dissociation occurs.

In conformity with the hypothesis that the formation of complexes between solvent and solute is the immediate cause of ionization, J. Kendall, J. E. Booge, and J. E. Andrews found that conducting solutions invariably afford evidence of the formation of complexes—*e.g.* the formation of stable hydrates is characteristic of strong acids, and the less the strength of the acid, the less the tendency to form stable hydrates. There is no indication of hydrate formation with weak organic acids unless the acid has also the character of a phenol base. Similar remarks apply to the bases. In general, therefore, there is a uniform increase in the ionization with the acids and bases most readily hydrated.

The proposition has not yet been established with salts, although A. Werner states that the stability of an aquo-salt decreases as the strength of the acid or base increases; but R. Abegg and G. Bodländer hold that salts of weak acids and bases are most extensively hydrated. With the mercuric salts also, all the highly ionized salts yield hydrates, and all slightly ionized salts are not hydrated. If ions are formed at all they are complexes formed by association with the molecules of the solvent. The ionic theory primarily assumes that the apparent *number* of solute "molecules" is increased by ionization, and in a general sense it may be said that it makes very little difference to the applications of the ionic theory whether it be assumed that each ion is isolated as a distinct individual, or whether each ion forms a complex with the molecules of the solvent. The number of ions is the same in both cases.

The explanation of the phenomena, particularly when solutions other than water are considered, is beset with many difficulties on account of the complex relations between the solvent and solute. So much is this the case that M. le Blanc (1907) considered "it to be very fortunate for the advance of electrochemistry that such complications are generally, though not always, absent in the case of the aqueous solutions. It is due to this fact that it has been possible to deduce simple laws from the study of aqueous solutions." On the other hand, O. N. Witt (1901) has said:

> Water is a very complicated substance, and the process of solution in that liquid must be attended by very great exceptions from the simple rules which exist for other solvents, not so complicated. It has therefore been a great mistake to study aqueous solutions and then other solutions. The chapters in treatises on physical chemistry entitled "Theory of Solution" should be rightly entitled "Theory of Aqueous Solution."

Several attempts have been made to work out a consistent explanation of the fundamental facts without a theory of charged ions, but with hypotheses based upon the formation of imaginary molecular complexes by a reaction between polymerized solvent and the molecules of the solute.

These controversial matters emphasize the fact that an explanation of a phenomenon may contain part of the truth, and yet not "the whole truth, and nothing but the truth." In that case, we try the hypothesis by the test indicated in the first chapter, and ask: Is the hypothesis useful? The answer is that the ionic hypothesis has done good work, and it promises to do more. An hypothesis is not always to be discarded as a first approximation, because troublesome exceptions crop up from time to time. Newton's theory of gravitation, for instance, appeared to be afflicted with such blemishes—particularly in its early days; so was the theory of opposing reactions once considered to be unreasonable folly; and the present-day theory of light seems highly absurd when it is remembered that it is based upon the existence of an æther pervading all space, an æther which is of the highest elasticity, and denser than steel. In spite of important difficulties, we shall try how the ionic hypothesis fits in with a few important phenomena.

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§ 6. The Electrolytic Conductivity of Solutions

> In electrolytic conduction, the electricity does not slip through between the molecules, it goes with them. The constituents of each molecule are free from one another, and while one set of atoms conveys positive electricity, the other set conveys negative electricity in the opposite direction, and so it is by a procession of free atoms that the current is transmitted. The atoms act as carriers. The free locomotion of charged atoms is essential for electrolysis.—O. J. LODGE (1892).

The process of electrolysis, according to the ionic hypothesis, is supposed to proceed somewhat as follows: When a salt—say, sodium chloride—is dissolved in water, (i) some of the dissolved molecules are, by hypothesis, ionized, and the ions immediately begin to recombine to form molecules. The speeds of the two reactions are supposed to behave analogously with those of opposing reactions, and a state of equilibrium is reached when the number of molecules reformed by the combination of the ions is equal to the number of molecules ionized in the same time. Still further, (ii) when the two poles of a battery—say platinum electrodes—are dipped in a solution of sodium chloride, all the chlorine ions, carrying a negative charge, are attracted to the anode or positively charged electrode, and the positively charged sodium ions are attracted to the cathode or negatively charged electrode. If a constant difference of potential be maintained between the electrodes of the battery, as each ion comes in contact with the electrode with a charge of opposite sign to its own, the charge is torn from the ion which thereby reverts to an ordinary atom of chlorine or sodium. The battery reproduces the same difference of potential as before by generating more electricity; this is again discharged at the electrodes; and so, by an alternate process of charge and discharge, electrolysis continues. (iii) The chlorine atoms, being unable to attack the water or the electrode, unite in pairs to form molecules of chlorine gas. As soon as the liquid in the vicinity of the anode is saturated with chlorine, this gas bubbles to the surface of the liquid. Similarly, the sodium ions are relieved from their charges at the cathode, and the resulting sodium atoms immediately attack the water, forming hydrogen gas and sodium hydroxide: $2Na+2H_2O=2NaOH+H_2$; the hydrogen bubbles off as a gas. (iv) The equilibrium between the un-ionized molecules and the ions is disturbed by the annihilation, so to speak, or the removal of ions at the electrodes. The difference of potential at the electrodes is maintained by the battery, and the supply of ions is kept up by the steady ionization of the salt as fast as the ions are de-electrified at the electrodes, until practically the whole of the salt in the solution has been electrolyzed. The charges drag the atoms to the electrodes, and only at the electrodes can the charges be torn from the atoms. Thus A. Smith (1890) said that "the ions do not transport the electricity of the battery, but their own." The charged ions are already present in the solution before connection is made with the battery.

Usually, the electrical conductivity of a solution is measured indirectly. The resistance which the solution offers to the passage of a current is directly measured. It is more convenient to take the reciprocal of the resistance and call it the conductivity of the solution. The **specific resistance** is first determined, that is, the resistance in ohms which is equivalent to the resistance of a cubical mass of the solution whose length of side is 1 cm., Fig. 5. The reciprocal of this quantity in *reciprocal ohms*, is the specific conductivity. Hence the **specific conductivity**, κ, represents the current in ampères which is produced in a cube of one centimetre side when a potential difference of one volt is applied to the opposite faces of the cube. From this, the so-called equivalent conductivity—symbolized λ—is calculated. **The equivalent conductivity of a substance represents the conducting power of one gram-equivalent of the substance dissolved in the solvent, and placed in a cell whose opposite walls, one centimetre apart, form the electrodes.** Otherwise expressed, the equivalent conductivity represents the conducting power of a layer of the solution 1 cm. thick, and containing one gram-equivalent of the substance in solution; or, **the quantity of electricity which, under a potential difference of one volt, passes per second between electrodes of indefinite extent, and one centimetre apart, between which is placed that quantity of solution which contains one equivalent weight of the ionizing substance.** If the conductivity be referred to a gram-molecule, and not a gram-equivalent, it is termed the **molecular conductivity** of the solution—symbolized μ.

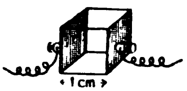

FIG. 5.

C. J. Reed[1] has pointed out the need for emphasizing the fact that electrical conductivity is a property of matter like transparency, diathermacy, magnetic permeability, and heat conductivity. The electrical conductivity of different substances is measured or compared by employing a unit in which there is a definite section across which the flux is measured, and a definite length in the direction of the flux. Units of this kind are defined by certain relations of form, in which the ratio of length to cross-section is a fixed ratio. He applies the terms *conductance* and *resistance* to bodies of definite form, length, and cross-section, while the terms *conductivity* and *resistivity* refer to properties of matter independent of shape, or form, or quantity. Conductivity is therefore specific conductance; and resistivity is specific resistance. The two ideas, however, are commonly merged in the one term conductivity or resistivity as the case might be.

When an electric current is passed through a cell composed of two metallic electrodes and an electrolyte, the total opposition to the passage of the current is made up of the resistance of the cell and the back electromotive force at the electrodes, which latter is the sum of the over-voltages at the two electrodes. The resistance of the cell is made up of the resistance of the electrolyte and the transfer resistance from electrode to electrolyte. The transfer resistance has been particularly studied by E. Newbery, etc.[2] The conditions which favour high transfer resistances are (i) low current density; (ii) low temperature; (iii) polished electrode surfaces; and (iv) high over-voltages.

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§ 7. The Number of Ions in a Solution

The greater the number of ions in a liquid the better is the liquid likely to conduct electricity.—O. J. LODGE (1892).

If water be progressively added to an aqueous solution of hydrogen chloride. containing, say, one gram-equivalent (36·5 grams) per litre, at 18°, the equivalent conductivity of the solution gradually increases as illustrated by the following numbers, when v denotes the number of litres of solution containing one gram-molecule of the solute, and λ the corresponding equivalent conductivity :

$v=$	2	8	16	32	128	512	1024
$\lambda=$	305·4	328·5	331·5	342·3	349·1	349·3	349·3 units

These numbers show that the electrical conductivity of the solution increases until a certain limit is reached. Subsequent additions of water have no further influence on the equivalent conductivity of the solution. This is further emphasized by the curve, Fig. 6, which represents the rapid rise in the equivalent conductivity of sodium chloride solutions with decreasing concentration ; the conductivity reaches a maximum very quickly, when the further additions of water have no further influence on the result. Hence **the equivalent conductivity of an electrolytic solution increases with dilution, reaching a maximum value approximately corresponding with infinite dilution.** This fact is called **F. Kohlrausch's first law.** When the dilution has reached the limit beyond which no further increase in the equivalent conductivity can be observed, it is supposed that the salt is all ionized, and no more ions can be supplied by the solute, however much more solvent be added. All the ions which can be obtained from the solute take part in conducting the electric current at infinite dilution.

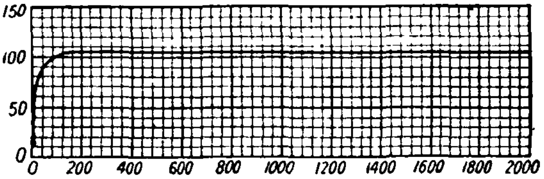

FIG. 6.—Effect of Concentration on the Equivalent Conductivity of Aqueous Solutions of Sodium Chloride.

The determination of the electrical conductivity of a solution.—Let R denote the resistance of the solution expressed in ohms. The cell containing the solution—the *conductivity cell*—is arranged as illustrated in the sketch and plan, Fig. 7, with a known resistance R (ohms) in the box of resistance coils ; a " metre " wire of known resistance ; a telephone, T ; a battery, B ; an electrolytic cell of resistance, S ; a key, K, for starting the current from the battery ; and an induction coil, N, which furnishes a rapidly alternating high potential current. It may be asked : How can there be anode and cathode when working with an alternating current ? If the impulse in one direction of the alternating current cannot bridge the gap between

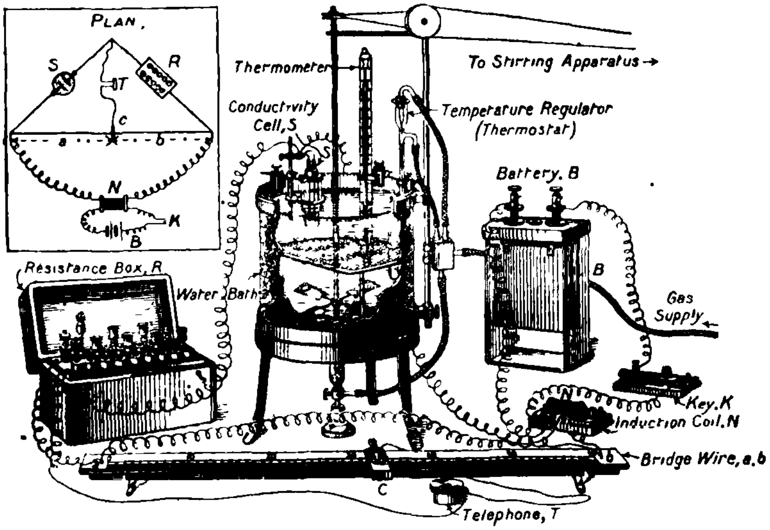

FIG. 7.—The Determination of the Electrical Conductivity of Solutions.

the electrodes, and the impulse in the other direction can, the general effect is that of an intermittent current in one direction. If the sliding contact of the bridge, C, be moved until the telephone is "silenced"—that is, makes least noise—the resistances on both sides of the system are in equilibrium. The readings are most accurate when the resistance R is so adjusted that the contact C is near the middle of the bridge. From the principle of Wheatstone's bridge—discussed in text-books on electricity—it follows that $S : R = a : b$, where a is the resistance of the bridge wire on the same side as the resistance R, and b the resistance of the wire on the other side. If the wire be 1000 mm., that is, one metre long, $b = 1000 - a$. Consequently,

$$\text{Observed conductivity} = \frac{1}{S} = \frac{b}{Ra} \text{ rec. ohms} \quad . \quad . \quad . \quad (1)$$

The specific conductivity—the reciprocal of the specific resistance—must be proportional to the observed conductivity, or, the specific conductivity is k times the observed conductivity, where k is the constant of proportion. Consequently,

$$\text{Specific conductivity} = \frac{k}{R} \cdot \frac{1000 - a}{a} \text{ rec. ohms} \quad . \quad . \quad . \quad (2)$$

The observed conductivity depends upon the *capacity of the cell* employed, and this, in turn, depends upon the *surface area* and the *distance apart* of the electrodes. If these two magnitudes are known, it is possible to compute the specific conductivity of the solution from the observed conductivity. It is simpler, however, to determine the **constant of the cell** employed, by using a solution of known conductivity. All the factors, except k, are then measured, and k is calculated from (2). With the same cell, the conductivity of the given solution can be determined and the specific conductivity computed by (2).

In illustration, the specific conductivity of a $\frac{1}{10}N$-solution of potassium chloride at 18° is 0·0112. With a resistance of 10 ohms, the telephone was silenced when $a = 535$ mm. Hence, from (2), $0{\cdot}0112 = (k/10)(1000 - 535)/535$; or $k = 0{\cdot}1289$. Hence, for this particular cell, the specific conductivity $= 0{\cdot}1289(1000 - a)/Ra$ rec. ohms; with a $\frac{1}{10}N$-solution of potassium chloride for which $a = 490$, when $R = 12$, the specific conductivity $= 0{\cdot}1289(1000 - 490)/12 \times 490 = 0{\cdot}011199$ rec. ohms. If v denotes the number of cubic centimetres containing one gram-equivalent of the compound under investigation, the quotient obtained by dividing the specific conductivity by v will represent the specific conductivity of the $\frac{1}{10}N$-potassium chloride at the dilution v, hence, since a $\frac{1}{10}N$-solution of potassium chloride has one-tenth of a molecular weight of the salt expressed in grams per litre, one gram-molecule will be present in 10 litres, or $v = 10{,}000$ c.c., and, since κ denotes the specific conductivity, the equivalent conductivity κ/v will be $0{\cdot}011199/v$, or 111·99.

During the measurements, the conductivity cell must be kept at a constant temperature since the conductivity varies with changes of temperature. Hence, the need for the water-bath, stirrer, and thermostat (temperature regulator) shown in Fig. 6. If the conductivity of the solution be large, a form of cell is employed with electrodes further apart than is the case with the cell shown in the diagram for solutions of feeble conductivity. Details are discussed in any laboratory handbook.[1] It is becoming increasingly clear from the work of E. Newbery, S. F. Acree, etc., that this method of measuring conductivity can be made much more sensitive and accurate by directing attention on the nature of the electrodes, and the frequency of the alternating current.

It is now assumed that **the number of ions which take part in conducting the electric current at any particular concentration of the solution is proportional to the equivalent conductivity, λ, of the solution.** If the number of ions in a given solution be doubled, the conductivity will be doubled. Consequently, if α represents the fraction of a gram-equivalent which is dissociated into ions when the solution occupies v litres, we have, at dilution v, the conductivity $\lambda_v = k\alpha$, where k is the constant of proportion. At infinite dilution, the whole gram-equivalent is supposed to be ionized, and consequently, $\alpha = 1$, and therefore the conductivity, λ_∞, at infinite dilution, is $\lambda_\infty = k$. Substitute this value of k in the preceding equation, and we get

$$\alpha = \frac{\lambda_v}{\lambda_\infty}$$

which, by hypothesis, means that **the fractional number of molecules ionized in a solution is numerically equal to the equivalent conductivity of the solution divided by the equivalent conductivity of the solution at infinite dilution**; or,

$$\text{Degree of ionization, } \alpha = \frac{\text{Number of molecules ionized}}{\text{Total number of molecules}} = \frac{\lambda_v}{\lambda_\infty}$$

This formula enables the electrical conductivity of a salt to be expressed in terms of the degree of ionization of the salt in solution. Thus, the equivalent conductivity of a solution of hydrochloric acid is 305·4, and the same acid at infinite dilution has the equivalent conductivity 349·3. Hence, the degree of ionization is $305\cdot4 \div 349\cdot3 = 0\cdot874$ per gram-equivalent, or 87·4 per cent. ionization. This means that 12·6 per cent. of the molecules of the solution are present as un-ionized neutral molecules, HCl; and 87·4 per cent. of the molecules are present in the ionic form $\text{H}^{\cdot}+\text{Cl}'$. Or,

$$\underbrace{\text{HCl}}_{12\cdot6\text{ per cent.}} \rightleftharpoons \underbrace{\text{H}^{\cdot}+\text{Cl}'}_{87\cdot4\text{ per cent.}}$$

The **percentage ionization** must not be confused with the **absolute concentration of the ions.** The former may be the greater in dilute solutions, and the latter greater in concentrated solutions. The ionic hypothesis thus assumes that an aqueous solution of hydrochloric acid contains three distinct kinds of "solute molecules," electrically charged molecules (hydrogen and chlorine ions), and neutral hydrogen chloride molecules.

Table I shows the degree of ionization of normal solutions (unless otherwise stated) of a few typical acids, bases, and salts selected merely for illustrative purposes.

TABLE I.—DEGREE OF IONIZATION OF SOME TYPICAL ACIDS, BASES, AND SALTS.

Acids.		Bases.		Salts.	
Acid.	Fraction ionized.	Base.	Fraction ionized.	Salt.	Fraction ionized.
Nitric acid (62%) .	0·096	Potassium hydroxide	0·77	Potassium chloride	0·74
Nitric acid (dil.) .	0·820	Sodium hydroxide .	0·73	Ammonium chloride . . .	0·75
Sulphuric acid (dil.).	0·510	Lithium hydroxide.	0·63	Potassium nitrate	0·64
Carbonic acid ($\frac{1}{10}N$).	0·002	Ammonium hydroxide	0·01	Zinc sulphate .	0·24
Hydrosulphuric acid ($\frac{1}{10}N$) . . .	0·001	Calcium hydroxide ($\frac{1}{64}N$) . .	0·90	Copper sulphate .	0·22
Perchloric acid ($\frac{1}{2}N$)	0·880	Barium hydroxide ($\frac{1}{64}N$) . .	0·92	Silver nitrate .	0·58
Acetic acid ($\frac{1}{10}N$) .	0·013	Methylamine .	0·12	Barium chloride .	0·57
Trichloracetic acid ($\frac{1}{10}N$) . . .	0·850	Ethylamine . .	0·13	Potassium sulphate . .	0·24

The effect of increasing the concentration of a solution is to increase the internal friction. This retards the movements of the ions and thus diminishes the conductivity more rapidly than would occur if the results were not affected by this disturbing factor. As the concentration decreases, the friction diminishes; and, with the more dilute solutions, the effects of internal friction can be neglected. The two factors—internal friction and conductivity—do not change with dilution in the same way, and, in consequence, the conductivity may increase with increasing dilution; reach a maximum; and then decrease with increasing dilution. This is the case, for instance, with sulphuric acid, where the maximum conductivity occurs when 30 per cent. of acid is present. The application of the ionic theory to *concentrated* solutions is beset with many difficulties, and consequently the theory has been mainly developed from results obtained with *dilute* solutions.

Strong and weak acids and bases.—The terms "strong" and "weak" are sometimes applied to the acids and bases, and these terms refer to the conductivity or to the degree of ionization in aqueous solution of moderate dilution. A strong acid or base has a high conductivity and accordingly a high degree of ionization at moderate dilutions; while the converse is the case with a weak acid or base. There is no real line of demarcation between the two. Acids like carbonic and hydrosulphuric acids, and bases like ammonia, are weak. Their degree of ionization is less than one per cent. If the degree of ionization exceeds 70 per cent. the acid is undoubtedly strong. Electrolytes like solutions of sodium chloride are good conductors, and some solutions with a conductivity midway between good conductors and non-conductors are sometimes called semi- or half-electrolytes. Most salts are highly ionized, even at moderate dilutions, but there are many exceptions, *e.g.* mercuric chloride, the cadmium halides, and mercuric cyanide are but slightly ionized in moderately dilute solutions.

W. Ostwald[2] noted that, as a rule, the ionization of analogous salts is the greater the further apart the anions and cations are in the electrochemical series. R. Abegg and G. Bodländer found that the tendency to form complex ions increases as the tendency of the salt to ionize decreases. The electrical conductivity of aqueous solutions increases with a rise of **temperature,** and F. Kohlrausch[3] represented his observations at 0° by the formula $K=K_0\{1+a(\theta-\theta_0)+b(\theta-\theta_0)^2\}$, where θ_0 represents the initial temperature, in the present case 18°. The constants a and b are characteristic of each solution of a given electrolyte. Thus, for nitric acid, $a=0{\cdot}0163$, $b=-0{\cdot}000016$; potassium chloride, $a=0{\cdot}0197$, $b=+0{\cdot}000047$; etc. F. Kohlrausch suggested that on a falling temperature, the conductivities of all aqueous solutions approach zero at about the same temperature, because of the decreasing fluidity or increasing viscosity of the solvent. J. Kunz found this temperature approximates to −40°. Owing to the opposite effects of viscosity and temperature on conductivity, negative coefficients might be anticipated, and S. Arrhenius found this to be the case with phosphoric acid. There is also a maximum in the curve with many salts—and the more concentrated the solution the lower the temperature at which a maximum occurs. There does not appear to be any anomaly in the conductivity as the temperature passes 4°, or even with undercooled solutions in passing through the freezing point.

The effect of **pressure** has been studied by G. Tammann, J. Fanjung, A. Bogojawlensky, etc.[4] If k represents the ionization constant; p, the pressure; R, the gas constant; T, the absolute temperature; and dv, the decrease in volume which occurs during the ionization of a gram-molecule of the salt, then, M. Planck's formula at constant temperature, $(d \log k)/dp=dv/RT$, describes the results of observation.

G. Wiedmann[5] noticed a relation between the conductivity and the **viscosity** of a solution, and O. Grotrian noted that there is a parallelism between the two variables, but not strict proportionality. According to H. von Euler, the viscosity η of a solution of a binary electrolyte is $\eta=\eta_1{}^{C(1-\alpha)}(\eta_2\eta_3)^{C\alpha}$, where α represents the degree of ionization; η_1, η_2, and η_3 respectively denote the viscosity coefficients of the un-ionized salt, the cation, and the anion; and C denotes the total concentration. If the electrolytic mobilities of the ions be plotted as abscissæ, and the viscosity coefficients as ordinates, the values for most of the salts lie on a straight line. M. G. Levi did not find that the stiffening of a solution with gelatine made an appreciable difference on the conductivity, but in very concentrated gelatine solutions, E. Wiedemann, C. Lüdeking, and B. von Tietzen-Hennig found that the conductivity is diminished; similar observations were made by C. Stephan, S. Arrhenius, and P. Massoulier with respect to solutions containing sugar or glycerol. W. von Beetz, B. von Tietzen-Hennig, and M. Oker-Blum studied the influence of suspensions of sand, gypsum, and blood corpuscles on the conductivity of salts.

J. Bosi,[6] E. H. Hall, and J. Nabl investigated the effect of the **agitation** of the solution on the conductivity, but no marked difference was observed. F. Neesen. H. Bagard, and G. Melani studied the effect of **magnetism** on the conductivity but without establishing any definite conclusion. C. H. Wind, E. van Everdingen, H. Bagard, F. Florio, and F. Chiavassa have studied the **Hall effect** with electrolytes. F. Kohlrausch, H. M. Goodurn, A. Wiener, and A. Miolate, etc.,[7] noticed that some electrolytes when diluted, mixed together, etc., show a transient change in the conductivity; this is attributed to chemical action. Light may also set up chemical reactions. According to J. Gibson, **light** always acts in such a way as to increase the conductivity, but whether the effect is reversible is not clear. The effect of **X-rays** has also been examined.[8]

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§ 8. The Migration of Ions

It is impossible to get one kind of ion liberated at one electrode without having a precisely equivalent quantity of an oppositely charged ion appearing at the other electrode;

> **it is impossible to have a procession of positive atoms through a liquid without a corresponding procession of negative ones. In other words, an electric current in a liquid necessarily consists of a flow of positive electricity in one direction combined with a flow of negative electricity in the opposite direction.—O. J. Lodge (1892).**

Many early investigators—*e.g.* M. Faraday (1834),[1] J. F. Daniell and W. A. Miller (1844), etc.—noticed that changes in concentration are produced about the electrode during the electrolysis of a solution, and that although the quantities of anions and cations liberated at the electrodes during electrolysis are always strictly equivalent, nevertheless, the rates at which the concentrations of the electrolyte changes about anode and cathode are not the same. W. Hittorf studied the effect of strength of current, concentration of solution, and temperature on the phenomenon which was attributed to differences in the speeds at which the anions and cations drifted in the solution.

The changes of concentration about the electrodes are illustrated by an experiment due to A. A. Noyes and A. A. Blanchard. A U-tube contains a solution of gelatine colored with cupric chloride and covered with a layer of sodium chloride. The object of the gelatine is to prevent any movement of the liquid. When electrolyzed, the blue colour rises into the sodium chloride at the cathode side, and descends below the level of the gelatine on the anode side. With potassium dichromate instead of cupric chloride, the yellow colour rises at the anode side and descends at the cathode side. With copper dichromate, the yellow colour rises in the anode compartment and the blue in the cathode. The ionic theory interprets these experiments by assuming that in the case of cupric chloride, blue copper ions travel towards the cathode and colourless chlorine ions towards the anode; in the second experiment, that yellowish Cr_2O_7''-ions travel towards the anode and colourless potassium ions towards the cathode; and in the third experiment, blue copper ions travel towards the cathode and yellow dichromate ions towards the anode. The fact observed is that *the electrolysis of the coloured solutions occurs at the boundary surfaces between the gelatine and the supernatant solution.* M. Faraday (1833) has described experiments illustrating the phenomenon: "the surfaces of separation of liquids in contact act as electrodes to each other, and separation may there occur just as at a plate."

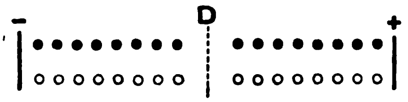

Fig. 8.

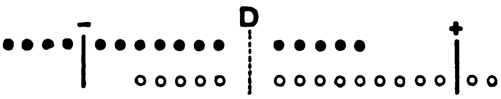

Fig. 9.

By a modification of these experiments, it is possible to measure the rates at which the concentration of the solution changes about the electrodes, or, in the language of the ionic theory, the rates at which the anions of copper, etc., drift towards the electrodes. Let the cations be represented by ● and the anions by ○, and suppose the two sets of anions to be arranged in rows as shown diagrammatically in Fig. 8, with an equal number on each side of a porous diaphragm in the electrolytic cell. There are eight molecules in each compartment, and the concentration of ion about each electrode can be represented by eight. If the cations move twice as fast as the anions, then, after a certain interval, the conditions may likewise be represented by Fig. 9, where each ion with no partner is supposed to have been discharged at the electrodes. Six cations and six anions have therefore been set free. The concentration in the cathode compartment has decreased from 8 to 6, and in the anode compartment from 8 to 4, with a loss of 2 and 4 respectively. Hence the loss in concentration about the cathode is to that about the anode, as the velocity of the anion is to that of the cation; that is, the losses in concentration about the electrodes are inversely as the speed of the correspondingly named ions. The relative velocities of the ions through the solution under a potential-gradient of 1 volt per cm. are best termed **Hittorf's transport numbers** of the ions.

If a solution of silver nitrate of known concentration be electrolyzed between silver electrodes in an apparatus similar to that illustrated in Fig. 7, the only change in the solution is a transfer of silver from the anode to the cathode, and a change in the concentration of the silver salt round the two electrodes; for the apparatus is constructed so as to reduce the mechanical convection of the dissolved salt to a minimum. The change in the concentration of the solution, after a few hours' electrolysis, can be measured by withdrawing about half the solution from the apparatus, *viâ* the stopcock, and determining the amount of silver in the solution by analysis. From the results, numbers can be obtained which are supposed to represent the speeds of migration of the anions and the cations. The following numbers, due to W. Hittorf (1853–59), serve to illustrate the principle.

W. Hittorf's experiment.—A solution of silver nitrate containing one part of silver to 49·44 parts of water was electrolyzed for nearly an hour in a cell with silver electrodes. Silver dissolved from the anode and a similar quantity deposited on the cathode. The concentration of the whole solution remained unchanged, but the concentration of the solution about the cathode decreased while that about the anode increased. In the cathode compartment, W. Hittorf found

Silver before electrolysis	0·7162 gram
Silver after electrolysis	0·5862 „
Loss	0·1300 „

The solution about the cathode thus lost 0·1300 gram of silver, and the solution about the anode must have increased by this amount owing to the action of an equivalent quantity of nitric acid on the silver electrode.

At the same time, by the simultaneous interposition of a silver voltameter in the circuit, it was found that sufficient electricity had passed through the electrolyte to deposit 0·2470 gram of silver at the cathode. If no silver ions have passed from the anode chamber, the quantity of silver in the anode chamber would have increased by 0·2470 gram owing to the transport of NO_3'-ions from the cathode chamber. The observed increase was only 0·1300 gram of silver; hence 0·2470 less 0·1300 gram; in all, 0·1170 gram of $Ag^{\cdot}$-ions were transported from the anode chamber to the cathode chamber while the cathode chamber simultaneously lost 0·1300 gram of silver due to the deposition of 0·2470 gram of silver on the cathode. Hence since *the relative speeds of the ions are proportional to the fall of the concentration about the oppositely named electrodes*, or

$$\frac{\text{Loss in cathode chamber}}{\text{Loss in anode chamber}}=\frac{0{\cdot}1300}{0{\cdot}1170}=\frac{\text{Speed of anion, }NO_3'}{\text{Speed of cation, }Ag^{\cdot}}$$

or the rate of transport of the anions is to the rate of transport of the cations as 130 : 117; or the NO_3'-ions migrate 1·1 times as fast as the $Ag^{\cdot}$-ions.

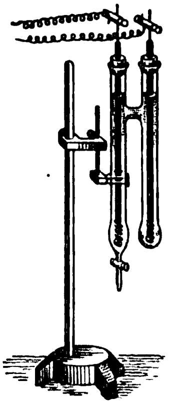

Fig. 10.—Determination of the Speed of Ionic Migration.

The mobility of the elementary ions was found by G. Bredig to vary periodically with the atomic weight; and with complex ions, W. Ostwald and G. Bredig[2] noted that the mobility decreases as the combining weight increases, and with isomeric ions the mobility is approximately the same.

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§ 9. The Speeds of Moving Ions—Kohlrausch's Laws

If the anions in a solution remained stationary, the whole current would be carried by the cations; but if both ions be moved, the current will be shared between them, and the share of each will be proportional to the speed at which it moves.[1] Let $v^{\cdot}$ represent the speed of migration of the cations, and v' that of the anions. The total current carried from one electrode to the other will be proportional to the rate at which the ions separate—that is, to the joint velocity of the two ions $v^{\cdot}+v'$. Accordingly the current carried across the electrolyte is shared in such a way that the

$$\text{Anions share} = \frac{v'}{v^{\cdot}+v'}, \quad \text{Cations share} = \frac{v^{\cdot}}{v^{\cdot}+v'}$$

Hence in W. Hittorf's experiment, the relative speeds of the $Ag^{\cdot}$- and NO_3'-ions were as 0·117 : 0·130, $=v^{\cdot} : v'$, the **transport numbers** are respectively 0·130/(0·130+0·117)=0·52 and 0·117/(0·130+0·117)=0·48. Hence, if n denotes the transport number of one ion, $1-n$ will represent the transport number of the other. It might be observed that the change in the concentration of the solution about one anode is sufficient to compute the relative speeds of migration of the anions and cations under the given conditions. In W. Hittorf's experiment just cited, the solution before the passage of the current contained the equivalent of 0·7162 grm. of silver, and the anode compartment lost 0·1170 grm. of silver. The total quantity of electrical energy transported through the cell was equivalent to the 0·2470 grm. of silver deposited in the voltameter. The fraction transported by the silver ions is therefore 0·1170/0·2470=0·473. If $n^{\cdot}$ denotes the transport number of the anion, and n' that of the cation, $n^{\cdot}+n'=1$. Hence, the transport number of the NO_3'-ions is obtained by subtracting 0·473 from unity; the result 0·527 agrees with that obtained from the ratio 0·1300/0·2470=0·527. Obviously the ratio 0·473 : 0·527 is the same as 117 : 130.

EXAMPLES.—(1) F. Vogel (1903)[2] found that 100 c.c. of a solution of barium nitrate contained the equivalent of 0·4419 grm. of barium, and it weighed 100·6660 grms. This solution was electrolyzed in a suitable apparatus while a silver voltameter deposited 0·5618 grm. of silver, which is equivalent to 0·3577 grm. of barium, 187·2880 grms. of the anode solution contained the equivalent of 0·6728 grm. of barium; the concentration of the solution between the two electrodes did not change. Compute the transport numbers of anion and cation. Since 187·2880 grms. of the electrolyte before electrolysis contained the equivalent of 0·8223 grm. barium, and after electrolysis 0·6728 grm. Hence, the loss in the anode chamber was 0·1495 grm. of barium. The transport number of the cation, $Ba^{\cdot\cdot}$, is therefore 0·1495/0·3577=0·418; and of the anion, NO_2', 1−0·418=0·582.

(2) F. Warschauer (1903) found that a solution of sodium metaphosphate $NaPO_3$ contained the equivalent of 0·1775 grm. of P_2O_5 per 25 c.c. or 25·1998 grms. Before the electrolysis the anode solution contained 91·6632 grms. of liquid; hence, it contained the equivalent of 0·6384 grm. P_2O_5; 0·2792 grm. Na_2O; and 90·7456 grms. of water. After electrolysis 0·7370 grm. P_2O_5; 0·3223 grm. Na_2O; and 90·6039 grms. of water. Hence, 90·6039 grms. during the electrolysis gains 0·7370−0·6374=0·996 grm. P_2O_5, and this is equivalent to 0·1108 grm. PO_3. While the electrolysis was in progress, a solution containing 6·0035 grms. of silver nitrate per half litre deposited 0·2625 grm. of silver during the electrolysis. This amount of silver is equivalent to 0·1922 grm. of PO_3. Hence the transport number of the PO_3'-ion is 0·1108/0·1922=0·58, and that of the $Na^{\cdot}$-ion is 1−0·58=0·42.

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The behaviour of electrolytes with a bivalent radicle united with two univalent radicles is a little more complex. For example, solutions of sulphuric acid may furnish two $H^{\cdot}$-ions, and one SO_4''-ion, or one $H^{\cdot}$-ion and one HSO_4'-ion. This is given as an explanation of the fact why the transport numbers for such solutions show appreciable differences when determined in dilute and in concentrated solutions. Thus, the anion of barium chloride in aqueous solution varies from 0·611 to 0·555 by progressive dilution as shown in the following scheme:

Normality of solution . . .	0·50	0·20	0·10	0·05	0·02	0·01
Transport numbers . . .	0·61	0·59	0·57	0·56	0·56	0·56

The concentration of the solution determines whether the ionization proceeds $H_2SO_4 \rightleftharpoons H^{\cdot} + HSO_4'$ or $H_2SO_4 \rightleftharpoons 2H^{\cdot} + SO_4''$. With decreasing concentration the ions become less complex, the solution yields transport numbers approaching a constant value. The variation is due to changes in the relative proportions of the anions and cations with increasing dilution: $BaCl_2 \rightleftharpoons BaCl^{\cdot} + Cl' \rightleftharpoons 2Cl' + Ba^{\cdot\cdot}$. All the molecules of the solute at infinite dilution are *ex hypothesi* ionized and take an active part in conducting the current, while the number of molecules which take an active part in conducting the current at any particular dilution is proportional to the molecular conductivity, μ, and therefore, if x represents the fraction of a gram-molecule which is ionized when the solution is diluted to v litres, $\mu = kx$, where k is the constant of proportion. At infinite dilution, the whole molecule is ionized, and consequently $x=1$; $\mu_\infty = k$; and $\mu = \mu_\infty x$. On comparing the molecular conductivities of a number of different salts at infinite dilution, F. Kohlrausch (1876) noticed a curious fact: The difference in the molecular conductivities of potassium and sodium chlorides is equal to the difference between potassium and sodium nitrates; and this in turn to the difference between sodium and potassium fluorides; etc. In illustration:

	KCl NaCl	KNO_3 $NaNO_3$	KF NaF
μ_∞	129·1 − 108·1	125·5 − 104·5	110·5 − 89·4
Difference . . .	21·0	21·0	21·1

The difference in each pair of salts with a common anion thus depends on the difference in the speeds of migration of the cations—$K^{\cdot}$ and $Na^{\cdot}$—and this is constant. Similar relations hold good for other salts containing a common cation. It is thence inferred that **the molecular conductivity at infinite dilution is the sum of two factors, one dependent upon the nature of the anion, the other on the cation** —this is **Kohlrausch's second law.** At infinite dilution, the molecular conductivity is represented by **Kohlrausch's equation :** $\mu_\infty = v^{\cdot} + v'$. Consequently, the speed of migration of any particular ion in a particular solvent is constant at infinite dilution, is dependent on its own chemical nature, and is independent of the nature of the other ion or ions which may be present. Otherwise expressed, **the speeds of migration of the different ions in a solution are independent of one another.** In illustration, the speeds of migration of the chlorine ion in 0·0001N-solutions of lithium, sodium, and potassium chlorides were respectively 65·7, 65·7, and 65·6.

W. Hittorf showed how to determine the numerical value of the ratio $v^{\cdot}/v'$, and F. Kohlrausch's equation furnishes the numerical value of $v^{\cdot} + v'$. Hence it is possible to compute the absolute velocities of the anion and cation. The results agree closely with those obtained by direct measurement.

EXAMPLE.—The molecular conductivity of a solution of silver nitrate at infinite dilution is 115, at 18°. This means that 115 coulombs of electricity are carried 1 cm. per second; but each gram ion of silver nitrate carries 96,540 coulombs (Faraday's law), hence 115 coulombs are carried $115 \div 96540 = 0{\cdot}00121$ cm. per second. This represents the velocity at which the two ions draw apart. The carriage of the electric charge is shared by both ions; the migration constants of the two ions are $Ag^{\cdot}$ 54, and NO_3' 62. The ratio $v^{\cdot}/v' = 54/62 = 0{\cdot}87$. Hence $v^{\cdot} = 0{\cdot}87v'$. From Kohlrausch's equation $0{\cdot}00121 = v^{\cdot} + v'$ or $1{\cdot}87v' = 0{\cdot}00121$, or $v' = 0{\cdot}00065$, and $v^{\cdot} = 0{\cdot}00056$ cm. per second.

F. Kohlrausch's equation was extended by W. Ostwald to represent other than infinite dilutions by introducing the term $\mu=a\mu_\infty$. Hence, when ionization is not complete, Kohlrausch's equation becomes $\mu=a(v^{\cdot}+v')$. As the solution is diluted more and more the term a becomes more and more nearly equal to unity, and finally when ionization is complete, $a=1$ and Kohlrausch's equation $\mu_\infty=v^{\cdot}+v'$ appears. The expressions assume a similar form if the equivalent conductivities be in question.

Example.—The transport numbers for the ions in a solution of sodium metaphosphate are 0·573 for PO_3', and 0·427 for $Na^{\cdot}$. The maximum equivalent conductivity of the solution is 126·2 units. What are the relative speeds of migration of the two ions ? If n be the transport number of the cation, $1-n$ will be the transport number of the anion, and $n/(1-n)=v'/v^{\cdot}$; and $\lambda=x(v^{\cdot}+v')$; by substitution therefore $v^{\cdot}a=(1-n)\lambda$, and $v'x=n\lambda$. When the equivalent or molecular conductivity is a maximum, ionization is complete, and $a=1$. Accordingly, $n=0·427$; $1-n=0·573$; $\lambda=126·2$. Hence, the relative speeds of migration of the cation $Na^{\cdot}$ is 53·9, and of the anion PO'_3, 72·3 ; or the sodium ion travels $53·9 \div 96540=0·00056$ cm. per second when the electromotive force is one volt, etc.

By measuring the rate of rise of the blue colour in A. A. Noyes and A. A. Blanchard's experiment, the velocity of copper ions can be determined under standard conditions, and in that way, with other solutions, a series of numbers have been obtained which represent the velocities of migration of the respective ions. In O. J. Lodge's experiment (1886) a current was passed through a ⊓-shaped tube containing a stiff gelatine solution of sodium chloride coloured red with phenolphthalein and a trace of sodium hydroxide. The ends of the tube dipped in beakers contained dilute sulphuric acid. The time taken to decolorize a certain measured distance was determined, and this was corrected by the time taken for the acid to diffuse in the jelly when no current was passing. In this way it was found that the hydrogen ions travelled through the jelly at the rate of 0·0026 cm. per second when a difference of potential of one volt was applied to the electrodes. H. B. Denison and B. D. Steele, and G. M. Lewis used the method of moving boundaries for measurements of the transport numbers.

The transport numbers are expressed in the same units as the equivalent and molecular conductivities, and they are proportional to the velocities of the ions. The speeds of the ions are decreased by increasing the viscosity of the solution, say, by adding non-electrolytes like cane sugar, alcohols, ether, etc. Gelatine has very little influence. The decrease in viscosity which occurs on raising the temperature is also of influence. The speeds of the ions are also augmented by using currents of greater electromotive force. Hence, the rate of motion of any given ion is determined (i) by the intensity of the electric pressure which directs or drives the ions to the electrodes; (ii) by the damping effect of the liquid on the moving ion.

It must be remembered also that the raising of the temperature or the addition of a third substance to the solution may materially modify or even mask the normal relations between solvent and solute. The conductivity of a solution may virtually vanish suddenly at the point of solidification of a cooling liquid; so that by plotting the conductivity of a molten salt cooling through a range of temperature, there will be an abrupt change in the direction of the curve at the freezing temperature, and it has been proposed to apply this principle to determine transition temperatures—solid or liquid, etc.

Many solids are poor conductors at ordinary temperatures but good conductors at temperatures above their melting points. One explanation assumes that the conductivity of fused salts is due to self-ionization, in other words, that a small portion of fused substance is ionized. Glass and porcelain are poor conductors at ordinary temperatures, but they conduct very fairly at more elevated temperatures, and this principle has been utilized in the so-called Nernst lamp.

At 18°, with a difference of potential of one volt between the electrodes, the absolute velocities of some ions are :

Anions . .	OH'	Cl'	I'	NO_3'	ClO_3'
Speeds . .	5·6	2·12	2·19	1·91	1·70 cm. per hour
Cations . .	$Cs^{\cdot}$	$Rb^{\cdot}$	$K^{\cdot}$	$Na^{\cdot}$	$Li^{\cdot}$
Speeds . .	2·32	2·32	2·05	1·26	1·11 cm. per hour

Under similar conditions, the charges carried by different ions may be equal; their speeds are different. The heaviest ions, in the alkali series of elements—that is, the ions with the greatest "atomic" weights—here appear to move fastest. This has been supposed to be due to the slower-moving ions dragging along with them a number of molecules of the solvent. This assumption seems to be justified by experiments with dilute solutions, but with concentrated solutions there is a discrepancy between results obtained by W. Hittorf's method and the method of moving boundaries, which is explained by assuming that in dilute solutions the change in the concentrations is negligibly small, whereas in a concentrated solution the difference in the concentration of the ions at each electrode must be affected by the water carried by the ions. W. Hittorf's method does not distinguish between changes of concentration about the electrodes due to the transport of ions and those due to the carriage of water by the ions.[3] In Hittorf's method it is assumed that the solvent is quite stationary during the electrolysis, and that no solvent is transferred from the one electrode to the other. If the ions are hydrated, not only the electrolyte but some of the solvent will be transferred from the one electrode to the other, unless the respective ions happen to be equally hydrated. This argument has been tested by W. Nernst, G. Buchböck, etc., by using solutions of an electrolyte containing a third substance—raffinose, mannite, sugar, etc.—not affected by the electrolysis, as a standard of reference for the concentration of the water. As a result, it was found that the numbers are not generally in agreement with Hittorf's transport numbers although they agree with those obtained by the method of moving boundaries; it was also found that during the electrolysis of hydrogen, sodium, potassium, and lithium chlorides, the ratio water : sugar decreases at the cathode and increases at the anode under conditions where no change occurs in the absence of the electrolyte. This fact can be explained either by assuming that the non-electrolytic sugar is carried from cathode to anode; or that water is carried from anode to cathode during the passage of the current. The former hypothesis assumes that the ions (or electrolyte) form a complex with the sugar, and for this there is no satisfactory evidence; the ionic hypothesis assumes that the ions are hydrated, and carry the water molecules as well as their electric charges. The molecular equivalents of water transferred from anode to cathode per farad of electricity when the electrolyte has normal concentration:

HCl	KCl	NaCl	LiCl
0·24	0·60	0·76	1·5

These numbers taken in conjunction with the transport numbers show that the degree of hydration varies with the different ions and with the concentration of the solution. The relative degrees of hydration for the different ions (chlorine assumed to be unity) are:

Cl'	$H^{\cdot}$	$K^{\cdot}$	$Na^{\cdot}$	$Li^{\cdot}$
1	0·46	2·3	3·6	7·0

the row of numbers must represent minimum values since a negative value for chlorine is impossible. Hence all the cations in the above-mentioned solutions must be hydrated, and the hydration increases markedly in passing along the series H, K, Na, Li. If the speeds of migration of the different ions be plotted on squared paper against the atomic weights of the elements, a periodic curve is obtained. H. Remy has calculated hydration numbers from the changes in volume which occurred in the anodic and cathodic solutions during electrolysis.

Evidence indicating the union of ions with the solvent has been sought in the changes which occur with boiling points and freezing points of concentrated solutions. These phenomena depend on the ratio of the number of molecules (or ions) of solute and of solvent. If union occurs, the number of molecules (or ions) is not changed, but only their size. The combination in dilute solutions can remove but a relatively small amount of solvent from the field, and the consequent effect is inappreciable. Even in concentrated solutions the deviations from the theoretical values do not show whether it is the free ions that are so combined, or whether it is not the result of something else. Measurements of the boiling and freezing points of solutions of hydrated salts in other solvents have also been made with the idea of finding if the water of crystallization remains attached to the salt. In virtually all cases the evidence points one way : the ions do unite with molecules of the solvent, and thus move more slowly than if they were not harnessed with the molecules of the solvent.

The data show that the rates at which ions move through water are surprisingly small—one centimetre per hour for the $K^{\cdot}$-ion under a pressure of one volt. And it requires a pressure equivalent to about 300,000 tons to drive a gram ion of hydrogen, $H^{\cdot}$, through water at this speed.

EXAMPLE.—By definition 10^7 dynes of energy are required to drive a coulomb of electricity one centimetre against a potential difference of one volt. A force of 10^7 dynes is equivalent to 10·18 kilograms. Hence, the force required for a gram-ion charged with 96,540 coulombs will be 96,540 × 10·18 = 983,000 kilograms ; and measurements of the absolute velocity of the hydrogen ion show that this force is required to drive these gram-ions with a velocity of 0·00325 cm. per second. Hence to drive the gram-ion with a velocity of one centimetre per second will require a force of nearly 983,000 ÷ 0·00325 = 302,000,000 kilograms. One ton is nearly equivalent to 1016·05 kilograms, and therefore 302,000,000 kilograms is nearly equivalent to 297,000 tons.

W. Hittorf's results can be deduced from the assumption that both the solvent and the solute conduct the current, for if, say, silver nitrate conducts the whole current, free acid appears only at the anode ; if the water conducts the whole current, free acid appears only at the cathode ; and if both salt and solute conduct the current, free acid appears at both electrodes, and the current can be portioned between the solvent and solute so as to make the observed facts fit the hypothesis. Hence, W. Hittorf's migration data do not prove that ions travel at unequal rates, for the observed facts can be explained by at least two plausible hypotheses.

In these experiments the *fact* observed is the changing molecular concentration of the solution about the anode and cathode during electrolysis ; the *hypothesis* is that during the passage of the current the anions and cations move in the same electrolyte with different velocities, and are yet the anions and cations given off at the respective electrodes at the same time.

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§ 10. "Abnormal" Osmotic Pressures and Ionization

It is natural to assume that substances are ionized which give in aqueous solution osmotic pressures which are too great.—S. ARRHENIUS.

We are now in a position to resume our study of the abnormal osmotic pressures furnished by solutions of electrolytes. Just as the abnormally high vapour density exhibited by hydrogen fluoride was traced to polymerization : $2HF \rightleftharpoons H_2F_2$, and the abnormally low vapour density of iodine above 700° was traced to the dissociation : $I_2=2I$, so S. Arrhenius argued that salts in solution which give an abnormally high osmotic pressure are similarly dissociated. Suppose that one molecule of an electrolyte furnished m ions, and further let a denote the fraction ionized when a gram-molecule of the electrolyte is dissolved in water. The solution will then contain $(1-a)$ non-ionized molecules, and ma ions. The total number of individual molecules in the solution—that is, electrically charged molecules (ions) and neutral molecules—will be $(1-a)+ma$. As in our previous study of solutions, let n denote the total number of individual molecules formed by the ionization of a substance in a given solution. Then $n=1+ma-a$. The numerical value of n, as we have seen, can be determined from conductivity data, and from osmotic pressure and related phenomena—freezing and boiling point determinations. If the value of n so determined be divided into the value of n calculated on the assumption that no ionization occurs, the value of a can be computed ; and if a be known, the value of n can be computed.

EXAMPLES.—(1) The solution of hydrochloric acid just studied gives $a=0{\cdot}874$ and $m=2$. Hence $n=1+(m-1)a$ becomes $n=1{\cdot}874$. Hence every 100 molecules of HCl furnish the equivalent of 187·4 individual molecules. If the electrolyte has been non-ionized, n would have been unity ; and if completely ionized, n would have been 2.

(2) The boiling point of a solution of 3·400 grms. of barium chloride, $BaCl_2$, in 100 grms. of water is 100°-208°, what is the degree of ionization of the solute ? From the above expression, there will be $1+ma-a=1+3a-a=1+2a$ "molecules" in the solution, *viz.* $Ba^{\cdot\cdot}$, $2Cl'$, and hence one molecule of barium chloride furnishes the equivalent of 208/85 $=2{\cdot}447$ "molecules." Consequently, $2{\cdot}447=1+2a$, or $a=0{\cdot}723$; or 72·3 per cent. of the salt is ionized.

(3) A solution of 11·07 grms. of barium nitrate in 100 grms. of water raised the boiling point 0·466°. What proportion of the salt is ionized ? Ansr. 55·8 per cent.

(4) A solution of 0·3668 grm. of sodium chloride in 100 grms. of water freezes at −0·221°. What proportion of the salt is ionized ? Ansr. 89·2 per cent.

A comparison of the values of n calculated from osmotic pressure, freezing point, and electrical conductivity data is indicated in Table II. The numbers in the last three columns show that the values determined by independent processes are strikingly concordant; and it is therefore inferred that the abnormal osmotic pressures indicated in Table VI, Cap. X, arise from the more or less complete ionization of the electrolytes in aqueous solution.

TABLE II.—MOLECULAR WEIGHTS OF SOME ELECTROLYTES IN SOLUTION.

Salts.	Molecular concentration.	Values of n.		
		Osmotic pressure.	Freezing point.	Conductivity.
Calcium nitrate, $Ca(NO_3)_2$	0·18	2·48	2·47°	2·46
Magnesium sulphate, $MgSO_4$	0·38	1·25	1·20°	1·35
Strontium chloride, $SrCl_2$	0·18	2·69	2·52	2·51
Potassium chloride, KCl	0·14	1·81	1·86°	1·86
Lithium chloride, LiCl	0·13	1·92	1·94°	1·84
Magnesium chloride, $MgCl_2$	0·19	2·79	2·68°	2·48

Modes of Ionization.—The ionization of some of the bivalent electrolytes—H_2CO_3 ; H_2SO_4 ; $BaCl_2$; $CdCl_2$; K_2SO_4 ; $CuSO_4$; etc.—in moderately dilute solutions appears to furnish complex ions. Thus, cadmium chloride, $CdCl_2$, not only furnishes $Cd^{\cdot\cdot}+2Cl'$, but also $Cd^{\cdot\cdot}+CdCl_4''$; sulphuric acid, H_2SO_4, not only gives $2H^{\cdot}+SO_4''$, but also $H^{\cdot}+HSO_4'$; carbonic acid, H_2CO_3, gives $2H^{\cdot}+CO_3''$; and $H^{\cdot}+HCO_3'$; copper sulphate, $CuSO_4$, not only gives $Cu^{\cdot\cdot}+SO_4''$, but also $Cu_2SO_4^{\cdot\cdot}$ and $Cu(SO_4)_2''$; etc. If, however, the solutions be still further diluted, the complex ions break down into simpler ones. Hence the ionization of concentrated polybasic acids like H_2SO_4 proceeds in stages: first $H_2SO_4=H^{\cdot}+HSO_4'$; followed by $H^{\cdot}+HSO_4'=2H^{\cdot}+SO_4''$.

§ 11. Equilibrium between Ionized and Non-ionized Solute

> The evidence is so un-ambiguous and convincing that ions and some molecules combine with more or less of the solvent that it seems that it can now be accepted as a fact of science.—H. C. Jones (1913).

Reference has previously been made to the assumption that the molecules of an electrolyte, when dissolved in water, are ionized; that the ions, at the same time, recombine to form neutral molecules; and that equilibrium will ensue when the speeds of the two opposing reactions—ionization and de-ionization—are equal. Consider the ionization of ammonium hydroxide, NH_4OH, represented by $NH_4OH \rightleftharpoons NH_4^{\cdot}+OH'$. Here the process of ionization bears some analogy with the dissociation of iodine by heat: $I_2=I+I$. Let $[NH_4OH]$ denote the concentration of the ammonium hydroxide; $[NH^{\cdot}_4]$, that of the concentration of the ammonium ion; and $[OH']$, that of the hydroxide ion. Then, applying the principle of opposing reactions, the condition for equilibrium is: $[NH_4^{\cdot}]\times[OH']=K[NH_4OH]$. If this theory applies to ions, it follows that the numerical value of the equilibrium constant, K, now called the **ionization constant**, remains unchanged whatever be the concentration of the solution. This relation is sometimes called **W. Ostwald's dilution law**,[1] or Ostwald's mass law, and, for univalent electrolytes, it is also symbolized:

$$\frac{a^2C}{1-a}=K\text{; or, }\frac{C_i^2}{C_u}=K\text{; or }\frac{a^2}{(1-a)v}=K$$

where a denotes the degree of ionization; C, the total concentration; C_i, the concentration of each of the ions; C_u, the concentration of the non-ionized part; and v the number of litres of solvent containing a gram-molecule of the salt.

Example.—In a solution containing 0·125 gram-molecules of NH_4OH per litre, the equivalent conductivity shows that 0·0135 gram-molecules are ionized, and hence, 0·0135 $\times$0·125=0·0017 represents the molecular concentration of the ammonium hydroxide which is ionized. This number thus represents the concentration of the $NH_4^{\cdot}$-ions. But every $NH_4^{\cdot}$-ion is accompanied by one OH'-ion, and accordingly, 0·0017 also represents the concentration of both the $NH_4^{\cdot}$- and the OH'-ions. Hence, from Ostwald's dilution law, 0·0017 $\times$0·0017$\div$(0·125$-$0·0017)=0·000023. This last number represents the value of the ionization constant for a seminormal solution of ammonium hydroxide.

It follows from this rule that the greater the dilution v the greater will be the **percentage amount of ionization** (although, of course, the **actual concentration of the ions** must decrease). Since $a=\lambda_v/\lambda_\infty$ the value of K can be readily computed; and this has been done by W. Ostwald for a large number of organic acids, and by G. Bredig for organic bases, with results so very satisfactory that S. Arrhenius could say "in no other field has the law of mass action been applied with such good results"—the converse of this statement applies with strong electrolytes. Table III represents values for the ionization constant for solutions of ammonium hydroxide of different strength.

The constancy of the value K means that although the last-named solution of ammonium hydroxide is nearly 300 times more dilute than that named first, and the degree of ionization of the last is nearly 16 times as great as the first, the expression represented by K, deduced on the supposition than the process of ionization follows the rule for opposing reactions, is constant within the limits of experimental error.

It will be observed that two important assumptions have been tacitly made in deriving the formula: (1) that the concentration of the ions can be obtained from the conductivity ratios; and (2) that the ions and un-ionized molecules of an electrolyte follow the laws of ideal solutions. In spite of the very successful results obtained with the feebler acids and bases, for some unknown reason, the application of the dilution law to the stronger electrolytes has been a signal failure, and the so-called anomaly is regarded as the *bête noir* of S. Arrhenius' ionic hypothesis. The numerical value of K, instead of remaining constant, increases rapidly with increasing concentration. In the first place, the equivalent conductivity of a univalent substance is $\lambda=aF(v^{\cdot}+v')$, where a is the fraction of the substance ionized, and F the quantity of electricity associated with each equivalent ion; and the equivalent conductivity at zero concentration or infinite dilution is $\lambda_\infty=F(v^{\cdot}_\infty+v'_\infty)$. Hence,

TABLE III.—EFFECT OF DILUTION ON THE IONIZATION OF AQUEOUS AMMONIA.

Ammonium hydroxide. (Gram-molecules per litre.)	Proportion ionized.	Molecular concentration of $NH_4^{\cdot}$ and of OH' ions. (Gram "ions" per litre.)	Molecular concentration of non-ionized NH_4OH. (Gram-molecules per litre.)	K
1·0000	0·0047	0·0047	1·0000–0·0047	0·000023
0·1250	0·0135	0·0017	0·1250–0·0017	0·000023
0·0159	0·0376	0·0006	0·0159–0·0006	0·000023
0·0039	0·0754	0·0003	0·0039–0·0003	0·000023

$$\frac{\lambda}{\lambda_\infty}=a\frac{v^{\cdot}+v'}{v^{\cdot}_\infty+v'_\infty}$$

which shows that λ/λ_∞ is equal to a only when the mobilities of the ions are constant for the concentrations under consideration, for only then does $v^{\cdot}+v'=v^{\cdot}_\infty\pm v'_\infty$. In view of the possible electrical effects resulting from the large electric charges on the ions, this assumption is by no means certain.

Again, S. Arrhenius and W. Ostwald [2] inclined to the view that the cause of the discrepancy is due to the failure of the mass law with strong electrolytes; H. Jahn believed that imperfections in the method of measuring λ_v/λ_∞ render the ratio an imperfect measure of a; and C. A. Kraus suggested introducing a correction term for the viscosity of the medium, $\lambda_v\eta_0/\lambda_\infty\eta=a$, when η_0 and η respectively denote the viscosities of solvent and solution. E. W. Washburn proposed $\lambda\phi_\infty^m/\lambda_\infty\phi^m=a$, where ϕ represent the fluidities of the media; for solutions less than normal, $m=0{\cdot}94$, but F. G. Donnan and W. E. Garner showed that the value of m decreases with increasing concentration for $2N$- to $12N$-solutions of lithium chloride. Another set of workers—S. Arrhenius, C. A. Kraus and W. C. Bray, J. Kendall, and W. R. Bousfield, etc.[3]—have corrected the results for the effect of traces of impurity in the solvent on the conductivity measurements. A. A. Noyes and W. C. Bray, J. Walker, etc.,[4] have suggested that the deviation is to be ascribed to the abnormal behaviour of the un-ionized molecules of strong electrolytes slightly increasing the concentration of the ions. The stimulating effect of the un-ionized molecules on ionization is also assumed by B. de Szyszkowsky. P. Walden [5] suggested that the solute increases the dielectric constant of the solvent and this augments its ionizing power. H. Jahn and G. N. Lewis have suggested that there is an increase in the ionic mobility with increasing ionic concentration. J. C. Ghosh assumes with W. Sutherland that the electrolyte is completely ionized, but that part of the ions are free to move as contemplated by the kinetic theory, and part are bound so as to hold fixed positions in the solvent-like structural units in the space lattice of a crystal. Another hypothesis assumes that a Grotthus chain conductivity is superposed on the ionic conductivity, a view negatived by the work of C. A. Kraus and W. C. Bray; [6] yet another hypothesis suggests that the solvent in the solution also conducts some of the current.

The question was raised by O. J. Lodge in 1886, if pure water and pure hydrogen chloride are non-conductors, and the conductivity of hydrochloric acid is due to the ionization of the hydrogen chloride by water; presumably also the effect is not one-sided, and the water is likewise ionized by the acid.[7] J. W. McBain has pointed out that if the movement of the cation and anion add up to unity, the solvent cannot have taken a share in the conductivity, and this conclusion is not affected by the presence of various kinds of complex ions. The work of G. Poma and B. Tanzi[8] makes it appear as if the water in the presence of sodium chloride is not so much ionized as the solvent alone. W. Palmaer and K. Melander draw the opposite conclusion with respect to aqueous solutions of calcium and lithium chlorides, so also did H. S. Harned with respect to solutions of sodium bromide or the chlorides of the alkalies and alkaline earths in hydrochloric acid. A. Sachanoff found that with solvents of low dielectric constant, an increased ionization occurs when other electrolytes are added, although with water there is a decrease.

The failure has been attributed to the gradual hydration of the ions during dilution. If so, the mobility of the ions will be constant only when the hydration is complete. The conductivity, therefore, will not depend upon ionization alone, but will also depend on the degree of hydration of the ions. If the dissolved substance combines with the solvent, then, in the more concentrated solutions, part of the liquid in which the substance is dissolved will no longer function as solvent because it is in combination with the ions and the non-ionized molecules of the solute. This is virtually the **solvate theory of solution** which so much attracted H. C. Jones.[9] However, this does not affect the principles which are based upon the dilution law, for it is merely necessary to introduce an additional factor to provide for the fact that the solution is much more concentrated than it would be if all the liquid in which the substance is dissolved is doing the work of a solvent. H. C. Jones, for instance (1913), has given very good evidence for assuming that what we call a normal solution of aluminium chloride and of several other substances in water is about twice normal because about five-eighths of the water is actually combined with the dissolved substance.

Numbers of formulæ[10] have also been proposed by M. Rudolphi, L. Storch, J. H. van't Hoff, F. H. McDougall, C. A. Kraus, and W. C. Bray, etc., in place of the one based on the law of mass action. In most of these, empirical changes are made in the indices or terms are added to the simple dilution law. The results are satisfactory only when empirical correspondence with fact is desired. The present position of the theory of ionization discussed at the Faraday Society[11] (1919), made it very clear that in spite of twenty years' labour there is something fundamentally wrong in the application of the mass law to ionization, excepting in the case of weak electrolytes and of very dilute solutions of the stronger electrolytes. The general conclusion to be drawn from the work is that electrical conductivity is not an accurate measure of ionic concentration, and for strong electrolytes in concentrated solutions, λ_v/λ is not equal to a. This is confirmed by a comparison, by H. N. Lewis and G. A. Linhart, of A. A. Noyes and K. G. Falk's value of a from the ratio λ/λ_∞ and the value computed from thermochemical data for solutions with 0·01 gram-molecule of the salt per litre. The discrepancies are very pronounced :

	KCl	NaCl	KIO_3	$NaIO_3$	K_2SO_4	$BaCl_2$	$CdSO_4$	$CuSO_4$	$La(NO_3)_2$
a . .	0·925	0·925	0·872	0·872	0·687	0·716	0·338	0·290	0·571
λ/λ_∞ .	0·941	0·936	0·928	0·917	0·872	0·883	0·614	0·629	0·802

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§ 12. The Solubility Law

In the case of an aqueous solution of sodium chloride, containing, say, 58·5 grams, that is, one gram-molecule per litre, we have: $NaCl=Na^{\cdot}+Cl'$, where 68 per cent. of the salt is ionized. The condition of the equilibrium, according to the dilution law, is

$$\frac{[Na^{\cdot}][Cl']}{[NaCl]}=K;\quad \frac{0\cdot68\times0\cdot68}{0\cdot32}=K;\text{ or }K=1\cdot44$$

If Cl'-ions be added they must necessarily be accompanied by an equivalent number of oppositely charged ions of, say, $K^{\cdot}$, from, say, a solution of potassium chloride; or of $Na^{\cdot}$-ions from, say, sodium hydroxide; $NaOH\rightleftharpoons Na^{\cdot}+OH'$; etc. If either $Na^{\cdot}$- or Cl'-ions be added to the solution—say, hydrogen chloride—making the concentration of the Cl'-ions 0·75 instead of 0·68—then, in order to preserve the constancy of the ratio 1·44, the concentration of the $Na^{\cdot}$-ions must be diminished. This can only occur by the union of some of the $Na^{\cdot}$- and Cl'-ions to form NaCl until the ratio K is again 1·44.

Solubility of mixtures with a common ion.—Sodium chloride is in equilibrium with its aqueous solution, when, at a given temperature, the concentration of the substance in solution has a certain definite and constant value—the solubility of the substance at the given temperature. Since the sodium chloride in solution is partly ionized, there are two equilibria to consider: first, the relation between the non-ionized and the ionized salt in solution, $NaCl \rightleftharpoons Na^{\cdot} + Cl'$ just indicated; and second, the relation between the non-ionized salt and the solid. If the solution be saturated, we have:

$$NaCl_{solid} \rightleftharpoons NaCl_{solution} \rightleftharpoons Na^{\cdot} + Cl'$$

If the concentration of the $Na^{\cdot}$ or the Cl' be augmented by the addition of hydrochloric acid, some of the $Na^{\cdot}$- and Cl'-ions will recombine to form non-ionized NaCl as indicated above. Consequently, some sodium chloride will be precipitated or the solution will be supersaturated. Hence **the solubility of a salt is usually diminished in the presence of another compound with a common ion.** If the solution of the hydrochloric acid had been isohydric with the salt solution—*i.e.* if the number of chlorine ions per cubic centimetre had been the same—no alteration in the concentration of the ions would occur, and therefore no salt would be precipitated on mixing the solutions, provided no disturbing secondary action occurs. The solubility of potassium nitrate is influenced in the same way by equivalent solutions of potassium chloride and bromide. Hence, it follows that the two latter salts are ionized to the same extent. A familiar example of this phenomenon is the precipitation of sodium chloride from its saturated solution by the action of hydrogen chloride or a concentrated aqueous solution of the acid.

The solubility of sodium chloride in the presence of increasing amounts of hydrochloric acid, decreases more rapidly than corresponds with the simple theory. The phenomenon is complicated by the chemical union of hydrochloric acid with some of the water, as is evidenced by the development of heat during the reaction. This increases the concentration of the sodium chloride solution by removing some of the effective solvent. The precipitation of sodium chloride by the addition of alcohol to a saturated solution of that salt is due to the union of the solvent with the alcohol, so that less solvent is available for the sodium chloride. The phenomenon is quite general; for example, potassium chloride in saturated solution is precipitated by hydrochloric acid, sodium chloride, or potassium sulphate; copper sulphate by copper nitrate, or sulphuric acid; barium chloride by hydrochloric acid, or sodium chloride; calcium sulphate, by sulphuric acid, potassium sulphate, or calcium nitrate. Again, nitric acid will precipitate barium nitrate from concentrated aqueous solutions; a nearly saturated solution of silver bromate will give a precipitate of silver bromate, if either silver nitrate or sodium bromate be added to the solution; sodium chlorate added to a saturated solution of potassium chlorate furnishes a precipitate of the last-named salt.

Solubility product.—It is sometimes convenient to discriminate between the total or **apparent solubility** of a salt, and the amount of the non-ionized salt present in the solution. The latter is sometimes called the **real or molecular solubility** of the salt. According to W. Nernst, if W. Ostwald's law applies to solutions, in a saturated solution the real solubility, like the apparent solubility, is regarded as constant. Hence, in the dilution law for sodium chloride: $[Na^{\cdot}][Cl'] \rightleftharpoons K[NaCl]$, indicated above, the concentration [NaCl] is invariable, K is constant, and consequently also the product of the two is constant. Therefore, for saturated solutions:

$$[Na^{\cdot}][Cl'] = \text{Constant}$$

This relation means that **in a saturated solution, the product of the "molecular" concentrations of the ions is constant.** This product is sometimes called the **solubility product** because, from what has been already stated, the product of the two ion concentrations determine the magnitude of the "real" solubility of the substance.

Rule for precipitation.—The solubility product of sodium chloride in solution is not very great, and, in consequence, if concentrated hydrochloric acid be added to a concentrated solution of sodium hydrogen sulphate, $NaHSO_4$, the solubility product of sodium chloride may be exceeded, and that salt will be precipitated. The condition of equilibrium of the mixed solutions is:

$$\begin{array}{rllll}
\mathrm{NaHSO_4} \rightleftharpoons & \left\{\begin{array}{l}\mathrm{Na^{\cdot}} \\ + \\ \mathrm{Cl'}\end{array}\right. & \begin{array}{c} + \\ \\ + \end{array} & \left\{\begin{array}{l}\mathrm{H^{\cdot}} + \mathrm{SO_4''} \\ + \\ \mathrm{H^{\cdot}}\end{array}\right. \\
\mathrm{HCl} \rightleftharpoons & & & \underbrace{\qquad\qquad} \\
 & \quad\upharpoonleft\!\downharpoonright & & \quad\upharpoonleft\!\downharpoonright \\
 & \mathrm{NaCl} & & \quad\mathrm{H_2SO_4}
\end{array}$$

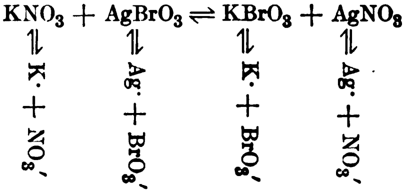
Hence, if the product of the "molecular" concentration of any pair of ions (with equal and opposite electrical charges) in a solution be greater than the solubility product for the saturated solution formed by the union of these ions, that substance will be precipitated; and conversely, if a substance be present in excess, it will be dissolved if the product of the "molecular" concentration of any pair of ions (with equal and opposite electrical charges) in a solution be *less* than the solubility product for the saturated solution formed by the union of these ions.

Apparent exceptions to the solubility law.—There are some apparent exceptions. The solubility of silver sulphate is increased, not diminished, by the addition of potassium or ammonium sulphate. Lead chloride is not precipitated from its saturated solution by lead nitrate, nor is barium chloride precipitated by barium nitrate. In both these cases a precipitate is produced by the addition of alkali chloride or hydrochloric acid. Calcium sulphate is not precipitated by sodium or ammonium sulphate, but it does separate on the addition of potassium sulphate or sulphuric acid; potassium sulphate is not precipitated from its saturated solution by sulphuric acid, but it does separate on the addition of potassium chloride or sodium sulphate. The explanation is that in each case double or complex salts are formed, which really *diminish* the number of lead or chloride ions in the case of lead chloride by forming a lead chloronitrate, $\mathrm{PbClNO_3}$. Similarly, in the other cases $\mathrm{BaClNO_3}$, $\mathrm{CaNa_2(SO_4)_2}$, $\mathrm{Ca(NH_4)_2(SO_4)_2}$, $\mathrm{KHSO_4}$, etc. In many cases the solubility of the double or complex salt so formed is less than the solubility of either constituent, and when such a solution is concentrated, the double compound separates in preference to the single components, *e.g.* potassium sulphate has a solubility of 12·5; aluminium sulphate, 8·5; and the double salt, $\mathrm{KAl(SO_4)_2.12H_2O}$, 9·5; potassium sulphate, 12·5; nickel sulphate, 6·7; and the double salt, $\mathrm{K_2Ni(SO_4)_2.6H_2O}$, 6·3; potassium carbonate, 110; sodium carbonate, 21; the double salt, $\mathrm{KNaCO_3.6H_2O}$, 13. With potassium and calcium sulphates the solubility of the latter (0·205) is less than the solubility of either potassium sulphate (12·5) or the double salt $\mathrm{CaK_2(SO_4)_2.H_2O}$—0·25. Calcium sulphate is accordingly precipitated in preference to the double salt.[1]

The solubility law developed by W. Nernst (1889) and A. A. Noyes (1890) [2] is based on assumptions which are not always valid. For example: (i) That the ionization conforms with W. Ostwald's law of mass action. As a matter of fact the ratio of the product of the concentrations of the positive and negative ions to the concentration of the un-ionized salt becomes greater as the concentration of the salt increases, otherwise expressed, the value of K in, say, $[\mathrm{M^{\cdot}}][\mathrm{Cl'}]=K[\mathrm{MCl}]$ increases with increasing concentration. (ii) It is assumed that the concentration of the un-ionized molecules of an electrolyte in solution and in equilibrium with its solid phase is always constant. S. Arrhenius, however, has shown that this is not in accord with fact, for the concentration of the un-ionized salt, *i.e.* the molecular solubility, diminishes as the total concentration of the salt in solution is increased. S. Arrhenius (1899) argued that the non-ionized part of a salt in a saturated solution is not a constant because the non-ionized part of thallous chloride, TlCl, in aqueous solution, as calculated from the electric conductivity, is 0·00179N, while if 0·8N-potassium chloride is present, the total solubility of thallous chloride is 0·00170N, or less than that of the non-ionized salt in aqueous solution—of this, 0·00170, perhaps 40 per cent., is ionized, leaving the non-ionized part of less concentration than in aqueous solute. (iii) It is assumed that the degree of ionization is independent of the presence of other electrolytes. S. Arrhenius, W. D. Harkins, M. S. Sherrill, have shown that this postulate is not in accord with fact. The solubility of calcium sulphate is increased up to a certain point by the addition of sodium chloride, and beyond that is diminished. A. E. Hill (1909) found that the solubility of silver sulphate in nitric acid behaves similarly. In both cases an increased solubility might have been anticipated owing to the formation of new compounds which would be opposed by a *small* decrease in the amount of un-ionized salt in solution, for with highly ionized salts like gypsum and silver sulphate in aqueous solution, the increased ionization is negligibly small. The diminution in the total solubility is therefore an effect of a diminution in the concentration of the ions of the solute, as distinct from chemical interaction, called by S. Arrhenius (1899) *the neutral salt effect*. According to this phenomenon, the presence of neutral salts increases the ionization of weak acids present with them in solution, either by the water acquiring a greater ionizing power, or the salt itself acting as a dissociating medium. The *Neutralsalzwirkung* has been studied by many workers. G. Poma and A. Patroni found that the ionization of cupric nitrate is augmented in aqueous solution by the presence of other nitrates—excepting those of potassium and rubidium. A. Sachanoff and P. J. Gontscharoff found the ionization of silver nitrate to be depressed by the addition of other salts—*vide* § 13. In general, observations indicate that the addition of sodium chloride to an acid solution results in an increase in hydrogen-ion concentration, whereas adding it to an alkaline solution causes an increase in concentration of the hydroxide ion.

The constancy of the solubility product is not maintained, for the work of F. K. Cameron and of A. E. Hill and J. P. Simmons has shown that the product of the concentration of the ions diminishes in value as the concentration of the electrolyte increases—*e.g.* the solubility of gypsum increases with the addition of sodium chloride up to a certain concentration beyond which it decreases; similarly, with silver sulphate and nitric acid; thallous chloride in acetic acid; with tetramethylammonium iodide in potassium hydroxide; etc. A continuous increase in solubility due to the formation of new compounds might have been anticipated; this will be opposed by a small decrease in the amount of an ionized salt as indicated by S. Arrhenius' experiments, but not sufficient to counterbalance the increase due to chemical action, since the quantity of un-ionized salt is negligibly small with such salts as silver sulphate and calcium sulphate. Hence, in order to explain the diminution in the solubility product it seems necessary to assume that the concentrations of the ions of the solute have been lessened. The solubility of mercuric chloride is increased by the addition of hydrochloric acid owing to formation of a combination of hydrochloric acid and mercuric chloride, which has a greater solubility than mercuric chloride alone. Again, a concentrated solution of cupric potassium sulphate, $K_2Cu(SO_4)_2.6H_2O$, can be separated into its components, potassium and cupric sulphates, by diffusion. A solution saturated with respect to both salts is possible in which the two salts are present in the ratio of their solubilities, but this condition is disturbed by the tendency of the more soluble salt to crystallize out. Either salt added in a soluble form will not drive the other out of its saturated solution, but there is a definite state of equilibrium when the solution is not changed by further additions. Equilibrium is the same whether one salt be added to a saturated solution of the other, or directly to the double salt. These facts strike at the foundations of the solubility product law, for the constancy of both relations was assumed in deducing that law. *The solubility product is not constant, but diminishes in value in the presence of other electrolytes.* With a decreasing value of [MR] and an increasing value for the whole proportion, it follows that the ion product $[M^\cdot]\times[R']$ might remain approximately constant if perchance the proportion grows larger to the same extent as the true solubility grows smaller. Hence, although the premises from which the solubility product law has been deduced are not the whole truth, yet it is conceivable that the law itself might be a sufficiently close approximation to be of practical assistance in the study of reactions involving precipitation, solution, etc. This alternative has been tested by J. Stieglitz (1908) with respect to the solubility of the silver salts of a number of organic acids. He finds that the solubility product must be treated as an "approximate empirical principle" without a theoretical foundation. This conclusion is confirmed by A. Findlay's experiments (1900) on the relative solubility of lead iodide and sulphate; G. Bodländer's work (1900) on the solubility of calcium carbonate in aqueous solutions of carbon dioxide; A. A. Noyes (1890–1903) on the solubility of lead iodide in solutions of potassium iodide, of lead chloride in solutions of potassium chloride, of calcium hydroxide in presence of ammonium chloride; etc.

Solubility of mixtures with no common ion.—If potassium nitrate be added to a saturated solution of silver bromate, a number of molecules of silver nitrate and potassium bromate will be formed by double decomposition, and the solution will be in equilibrium when these four salts have attained a definite concentration, and each salt is itself ionized and is in equilibrium with the corresponding ions. The condition of equilibrium is therefore complex. It may be symbolized:



$$\begin{array}{ccccccc} KNO_3 & + & AgBrO_3 & \rightleftharpoons & KBrO_3 & + & AgNO_3 \\ \upharpoonleft\!\downharpoonright & & \upharpoonleft\!\downharpoonright & & \upharpoonleft\!\downharpoonright & & \upharpoonleft\!\downharpoonright \\ K^{\cdot}+NO_3' & & Ag^{\cdot}+BrO_3' & & K^{\cdot}+BrO_3' & & Ag^{\cdot}+NO_3' \end{array}$$

The net result is that the number of ionized and non-ionized molecules of silver bromate in the solution is lessened, and the equilibrium:

$$AgBrO_{3\,\text{solid}} \rightleftharpoons AgBrO_{3\,\text{solution}}$$

is disturbed. The original relation is restored by the passage of more silver bromate into solution. Similarly, when nitric acid is added to a saturated solution of silver acetate, some silver nitrate is formed, and the equilibrium:

$$\text{Silver acetate}_{\text{solid}} \rightleftharpoons \text{Silver acetate}_{\text{solution}}$$

can only regain its former value by the passage of more silver acetate into solution. Consequently, **the solubility of a salt may be increased in the presence of a compound containing no common ion.** There are a number of complications in special cases owing to the dehydration of the solution by the added substance; the solute may form polymerized molecules in the presence of the solvent; etc. The dehydrating action is illustrated in the familiar method of preparing hydrogen chloride by dropping concentrated sulphuric acid into a concentrated hydrochloric acid. The sulphuric acid abstracts water, and thus diminishes the effective amount of the solvent, the hydrogen chloride is then evolved as a gas. The action is in part attributed to the repression of the ions of hydrogen chloride at the same time, and the consequent elimination of molecules from the water already saturated with molecules of the same kind. Similarly, an excess of sulphuric acid precipitates the di- or monohydrate of cadmium chloride almost completely; the particular hydrate formed depends on the amount of sulphuric acid added. Cadmium bromide, mercuric chloride or bromide, and copper and stannous chlorides or bromides behave similarly. The behaviour of many salts is thus not completely described by the solubility product law.

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§ 13. Acids and Bases according to the Ionic Hypothesis

> The ionization hypothesis enables us to place the whole subject of acidity upon a rational basis. Without this theory, the subject would still be only so many empirically established, disconnected, and meaningless facts.—H. C. JONES (1913).

Acids.—It will be remembered that C. Gerhardt defined acids to be "salts of hydrogen," the ionic hypothesis expresses a similar idea another way: "all acids, when dissolved in water, furnish hydrogen ions." Although many substances not usually called acids when completely ionized furnish hydrogen ions—*e.g.* potassium hydrogen sulphate, $KHSO_4$, etc.—yet their acidic properties are due to the presence of $H^{\cdot}$-ions, and consequently it has been said that "there is only one acid, and that is the $H^{\cdot}$-ion," and that "the two terms acidity and hydrogen ions are co-extensive."[1] Hydrogen ions thus become the primordial acid of the older chemists. The general and characteristic properties of acids are assumed to be the general and characteristic properties of $H^{\cdot}$-ions, and thus the $H^{\cdot}$-ions are said to have a sour taste, redden blue litmus, conduct electricity in solutions containing them, behave as univalent radicles, etc. The basicity of an acid is fixed by the number of $H^{\cdot}$-ions furnished by the complete ionization of one molecule of the acid. Thus monobasic hydrochloric acid, HCl, furnishes one $H^{\cdot}$-ion, $HCl \rightleftharpoons H^{\cdot} + Cl'$; and dibasic sulphuric acid furnishes two $H^{\cdot}$-ions, $H_2SO_4 \rightleftharpoons 2H^{\cdot} + SO_4''$. Sulphuric acid also furnishes the ions $H^{\cdot}$ and HSO_4', so that it behaves also as a monobasic acid when it forms the so-called "acid sulphates."

Why is the hydrogen ion acidic?—The action of a metal, say zinc, on an acid is usually represented by the equation: $Zn + 2HCl = ZnCl_2 + H_2$; the ionic hypothesis assumes that $Zn + 2H^{\cdot} + 2Cl' \rightleftharpoons Zn^{\cdot\cdot} + 2Cl' + H_2$; and that the different atoms have different affinities—**electro-affinities**—for the electric charges as assumed by H. von Helmholtz in 1881. Since the Cl'-ions are but little affected by the change, the last equation reduces to $Zn + 2H^{\cdot} = Zn^{\cdot\cdot} + H_2$. The action is thus independent of the negative ion, for it involves little more than a transfer of the positive electric charges from the two hydrogen ions to the zinc, and generally, such typical chemical reactions can be represented as the transfer of electrical charges from hydrogen to the metal. When the solution of zinc chloride is concentrated by evaporation the ionizing solvent is removed from the system and the $Zn^{\cdot\cdot}$- and $2Cl'$-ions recombine to form zinc chloride. **The hydrogen ion is an acid because it holds its charge less tenaciously than the metals hold their charges.** If it were otherwise, says H. C. Jones, if hydrogen held its charge as firmly as the average metal, the acids would not be acids.

Why is hydrogen acidic in some compounds and not in others?—The answer furnished by the ionic hypothesis is that hydrogen separates from the former compounds as ions, but not from the latter. Hydrogen chloride in aqueous solution is an acid because it furnishes $H^{\cdot}$-ions, but it is not an acid when dissolved in dry benzene or dry chloroform because it does not then furnish $H^{\cdot}$-ions. Hence, says

H. C. Jones, **an acid is a compound which yields hydrogen ions when dissolved in an ionizing solvent.** Dry benzene and dry chloroform are not ionizing solvents. A compound becomes an acid only when it is ionized into hydrogen ions, etc. Many substances contain hydrogen, and they are not regarded as salts of hydrogen. Methane, CH_4; ammonia, NH_3; alcohol, C_2H_5OH, etc. Again, H_3PO_2 only gives one hydrogen ion per molecule, and the remaining two hydrogen atoms are not ionizable, for they form an essential part of the cation H_2PO_2'. Silicic acid is very slightly soluble in water, so that its aqueous solution has no effect on blue litmus. Silicic acid is acid because it forms a salt, sodium silicate, Na_2SiO_3, which dissolves in water and ionizes: $Na_2SiO_3 \rightleftharpoons 2Na^{\cdot} + SiO_3''$, when electrolyzed. Neither pure dry hydrogen chloride nor pure dry sulphuric acid is acidic; neither compound is ionized; nor acts on metals; nor decomposes carbonates; nor colours blue litmus.

The chemical activity of different solutions containing equivalent amounts of the different acids is referred to the concentration of the $H^{\cdot}$-ions in the solution.—The concentration of the $H^{\cdot}$-ions depends upon the degree of ionization of the different acids. Hence, the relative strengths of the acids can presumably be expressed in terms of the electrical conductivity of equivalent solutions. The speed of a reaction dependent upon an acid is thus connected with the concentration of the $H^{\cdot}$-ions. Reverting to the measurements given previously for hydrochloric, sulphuric, and acetic acids, although the solutions contained equivalent quantities of replaceable hydrogen per litre, acetic acid has but one two-hundredth the activity of hydrochloric acid.

	Hydrochloric acid.	Sulphuric acid.	Acetic acid.
Fraction ionized . .	0·78	0·51	0·004
Relative strength . .	100	70	0·5

In hydrochloric acid, a greater number of hydrogen ions are ready to react with the metal than with acetic acid, and consequently the available hydrogen in hydrochloric acid is more rapidly exhausted than with acetic acid where but few ions are in a condition to react with the metal at any moment, and consequently the reaction progresses slowly for a long time; as fast as the available ions are exhausted, new ions are formed by the ionization of the molecule of acetic acid. The total number of hydrogen ions is the same in both cases, but the number in a condition to react with the metal at any moment is very different in all three cases.

Bases.—Just as an acid has been defined to be a substance which can furnish hydrogen ions when dissolved in water, so bases, according to the ionic hypothesis, are substances which yield HO'-ions when dissolved in water. The basic properties of bases are due to the OH'-ions, and in this sense it has been said that "there is only one base, and that is the OH-ion," and that "the two terms hydroxyl ions and base are co-extensive." The general and characteristic properties of the bases are supposed to be the general and characteristic properties of the OH'-ions. Thus the OH'-ions are said to have a soapy feel, turn red litmus blue, conduct electricity in a solution containing them, etc. The acidity of a base is fixed by the number of OH'-ions it furnishes on complete ionization of a molecule of the base. Thus, the monoacid bases, like sodium hydroxide, ionize: $NaO \rightleftharpoons Na^{\cdot} + OH'$; and the diacid bases, like barium hydroxide, ionize: $Ba(OH)_2 = Ba^{\cdot\cdot} + 2OH'$. In a non-ionizing solvent, the bases do not furnish hydroxyl ions, and they do not then behave like bases. Hence, says H. C. Jones, **a base is a compound which furnishes hydroxyl ions when dissolved in an ionizing solvent.** A compound becomes a base only when it is ionized into hydroxyl ions.

The strength of a solution containing equivalent quantities of the different bases is referred to the concentration of the OH'-ions in the solution.—The strength of a base depends upon the degree of ionization, or on the concentration of the OH'-ions. The strength of a base can thus be determined from the electrical conductivity. In equivalent solutions, bases, like acids, differ very much in strength. The alkalies and alkaline hydroxides are very strong bases, for they are ionized to very nearly the same extent as hydrochloric acid in aqueous solution. Ammonia is a comparatively feeble base. The following numbers represent the relative strengths of a few bases in $\frac{1}{40}N$-solution on the assumption that the strength of the base is proportional to the electrical conductivity:

	LiOH	NaOH	KOH	NH_4OH
Relative strength . . .	100	98	98	2

Reactions between acids and salts.—When a highly dissociated acid is mixed with a salt, the two react, forming another acid and salt. The change is reversible, and the reacting system is then a further illustration of the principle of opposing reactions. For instance, the action of dilute nitric acid on potassium hypochlorite, $HNO_3+KOCl \rightleftharpoons KNO_3+HOCl$. If both products are highly ionized, there will be no perceptible change in the system, but in the illustration just cited, hypochlorous acid is but feebly ionized, and, since the $H^{\cdot}$-ions of the nitric acid, and the OCl'-ions of the potassium hypochlorite, react to form feebly ionized hypochlorous acid, the result of the reaction in dilute solutions is ionized potassium nitrate, and feebly ionized hypochlorous acid:

$$\underbrace{H^{\cdot}+NO_3'}+\underbrace{K^{\cdot}+OCl'} \rightleftharpoons \underbrace{K^{\cdot}+NO_3'}+HOCl$$

Reactions between bases and salts.—Similar remarks apply, *mutatis mutandis*, to the action of a salt on a base, and this explains how feebly ionized ammonium hydroxide is formed in relatively large quantities when highly ionized solutions of potassium hydroxide and ammonium nitrate are mixed together. The reaction proceeds almost to the end:

$$\underbrace{NH_4^{\cdot}+NO_3'}+\underbrace{K^{\cdot}+OH'} \rightleftharpoons \underbrace{K^{\cdot}+NO_3'}+NH_4OH$$

When the base is insoluble, it will be precipitated, and the reaction will proceed to an end quite apart from the degree of ionization of the reacting compounds. This is the case, for example, with ferric, aluminium, zinc, and other hydroxides:

$$\underbrace{Fe^{\cdots}+3Cl'}+\underbrace{3Na^{\cdot}+3OH'} \rightleftharpoons \underbrace{3Na^{\cdot}+3Cl'}+Fe(OH)_3$$

The determination of the basicity of acids.—W. Ostwald (1887)[2] and P. Walden (1887) noticed empirically that if n_a denotes the valency of the anion, and n_c the valency of the cation, the difference D between the equivalent conductivity of the corresponding electrolyte dilutions $v=1024$ and $v=32$ is $D=Kn_an_c$, where K is a constant which is a function of the concentration of the solution, and for the $v=1024$ and $v=32$ is nearly 10. If the sodium salts be employed, $n_c=1$; and at 25°, the basicity of the acid is approximately $\frac{1}{10}D$. For monobasic acids D is nearly 10; for dibasic acids, 20; for tribasic acids, 30; etc.; otherwise expressed, **the equivalent conductivity of aqueous solutions of the sodium salts of *n* basic acids increases by about $n \times 10$ units on diluting a solution from $\frac{1}{32}N$ to $\frac{1}{1024}N$.** This empirical relation is sometimes called **Ostwald and Walden's rule.**

The unit of conductivity is now rather smaller than that used in 1887. The constant is now more nearly 10·8 than 10, so that the empirical rule is more nearly exact if the basicity of the acid be taken as one-eleventh of the difference, D, between the equivalent conductivities of the sodium salt at dilutions $v=32$ and $v=1024$. The amended rule then reads:

$$\text{Basicity of acid} = \tfrac{1}{11}D$$

Numerous tests of the rule have been made with organic acids. Table IV shows some results with inorganic acids.

EXAMPLES.—(1) G. von Knorre (1900) showed that the equivalent conductivity of the so-called sodium trimetaphosphate with a composition corresponding with $Na_3(PO_3)_3.6H_2O$ at dilutions $v=32$, and $v=1024$, is respectively 89·5 and 122·4. Hence show that these numbers are in agreement with the inference "Nach der Ostwald-Walden'schen Regel ist demnach die Trimetaphosphorsäure als dreibasische Säure zu betrachten." Here $\frac{1}{10}(\lambda 1024-\lambda 32)=\frac{1}{11}(122{\cdot}4-89{\cdot}5)=3{\cdot}3$ nearly; and the acid is accordingly tribasic.

(2) R. Kremann and W. Decolle (1907) found that the conductivity of sodium fluoride increases on dilution from $v=32$ to $v=1024$ by 20·8 units. Explain how it might be inferred that " hydrofluoric acid is dibasic."

TABLE IV.—THE EQUIVALENT CONDUCTIVITIES OF SOME SODIUM SALTS.

Sodium salt.	Equivalent conductivities.		Differences.	$\frac{D}{11}$	Basicity of acid.
	$v=32$	$v=1024$			
Chloride, $NaCl$	113·6	126·3	12·7	1·1	1
Chlorate, $NaClO_3$	101·3	112·3	11·0	1·0	1
Perchlorate, $NaClO_4$	112·9	121·2	12·3	1·1	1
Nitrate, $NaNO_3$	108·2	120·1	11·9	1·1	1
Sulphite, $NaSO_3$	94·5	114·6	20·1	1·8	2
Tungstate, Na_2WO_4	95·9	116·4	20·5	1·8	2
Cyanoplatinate, Na_2PtCy_6	110·6	130·4	19·8	1·8	2
Orthophosphate, Na_3PO_4	97·5	114·2	26·7	2·4	3
Orthoarsenate, Na_3AsO_4	101·2	127·6	26·6	2·4	3
Trimetaphosphate, $Na_3(PO_3)$	89·4	119·4	30·0	2·8	3
Fleitmann's metaphosphate, $Na_4P_4O_{12}.4H_2O$	85·6	126·2	40·6	4·1	4

At extreme dilutions, more particularly with inorganic salts, secondary reactions—*e.g.* hydrolysis—may interfere with the conductivity determinations; in other cases, the dilution $v=1024$ does not appear great enough to ionize all the salt. There are accordingly some difficulties, but, in a great many cases, the method furnishes circumstantial evidence of the basicity of the acid in question.

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§ 14. The Strengths of Acids and of Bases

I have no doubt that fixed salts choose one acid rather than another in order that they may coalesce with it in more intimate union.—JOHN MAYOW (1674).

I maintain that when several acids act upon one metallic base, the action of one acid does not overpower that of the others so as to form an insulated combination, but each of the acids has a share in the action proportionate to its capacity for saturation and to its quantity.—C. L. BERTHOLLET (1803).

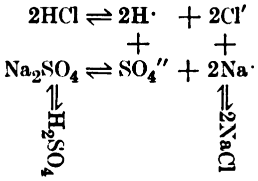
The **strength** of an acid or base refers to the extent to which the acid or base exhibits acidic or basic properties respectively. The terms *affinity*, *avidity*, and *activity* are sometimes employed synonymously with "strength," but there are objections to each of these. The term strength, too, is often used where concentration is really meant. **Concentration** refers to the "quantity in unit volume" expressed in, say, "grams per litre;" or in any other convenient form—say the number of gram-molecules per litre, etc.

The action of sulphuric acid on sodium chloride which results in the formation of hydrochloric acid, seems to prove that sulphuric acid is stronger than hydrochloric acid; again, when hydrochloric acid is added to a solution of silver sulphate, silver chloride is precipitated. The hydrochloric acid expels the sulphuric acid from its combination with silver: $Ag_2SO_4+2HCl=2AgCl+H_2SO_4$, and it seems as if hydrochloric acid is stronger than sulphuric acid. These two conclusions are contradictory, and there must therefore be a fallacy in our reasoning. We have wrongly assumed that the two acids were competing for sodium and for silver under similar conditions. This is not the case. When hydrochloric and sulphuric acids compete for the sodium, the hydrochloric acid, being volatile, escapes from the system as fast as it is formed; while the non-volatile sulphuric acid alone remains behind. Again, when sulphuric and hydrochloric acids are competing for silver, the hydrochloric acid carries the silver away from the sulphuric acid as an insoluble precipitate of silver chloride. Still further, hydrosulphuric acid is notoriously a very feeble acid, and yet it can displace relatively strong acids from combinations with the metals. Thus, it will precipitate lead sulphide from solutions of lead chloride; copper sulphide from solutions of copper sulphate, etc. Here, again, the feeble acid does its work by removing the metal from the solution as an insoluble sulphide.

To compare the relative strengths of the acids, and, *mutatis mutandis*, of the bases, it is necessary that the comparison be made under conditions where the reacting acids and the products of the reaction are in the same physical condition—say, all in solution. Thus, if an equivalent of a solution of sodium hydroxide be mixed with an equivalent of a solution of sulphuric and of hydrochloric acids, the two acids can compete for the one base under the same conditions, and hence the stronger acid will be able to unite with more sodium than the weaker acid. In 1803, C. L. Berthollet pointed out that:

> When a neutral salt is dissolved and an acid added to the solution, the free acid enters into competition with the combined acid, and they both act on the alkali base in the ratio of their respective concentrations as though no combination had existed. It cannot therefore be said that if all the conditions remain equal one acid displaces another from the base with which it has been united, but the base is shared between the two acids in the ratio of the concentrations and affinities of the respective acids.

It is found experimentally that the same result is obtained when equivalent quantities of sodium hydroxide, sulphuric acid, and hydrochloric acid are mixed together as when equivalent quantities of sodium sulphate and hydrochloric acid, or equivalent quantities of sodium chloride and sulphuric acid are mixed, provided, of course, the whole of the system has been allowed to stand long enough for equilibrium. This fact is represented by the equation: $2HCl + Na_2SO_4 \rightleftharpoons 2NaCl + H_2SO_4$, which, when translated into the language of ions, reads:



$$\begin{array}{ccccc} 2HCl & \rightleftharpoons & 2H^{\cdot} & + & 2Cl' \\ & & + & & + \\ Na_2SO_4 & \rightleftharpoons & SO_4'' & + & 2Na^{\cdot} \\ \downarrow\uparrow & & & & \downarrow\uparrow \\ H_2SO_4 & & & & 2NaCl \end{array}$$

The measurement of the relative strengths of acids and bases.—The proportions of a base shared between two acids, or of an acid between two bases, cannot be determined by the ordinary methods of chemical analysis without disturbing the equilibrium of the mixture. The distribution of an acid between two bases, or of a base between two acids, must be determined by physical processes which do not interfere with the solution.

In illustration, the heat of neutralization of sodium hydroxide by sulphuric acid is 31·38 Cals.; and by hydrochloric acid, 27·48 Cals. If, therefore, on mixing hydrochloric acid with sodium sulphate, all the sulphuric acid were displaced by the hydrochloric acid, the thermal effect resulting from the decomposition of the sodium sulphate, and the formation of the sodium chloride would be 27·48—31·38 = −3·9 Cals. After making a small allowance for secondary reactions between sodium sulphate and sulphuric acid, J. Thomsen found that the thermal value of the reaction was −2·6 Cals. Hence it follows that −2·6÷−3·9, or about two-thirds of the hydrochloric acid combines with about two-thirds of the base to form sodium chloride; and about one-third of the sulphuric acid combines with the other third of the base to form sodium sulphate.

A similar result was obtained with a mixture of sodium chloride and sulphuric acid, as with sodium sulphate and hydrochloric acid. Consequently, in the competition of sulphuric and hydrochloric acids for sodium under comparable conditions, the hydrochloric acid can hold twice as much of the base as the sulphuric acid, and consequently, hydrochloric acid is nearly twice as strong as sulphuric acid. Similar results have been obtained by measuring the specific gravity, index of refraction, absorption of light, etc. Some results obtained by three different methods are shown in Table V.

TABLE V.—RELATIVE STRENGTHS OF ACIDS.

Acid.	Thomsen's thermal process.	Ostwald's specific gravity process.	Molecular conductivity.
Hydrochloric acid	100	98	100·0
Nitric acid	100	100·00	99·6
Hydrobromic acid	89	95·00	100·0
Sulphuric acid	49	66·7	65·1
Phosphoric acid	25	—	7·3
Acetic acid	3	1·23	0·4

The relative strengths of the different acids and bases have also been determined by measuring the effects of the different acids on the speed of different reactions—*e.g.* the hydrolysis of acetamide, cane sugar, methyl acetate, etc. The actual numbers obtained by the different methods are not always quite the same, possibly because of the different conditions under which the experiments are made. If two acids are under the same physical conditions and differently influence the speed of a given reaction, the acid which induces the greater velocity is assumed to exert the greater chemical force. It has been found that in many cases the effects produced by one acid of different concentrations is roughly proportional to the electrical conductivity of its solution, which in turn is proportional to the concentration of the hydrogen ions. A. A. Noyes and A. A. Blanchard illustrate this by the following experiment:

> Mix 40 c.c. of 0·5*N*-KI, 40 c.c. of 0·5*N*-$KBrO_3$, 40 c.c. of starch solution, and make the whole up to two litres. Put 400 c.c. of this solution in each of four bottles and introduce 10 c.c. of each of the ½*N*-acids—hydrochloric, sulphuric, chloroacetic, and acetic acids—into each of the four cylinders, as quickly as possible. The bottles are immediately stoppered and shaken. The solution containing the hydrochloric acid turns deep blue almost immediately; the sulphuric acid in about half a minute; the chloroacetic acid in three or four minutes; and the acetic acid in three or four hours.

Again, the addition of an excess of foreign acid to the reaction between potassium chlorate, potassium iodide, and hydrochloric acid: $KClO_3+6HCl+6KI=7KCl+3H_2O+3I_2$, or to a mixture of bromic acid and hydriodic acid accelerates the change. The effect with different acids varies with their strength (affinity): HBr, HCl, HNO_3, H_2SO_4. This order is virtually the order as deduced from measurements of the degree of ionization of the different acids, and accordingly the catalytic effect is said to be due to the presence of hydrogen ions. Organic and other feebly ionized acids exert very little catalytic action. It was therefore postulated by W. Ostwald that the hydrolytic activity of acids is proportional to the degree of the assumed ionization.

S. Arrhenius found that the hydrolytic activity of strong acids is augmented by the addition of a neutral salt of the acid. Thus, the rate of hydrolysis of cane sugar by an aqueous solution of hydrogen chloride is considerably increased by the addition of sodium chloride or calcium chloride, although these substances decrease the degree of ionization of the acid. The effect was styled **neutral salt action** by S. Arrhenius. If the action of the acid is due to hydrogen cations, the presence of a neutral salt having the same anion should diminish the dissociation of the acid and consequently its activity, but this is not the case. Actual experiment yields results which are just the reverse of that which the theory of ions would indicate. J. W. McBain and co-workers have shown that the alleged effect can be accounted for on the assumption that the un-ionized salt is catalytically active without assuming that the solvent acquires a greater ionizing power, or that the salt acts as an ionizing medium.

Again, the molecular hydrolytic activity of strong acids is decreased by increasing dilution, whereas, if the activity were proportional to the degree of ionization, the reverse should obtain. Hence, G. Senter, H. C. S. Snethlage, S. F. Acree, etc.,[1] conclude that an electrolyte in solution may enter into chemical reactions not only by means of its ions, but also by means of its un-ionized molecules—otherwise expressed, the catalytic activity of acids is the joint effect of the hydrogen ions and of the un-ionized molecules. F. P. Worley has emphasized that instead of the rate of hydrolysis of ethereal salts and cane sugar being proportional to the concentration of the hydrogen ions, the two properties are altered in different directions by changes of concentration. For example, if n denotes the molecular proportions $H_2O : HCl$, H, the molecular hydrolytic activity, and a, the degree of ionization of hydrochloric acid,

n	30	40	50	60	80	100	200
H	385	323	290	269	243	229	201
a	0·725	0·778	0·813	0·837	0·859	0·871	0·901

Consequently, the catalytic activity of the acids is not proportional to the concentration of the hydrogen ions; and, adds F. P. Worley, "if hydrogen ions and un-ionized molecules are both chemically active, . . . in time, the extreme supporters of the ionic hypothesis may admit that both ions and un-ionized molecules may be concerned in electrolytic conductivity!"

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§ 15. The Neutralization of Acids and Bases

> The importance for chemistry of the fact that hydrogen and hydroxyl ions cannot remain in the presence of one another uncombined is difficult to over-estimate. Could these ions remain separate, then an acid would not neutralize a base, and all salt formation from the process of the neutralization of acids and bases would be excluded.—H. C. JONES (1913).

The term *neutral* has been used somewhat vaguely, implying that the substance is neither acidic nor basic. The test for acidity or basicity depended upon the behaviour of the solution towards a solution of litmus. If other indicators are used, the conclusions might be different, because a substance might appear acidic towards one indicator, and neutral towards another. The ionic hypothesis, as we have seen, refers acidity to the presence of hydrogen ions, and alkalinity to the presence of OH′-ions, and the term " neutrality " refers to the case where the concentration of both ions are the same, or both ions are absent. We have seen that water is a constant product of the reaction between the solution of an acid and of a base: $HCl+KOH \rightleftharpoons KCl+H_2O$; $H_2SO_4+2NaOH \rightleftharpoons Na_2SO_4+2H_2O$, etc. When solutions of an acid and base are mixed, the hydrogen and hydroxyl ions of acid and base respectively combine to form water, because water only ionizes to an inconceivably small extent, and the two kinds of ions—$H^{\cdot}$ and OH'—cannot remain in the presence of one another uncombined. Hence when aqueous solutions of acids and bases are mixed together, OH'- and the $H^{\cdot}$-ions are removed from the solution, and the reaction is almost completed:

$$\underbrace{H^{\cdot}+Cl'}+\underbrace{K^{\cdot}+OH'} \rightleftharpoons \underbrace{K^{\cdot}+Cl'}+H_2O$$

What is here stated with respect to hydrochloric acid and potassium hydroxide applies, *mutatis mutandis*, to any strongly ionized acid and base; and consequently, the neutralization of strongly ionized acids and bases involves little more than the formation of water: $H^{\cdot}+OH' \rightleftharpoons H_2O$, because the other ions present before the acids and bases are mixed remain after the reaction is over. If, however, the water be evaporated from the solution, the ions recombine to form the salt, and the result of the reaction is then correctly symbolized: $HCl+KOH \rightleftharpoons KCl+H_2O$. This reaction probably also occurs if very concentrated solutions or solids are mixed, whereas the **neutralization of acids and bases in dilute solutions involves the formation of water, not salt molecules.**

The heat of neutralization of dilute solutions.—This view is further supported by the fact that with dilute solutions of the strong acids and bases, the thermal value of the process of neutralization—heat of neutralization—is the same. For example,

	$LiOH$	$NaOH$	KOH	$Ca(OH)_2$	$Ba(OH)_2$
Hydrochloric acid . . .	13·7	13·7	13·7	13·8	13·8 Cals.
	HCl	HBr	HI	HNO_3	HIO_3
Sodium hydroxide . . .	13·7	13·8	13·7	13·7 .	13·5 Cals.

Hence, neutralization is an isothermal process; the heats of neutralization of dilute solutions of the strong acids and bases do not depend upon the specific nature of the acid or base; and the formation of water in these reactions is accompanied by the evolution of approximately 13·7 Cals. of heat.

The law only describes the thermal effect attending the neutralization of solutions sufficiently diluted to ensure complete ionization of acid, base, and salt; it presupposes that no new electrically neutral molecules are formed. As a corollary, it follows that if two completely ionized salts are mixed, there will be no thermal change provided the salts are completely ionized before and after the mixing, and no other electrically neutral molecules are formed. The fact that **if two neutral salt solutions at the same temperature are mixed together, no change of temperature occurs,** was discovered by H. Hess in 1841, and is called **Hess' law of thermoneutrality.** For example:

BEFORE MIXING.		AFTER MIXING.	
Calcium nitrate, $Ca(NO_3)_2$ . .	451	Calcium sulphate, $CaSO_4.2H_2O$.	642
Potassium sulphate, K_2SO_4 . .	601	Potassium nitrate, KNO_3 . .	409
Thermal value . .	1052	Thermal value . .	1051

The ionic hypothesis indicates clearly the conditions which must be fulfilled before Hess' law of thermoneutrality is applicable, and it would be difficult to find such a strikingly successful explanation by any other known hypothesis.

Heat of ionization.—If the acid and base are but partially ionized, the heat of neutralization is not only determined by the heat of formation of water—13·7 Cals.—but it is also determined by the thermal value of the energy required to complete the ionization of acid and base. When a dilute solution of hydrofluoric acid is neutralized by sodium hydroxide, for example, the sodium fluoride formed during the reaction is fully ionized, whereas the hydrofluoric acid at the commencement of the process: $HF+NaOH=NaF+H_2O+16{\cdot}27$ Cals. is not fully ionized. Hence in addition to the formation of water, there is a continuous ionization of hydrofluoric acid *during* the process of neutralization, and the fact that more heat is produced has been assumed to prove that the ionization of the acid is accompanied by the evolution of heat. The heat of neutralization of hypochlorous acid, HOCl, by sodium hydroxide, NaOH, is: $HOCl+NaOH=NaOCl+H_2O+9{\cdot}8$ Cals., a number less than the normal value 13·7 Cals. The salt, NaOCl, and the base, NaOH, are completely ionized; while the acid, HOCl, is but feebly ionized. Hence, it is assumed that the ionization of HOCl is an endothermal process. Similarly, when ammonia is neutralized: $NH_4OH+HCl=NH_4Cl+H_2O+12{\cdot}1$ Cals., it is assumed that the low results are due to the absorption of heat during the ionization of ammonium hydroxide. S. Arrhenius gives the following Table VI, in his *Recherches sur la conductibilité galvanique des électrolytes* (Stockholm, 1883):

TABLE VI.—HEATS OF NEUTRALIZATION OF ACIDS AND BASES.

	HCl	HNO_3	CH_3COOH	HCOOH	$\frac{1}{2}(COOH)_2$	$\frac{1}{2}H_2SO_4$	$\frac{1}{2}H_2S$	HCy	$\frac{1}{2}H_2CO_3$
NaOH .	13·7	13·7	13·3	13·4	14·3	15·85	3·85	2·9	10·2
KOH .	13·7	12·8	13·3	13·4	14·3	15·7	3·85	3·0	10·1
NH_4OH.	12·45	12·5	12·0	11·9	12·7	14·5	3·1	1·3	5·3
$\frac{1}{2}Ca(OH)_2$	14·0	13·9	13·4	13·5	18·5	15·6	3·9	—	9·8
$\frac{1}{2}Ba(OH)_2$	13·85	13·9	13·4	13·5	16·7	18·4	—	—	11·1
$\frac{1}{2}Sr(OH)_2$	14·1	13·9	13·3	13·5	17·6	15·4	—	—	10·5

Hess' law of thermoneutrality without the ionic hypothesis.—It would not be fair to pass by this explanation without indicating how H. Crompton (1897) showed that the phenomena could have been deduced without the aid of the ionization hypothesis. It follows from the calorimetric observations of J. Thomsen and of F. Stohmann and his co-workers[1] that for non-associated organic compounds—presumably non-ionized—the replacement of hydrogen, in a compound RH, by one and the same radicle M is attended by a constant heat change which is independent of the radicle R to which the hydrogen is attached; and generally, in non-associated organic compounds if M is constant, the thermal change in the reaction $RH+M=RM+H$ is constant and independent of R; and similarly, in the reaction $ROH+M=RM+OH$, the heat change will remain constant so long as M is constant.

In the neutralization of an acid by a base, in dilute solution, where the solutes may be assumed monomolecular, the changes which occur involve the splitting of the acid $HR=H+R+Q_1$ and of the base $MOH=M+OH+Q_2$, and the combination $M+R=MR+Q_3$, and of $H+OH=H_2O+Q_4$. First, if the base be constant and the acid varied, the terms Q_2 and Q_4 will be constant. The changes $HR=H+R+Q_1$ and $M+R=MR+Q_3$ are analogous with the changes which occur in the replacement of H by M in the non-associated organic compound RH. Hence, unless inorganic compounds behave quite differently from organic compounds, the heat of neutralization of an equivalent of any non-associated acid HR by an equivalent of one and the same non-associated base MOH, is always the same, and independent of the character of the acid. H. Crompton applies a similar argument to show that the heat of neutralization of an equivalent of any non-associated base MOH by the equivalent of one and the same acid HR is always the same and independent of the character of the base. These two conclusions are then generalized: The heat of neutralization of any acid by any base is independent of the character of the acid or base, so long as these are non-associated. H. Crompton further showed that in dilute solutions, the solute assumes a non-associated state.

The heat of neutralization of an acid by a base involves the heat of replacement $MOH+H=H_2O+M$, and the heat of replacement $HR+M=MR+H$, it therefore follows that since OH is a negative radicle like R, changing the radicle does not affect the heat of replacement of H by M or of M by H. Hence the heat of the first process should exactly balance that of the second, and an acid should be neutralized by a base without any thermal change whatever. With organic compounds the heat of formation of an ethereal salt from an acid and alcohol is usually very small—sometimes positive, sometimes negative, but the results are complicated by association phenomena and the heats of association are an integral part of the thermal values of the reactions. Again, with dilute solutions of acids and bases, the acid, base, and salt are in a very attenuated condition more or less comparable with the gaseous state; but the molecules of water produced in the reaction $MOH+HR=MR+H_2O$ will immediately pass to the liquid state characteristic of the solvent. The observed heat of the reaction is therefore mainly that caused by the condensation of the molecule of water from the gaseous to the liquid state and their subsequent polymerization or association. The molecular heat of condensation of water vapour is nearly 10·8 Cals. at 0°, and this is the same order of magnitude as the 13·4 Cals. observed by J. Thomsen for the heat of neutralization in dilute solutions. J. Thomsen also found that the heat of neutralization decreases with a rise of temperature in a way comparable with the effect of a rise of temperature on the heat of vaporization. These comparisons are closer than might have been anticipated. Hence, argues H. Crompton, the assumption that salts are ionized in aqueous solution is unnecessary to explain Hess' law of thermoneutrality; and "it is not only unnecessary, but it is inadequate, for it does not bring the behaviour of electrolytes, as far as the heat changes which accompany the formation of salts in aqueous solution are concerned, into line with the behaviour of non-electrolytes."

Hydrolysis.—It will be remembered that in hydrolysis, a salt reacts with water to form the free base and free acid, or free acid and a basic salt. **Hydrolysis is thus a reversion of the process of neutralization.** Reactions like those previously discussed are probably slightly reversible, but, in addition to those examples, there are many others where the back reaction is more pronounced. Hydrocyanic acid, HCy, for instance, ionizes: $HCy \rightleftharpoons H^{\cdot}+Cy'$. With potassium cyanide, KCy, in aqueous solution, $KCy \rightleftharpoons K^{\cdot}+Cy'$. In the latter case, some of the $H^{\cdot}$-ions of the water unite with the Cy'-ions of the salt to form molecules of hydrocyanic acid, HCy. The equilibrium is disturbed, and more molecules of water ionize: $H_2O \rightleftharpoons H^{\cdot}+OH'$. The new $H^{\cdot}$-ions combine with more Cy'-ions and the process continues until the concentration of the OH'-ions becomes large enough to prevent the further ionization of the water. The solution then contains an excess of OH'-ions, and free hydrocyanic acid, as well as potassium cyanide, and K'-and Cy'-ions. The free hydrocyanic acid can be recognized by its smell; and the OH'-ions can be recognized by the alkalinity of the solution.

The ionic hypothesis in analytical chemistry.—The language of the ionic hypothesis has penetrated analytical chemistry—more particularly the qualitative analysis taught in our schools—and as a result, tests for metals and acid radicles are described as tests for the ions. Many, however, doubt if anything is really gained by describing the facts of an essentially practical art in the language of so hypothetical a doctrine. Be that as it may, since both chlorides and hydrochloric acid are supposed to furnish chlorine ions: $HCl \rightleftharpoons H^{\cdot}+Cl'$, or $NaCl \rightleftharpoons Na^{\cdot}+Cl'$, it is assumed that the test for hydrochloric acid or for a chloride is a search for chlorine ions. The silver nitrate solution used in making the test is supposed to be ionized: $AgNO_3 \rightleftharpoons Ag^{\cdot}+NO_3'$; consequently, when silver nitrate is added to sodium chloride solution, the mixed solution momentarily contains: $Ag^{\cdot}+NO_3'+Na^{\cdot}+Cl'$; but, since a small proportion of silver chloride is ionized and the salt is but very slightly soluble in water, it precipitates at once. Silver chlorate, $AgClO_3$, is soluble in water, and accordingly, when silver nitrate is mixed with a solution of, say, potassium chlorate, there is no precipitation. The solution contains four different kinds of ions but no chlorine, Cl′-ions: $AgNO_3+KClO_3 \rightleftharpoons K^{\cdot}+ClO_3'+Ag^{\cdot}+NO_3'$. Hence, silver nitrate is a test for chlorine ions, but not for chlorate ions. If potassium cyanide KCy in aqueous solution be added to a solution of silver nitrate, $AgNO_3$, a precipitate of silver cyanide, AgCy, is obtained: $Ag^{\cdot}+NO_3'+K^{\cdot}+Cy'=AgCy+K^{\cdot}+NO_3'$. If an excess of potassium cyanide be added the precipitate redissolves, and it can now be shown that the solution no longer contains $Ag^{\cdot}$-ions in appreciable quantities, since (1) sodium chloride gives no precipitation of silver chloride; (2) on electrolysis silver is deposited on the anode not on the cathode, as is the case when a solution of silver nitrate is electrolyzed; (3) a crystalline compound, $KAgCy_2$, is obtained on concentrating the solution. The solution of silver cyanide in potassium cyanide indeed ionizes thus: $KAgCy_2 \rightleftharpoons K^{\cdot}+AgCy_2'$. Here again it matters very little whether the facts be described in terms of the ionic hypothesis or in terms of basic and acidic radicles. The choice can only be decided by personal opinion since the ions in solution still remain hypothetical units.

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CHAPTER XVI

ELECTRICAL ENERGY

§ 1. The Factors of Energy

> All the differences discoverable in the effects of electricity (obtained from different sources) may be owing to its being less intense but produced in much larger quantity from some sources rather than from others.—W. H. WOLLASTON (1801).
>
> The term electromotive force in electricity is equivalent to the term chemical activity or affinity just as the term quantity of electricity corresponds to the chemical notion of valency.—G. SALET (1867).

IT has been shown that every form of energy has a dual nature, for all the better-known forms of energy appear as if they were two dimensional in that they are compounded of two factors—one the capacity factor, the other the intensity factor. The latter determines whether a given change will occur. The capacity and intensity factors of heat energy are respectively entropy and temperature. The flow of heat is not determined by the quantity of heat in a given system, but rather by the difference of temperature. The heat in a furnace can do work not because it is hot, but because it is hotter than its surroundings. With electrical energy, the quantity of electricity expressed in suitable units—say coulombs—is the capacity factor, and the electromotive force expressed in suitable units—say, volts—is the intensity factor. The product of these two factors expresses the magnitude of electrical energy.

What are the factors of chemical energy ?—A. Butleroff (1861) pointed out that it is necessary to distinguish the quantity of affinity from its intensity, that is, the smaller or greater energy with which it tends to become active. If chemical energy can be resolved into two factors, the one factor must be analogous to the capacity, and the other to the intensity factor of thermal or electrical energy. J. W. Gibbs [1] calls the intensity factor of chemical energy the **chemical potential** ; G. H. Helm calls it the **chemical intensity**; and it is often called **the driving force of a reaction.** These terms are employed with the idea of evading the vagueness of the old term, **chemical affinity,** which is undoubtedly the correct designation for "chemical intensity." Now, the quantity of a substance which takes part in any chemical change is proportional to the *equivalent weight* of the substance, where the term equivalent weight refers to quantities of matter which have the same valency. Assuming then that the chemical equivalent is the capacity factor of chemical energy, we may write—

Chemical energy = Equivalent weight × Chemical affinity ; or,
Chemical energy = Equivalent weight × Chemical intensity.

Some follow G. Salet, *vide supra*, and hold that valency is the capacity factor, but that does not seem the right thing to do.

If two bodies at the same temperature be placed in contact, there will be no apparent conduction of heat from the one to the other ; but when the temperature of the one body—*i.e.* the intensity factor—is higher than that of the other, heat will pass from the hot to the cold body, so that the cold body is warmed and the hot body is cooled. So with chemical energy. We assume that **the molecules of every substance possess a specific amount of chemical energy, which has a**

definite intensity under certain specified conditions. One substance can only react with another when the intensity of the energy associated with the original mixture is greater than that of the final system. If the intensity of the energy associated with the original mixture be the same as that associated with the products of the reaction, no reaction will take place, for the system will be in stable equilibrium; if the intensity factors are not equal, the energy will not usually be in stable equilibrium. Just as the value of heat energy as a source of power depends on its temperature, so does the availability of chemical energy depend on the magnitude of its intensity factor.

W. Ostwald has drawn attention to the fact that if the chemical process be performed in a voltaic cell, the work derived from that process will be transformed into an equivalent amount of electrical energy. The quantity C of electricity generated when w grams of a compound are formed or decomposed in a cell will be $w=\epsilon C$, where ϵ denotes the electrochemical equivalent. This means that the capacity factor—quantity of electricity—is proportional to the quantity of matter decomposed, and that the capacity factor of the electrical energy is proportional to the capacity factor of the chemical energy. If the current does no work other than the chemical decomposition of the compound into its elements, and the difference of potential is E, the work done by the current will be EC. Again, if chemical affinity performs an amount of work W in building up w grams of a substance from its elements, wW units of work will be required. Accordingly, $wW=EC$. By substituting $w=\epsilon C$, and reducing the expression to its simplest terms, $\epsilon W=E$; otherwise expressed, the electromotive force of a cell E is equal to the chemical affinity per gram equivalent of the compound in question. Consequently, as G. Salet showed, the product of the quantity of electricity into electromotive force not only represents the electrical energy of a battery, but also measures the work of affinity which that energy transformation can perform. It therefore follows that the respective intensity factors of chemical and electrical energies are proportional, and since the electromotive force is proportional to the intensity factor of electrical energy, it follows that the **electromotive force is proportional to chemical affinity.** We see, then, that electromotive force and chemical affinity are manifestations of one form of energy; or, in the words of M. Faraday, " the forces called electricity and chemical affinity are one and the same." The problem is solved for conductors of electricity—electrolytes. Chemical action takes place when the electrical potential or the chemical affinity of the reacting substances is greater than that of the reacting products. We can to-day express the " affinity " between a number of reacting substances roughly in terms of difference of potential. The measurement of electrical potential of voltaic combinations under conditions where disturbing effects due to thermal changes, secondary reactions, etc., are eliminated, will represent the free energy or affinity of the reaction in question. How this may be done for non-conductors of electricity has not yet been determined.

The temperature or intensity factor of heat energy required for the decomposition of many substances—say calcium or potassium chloride—is so great that commercial methods of decomposing these substances by thermal energy are not profitable. A great many compounds thus appear to be very stable when heated at high temperatures; these can often be decomposed by electrical energy at a comparatively low voltage (intensity factor). This illustrates how the commercial production of metals like aluminium, calcium, etc., were not particularly successful until electrical methods were adopted. The prediction of C. L. Berthollet (1803) has been fulfilled :

> The electrical current has furnished chemistry with an agent whose energy may be carried to a degree, which as yet can scarcely be imagined, and which will furnish the means of producing in the formation and decomposition of chemical combinations, effects unforeseen, and superior to those which it is possible to obtain by the action of heat.

It has been suggested, too, that if a source of energy with a particularly high intensity factor were available, it would most likely be possible to decompose many of the so-called elements into still simpler substances, but this, of course, is merely a speculation.

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§ 2. Electrochemical Series of the Elements

> An electrochemical series is obtained by arranging substances in accord with their electrical properties, and this series is better than any other for giving a general idea of chemistry.—J. J. BERZELIUS (1825).
>
> The metals precipitate one another after a certain order.—T. BERGMANN (1779).

Near the beginning of the fourth century, Zosimus mentioned the fact that when iron is immersed in a solution of a copper salt, the iron acquires a coating of copper; and miners have frequently noticed that their iron tools become coated with copper when brought in contact with the water percolating through certain mines. We now know that such water may hold in solution copper sulphate from the oxidation of ores containing copper sulphide associated with iron sulphide, and we have also learned that when the copper is deposited, an equivalent amount of iron passes into solution. The reaction is represented in symbols, $Fe+CuSO_4=Cu+FeSO_4$. Curiously enough, even as late as the sixteenth century Paracelsus attributed the phenomenon to the transmutation of iron into copper. The transmutation hypothesis certainly appeared a very plausible explanation of the facts. As T. Bergmann emphasized near the middle of the eighteenth century in his *De præcipitatis metallicis*:

> The man who first saw a metal corroded by a limpid menstruum, in such a manner that a body so extremely ponderous and so opaque should gradually and entirely disappear, and afterwards, upon the addition of a suitable precipitant to a liquid which appeared to be simple and homogeneous, saw the metal separate and again come into view, that man, I say, who first saw this, must have been struck with astonishment and admiration. Persons accustomed to these wonderful phenomena neglect, perhaps too much, the accurate investigation of them, though these operations are of the highest importance, and form as it were the whole of the effective part of chemistry.

Metallic magnesium will displace hydrogen from dilute acids: $Mg+H_2SO_4=MgSO_4+H_2$; or in the language of the ionic hypothesis: $Mg+2H^{\cdot}+SO_4''=Mg^{\cdot\cdot}+SO_4''+H_2$. Magnesium will also precipitate zinc from a solution of a zinc salt: $Mg+ZnSO_4=MgSO_4+Zn$; or in the terms of the ionic hypothesis: $Mg+Zn^{\cdot\cdot}+SO_4''=Mg^{\cdot\cdot}+SO_4''+Zn$. Zinc in turn will precipitate iron from iron salts; iron will precipitate copper from copper salts; copper will precipitate silver from silver salts, etc. By treating the different metals in a similar manner it has been found possible to arrange them in a series such that, under like conditions, any metal in the list will displace those which follow it, and be displaced by those which precede it.

Again, when zinc is treated with dilute acids under suitable conditions in a voltaic cell, so as to eliminate disturbing effects, the reaction produces an electric current at a certain voltage. If the zinc be replaced by some metals—aluminium, magnesium, etc.—the voltage of the cell is increased; and conversely, if the zinc be replaced by other metals—cadmium, iron, cobalt, etc.—the voltage of the cell is diminished. It is thus possible to arrange the elements in a series representing the potential difference in volts which is developed between the metals and solutions of their salts. The list of the elements so arranged is called **the electrochemical series.** A more complete list is indicated in Table I. The order of the metals in the electrochemical series not only depends on the nature of the elements themselves, but also on the chemical composition of the solution in which they are placed, the degree of concentration, and its temperature. In an acid solution, for example, the following six metals have this order: zinc, iron, lead, copper, silver, antimony; and in 12·5 per cent. potassium cyanide solution the order zinc, copper, silver, antimony, lead, iron. When silver and potassium cyanide replace zinc and sulphuric acid in the Daniell cell, a strong current is developed and copper is precipitated; copper is usually supposed to precipitate silver, but silver here precipitates copper. These variations promised to obscure the use of the electrochemical series for predicting the course of chemical reactions. Again, tin precipitates lead from its solution in acetic acid, and lead precipitates tin from its solution in nitric acid. Calcium iodide at about 740° is reduced by metallic sodium, but the reverse action occurs above 800° for sodium is displaced by calcium; hence sodium is more electropositive than calcium at low temperatures, and less so at high temperatures. Similar phenomena occur with potassium and strontium. In many cases the displacement is so complete that the reaction is employed in quantitative analysis. The further apart any two elements are in the series: (1) The greater the electromotive force of the currents generated when the two elements are used as plates in a voltaic couple; (2) The greater the amount of heat liberated when the displacement occurs, *e.g.* when the zinc precipitates silver more heat is evolved than when it precipitates tin. (3) Similar remarks apply, *mutatis mutandis*, to the speed of precipitation. (4) The greater the amount of heat or electrical energy required for the decomposition of their compounds; (5) The greater their chemical affinity for one another.

TABLE I.—ELECTROCHEMICAL SERIES OF THE ELEMENTS.

Cæsium	"Metals."
Rubidium	
Potassium	
Sodium	
Lithium	
Barium	
Strontium	
Calcium	
Magnesium	
Aluminium	
Chromium	
Manganese	
Zinc	
Cadmium	
Iron	
Cobalt	
Nickel	
Tin	
Lead	
Hydrogen	
Antimony	
Bismuth	
Arsenic	
Copper	
Mercury	
Silver	
Palladium	
Platinum	
Gold	
Iridium	
Rhodium	
Osmium	
Silicon	"Non-metals."
Carbon	
Boron	
Nitrogen	
Selenium	
Phosphorus	
Sulphur	
Iodine	
Bromine	
Chlorine	
Oxygen	
Fluorine	

A similar table would be obtained if the elements were arranged in the order of their chemical activity. Thus, (1) The earlier members on the list oxidize or rust on exposure to the air. (2) Oxides of the metals succeeding manganese are reduced to metals when heated in a stream of hydrogen, while the metals which precede manganese, under the same conditions, may be reduced to lower oxides, but not to the metallic condition. (3) The oxides of the metals ranging from mercury to osmium may be decomposed into their elements by simply heating them to a comparatively low temperature. (4) The metals preceding hydrogen on the list can give hydrogen when treated with acids, although secondary actions may simultaneously lead to the formation of some product other than hydrogen. The metals succeeding hydrogen do not usually displace hydrogen from the acids. (5) With the possible exception of tin and lead (metals close to hydrogen) the freed elements are rarely, if ever, found in nature excepting possibly in meteorites. This arises from the fact that natural waters containing carbonic and other acids in solution attack these metals; consequently, even if these elements were produced by subterranean agents—volcanic or otherwise—they must eventually succumb to attack by natural waters.

It will be noticed that the series refers only to the action of the *free elements*, and it has no direct reference to the mutual action of chemical *compounds* of the elements upon one another. The order of the elements in the electrochemical series depends to some extent upon the temperature as well as on the nature and concentration of the electrolyte. For example, zinc and copper behave in what appears to be an abnormal manner in the presence of potassium cyanide. Thus copper and iron will precipitate zinc from potassium zinc cyanide, whereas zinc will precipitate copper from copper sulphate; and iron from neutral ferrous sulphate. Again, silver will displace hydrogen from aqueous hydriodic acid; copper will precipitate nickel from sodium nickel chloride; and platinum will liberate hydrogen from aqueous solutions of potassium cyanide. R. Abegg and G. Bodländer[1] have developed H. von Helmholtz's assumption that the ions hold their charges with different degrees of tenacity. The ions—$K^{\cdot}$, $Na^{\cdot}$, NO_3', Cl', etc.—which hold their charges very tenaciously, are called **strong ions**; and ions—$Hg^{\cdot\cdot}$, $Ag^{\cdot}$, OH', Cy', etc.—which readily lose their charge, are called **weak ions**. The degree of tenacity with which the ions of an element hold their charges has been called the **electro-affinity** of the element. The electro-affinities of the elements are roughly measured as decomposition voltages. Ions with strong electro-affinity are difficult to prepare in a free state, and conversely. If an element with a strong electro-affinity comes in contact with the ion of an element with a weak electro-affinity, the charge on the latter passes over to the former. Thus zinc has a stronger electro-affinity than copper, and, in consequence, as indicated above, zinc will precipitate copper from solutions of its salts: $Zn+Cu^{\cdot\cdot}=Zn^{\cdot\cdot}+Cu$. Zinc also has a stronger electro-affinity than hydrogen, and consequently zinc dissolves in dilute acids with the evolution of hydrogen: $Zn+2H^{\cdot}=Zn^{\cdot\cdot}+H_2$. Similarly, chlorine has a stronger electro-affinity than bromine, and bromine a stronger electro-affinity than iodine. In consequence, chlorine will displace bromine from aqueous solutions of the bromides: $Cl_2+2K^{\cdot}+2Br' \rightleftharpoons 2K^{\cdot}+2Cl'+Br_2$; and bromine will displace iodine from the iodides: $Br_2+2K^{\cdot}+2I' \rightleftharpoons 2K+2Br'+I_2$.

The attempt of R. Abegg and G. Bodländer to show that certain properties and reactions of the inorganic salts are directly dependent upon the electro-affinities of the respective + and − ions. These properties are especially (1) solubility—where it is supposed that the greater the electro-affinity of the + and − ions, the greater the solubility—*e.g.* the electro-affinity of sodium ion in sodium salts is usually very great and the salts are usually very soluble in water; whereas with silver salts, the silver ion has a weak electro-affinity and the salts are sparingly soluble. If one of the ions has a high and the other a low electro-affinity the salt is usually soluble, *e.g.* silver nitrate. (2) Tendency to form complex positive or negative ions—if the neutral compound of the complex ion has low electro-affinities, the tendency to form complex salts will be great—*e.g.* in potassium ferricyanide K_3FeCy_6, the complex ion $FeCy_6'''$ is composed of single ions $3Cy'$ and the neutral component $FeCy_3$, where the electro-affinities are weak. A further examination of these hypotheses by J. Locke shows that the relations deduced by R. Abegg and G. Bodländer are not generally applicable.

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§ 3. Solution Pressure—Contact Differences of Potential

> Whenever there is free energy present, or whenever there is potential energy seeking to become free when chemical affinities come into play in the *presence* of differential molecular structures or conditions, this energy takes the form of electrical potential.—J. T. SPRAGUE (1892).

If a spherical globule of mercury at the bottom of a watch glass—*a*, Fig. 1—be electrified at either the positive or negative pole of an electric machine, the globule flattens—*b*, Fig. 1—showing that the surface tension of the metal has diminished, and that changes in the surface tension of mercury accompany variations in its electrical condition. The greater the electric *charge* impressed on the metal, the smaller the surface tension. If σ denotes the surface tension; E, the potential difference between the metal and electrolyte; and ϵ, the quantity of positive electricity per unit surface of metal, G. Lippmann,[1] H. von Helmholtz, and W. Ostwald find $d\sigma/dE=\epsilon$.

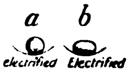


FIG. 1.—H. Herwig's Experiment.

In P. Lippmann's experiment (1873), two glass U-tubes, *A* and *B*, Fig. 2, each with one leg drawn to a capillary bore, were partially filled with mercury, and partially immersed in a beaker of dilute sulphuric acid (1 : 6) as shown diagrammatically in Fig. 2. The mercury rose to a higher level in the wider limb than in the capillary, and the finer the capillary the greater the difference of level in the two limbs—care must be taken to displace any bubbles of air in the capillary which would prevent the acid coming in contact with the mercury. Connect the mercury in the wider limbs by means of a source of electrical energy at a pressure not exceeding 0·5 volt. The meniscus of the mercury *a* through which the current enters the electrolyte—dilute sulphuric acid—will rise, and the meniscus *b*, through which the current leaves the electrolyte, will be depressed. The arrows show the direction of the current. If the meniscus in one capillary falls, the surface tension of the mercury must be increasing, and conversely, if the meniscus rises, the surface tension is diminishing. Hence, when the electrical connections were made the electrical potential of *a* was increased, and that of *b* decreased. If the potential difference between *A* and *B* were gradually increased from 0·5 volt, the meniscus at *a* would continue ascending, and that at *b* would continue descending until a potential difference of 0·93 volt is attained—after that, any further increase in the potential difference between *a* and *b* causes the mercury in *b* to rise. The explanation is that mercury in contact with dilute sulphuric acid normally acquires a potential difference of 0·93 volt, which, for convenience, is called the **contact difference of potential,** or the **electrode potential** of the mercury. Under the influence of an increasing potential difference, the positive charge is gradually augmented at *a*; and the increasing negative charge at *b* reduces the total charge on *b* by neutralizing the normal positive charge already there. When the difference of potential applied at *b* reaches 0·93 volt, the charge at *b* will be zero, and the mercury will have its maximum surface tension and *b* reaches its lowest level in the capillary. Any further increase in the difference of potential between *a* and *b* will cause *b* to be charged negatively and the mercury at *b* will begin to rise in the capillary. The mercury in both capillaries will continue rising until the difference of potential reaches 2 volts. The acid then begins to decompose.

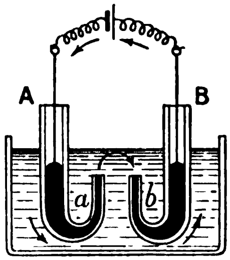


FIG. 2.—P. Lippmann's Experiment.

If the source of the electrical energy be removed and the two wires in *A* and *B* be joined, the mercury in each capillary will return to its former level. This experiment illustrates the principle of the so-called **capillary electrometer** used in various forms for measuring small differences of potential in the laboratory.

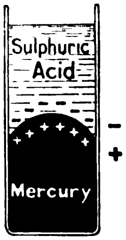


FIG. 3. — Helmholtz's Double Layer.

It is supposed that if the metal near its surface of separation from the dilute acid be positively charged—the surface of separation must act as an insulator or dielectric—and an equivalent negative charge will be induced in the acid—as represented diagrammatically in Fig. 3. The two layers of electricity of opposite sign are called **Helmholtz's double layer**—after H. von Helmholtz's investigations on this subject in 1879. Had dilute hydrochloric acid been used in place of dilute sulphuric acid, the maximum depression in the capillary *b* would have occurred with a difference of potential of 0·56 volt.

The contact difference of potential between the different metals in contact with normal solutions of their salts are indicated in Table II, due to N. T. M. Wilsmore.

TABLE II.—CONTACT POTENTIALS OF THE ELEMENTS.

	Volts.		Volts.		Volts.
K . .	(+2·92)	Fe . .	+0·063	Hg . .	−1·027
Na . .	(+2·54)	Tl . .	+0·045	Ag . .	−1·048
Ba . .	(+2·54)	Co . .	−0·045	Pd . .	< −1·066
Sr . .	(+2·49)	Ni . .	−0·049	Pt . .	< −1·140
Ca . .	(+2·28)	Sn . .	< −0·085	Au . .	< −1·356
Mg . .	(+2·26)	Pb . .	−0·129	F . .	(−2·24)
Mg . .	+1·214 ?	H . .	−0·277	Cl . .	−1·694
Al . .	+0·999 ?	Cu . .	−0·606	Br . .	−1·270
Mn . .	+0·798	As . .	< −0·570	I . .	−1·797
Zn . .	+0·493	Bi . .	< −0·668	O . .	−1·396 ?
Cd . .	+0·143	Sb . .	< −0·743		

A common method used in measuring contact difference of potential, or the relative e.m.f.—electromotive force—of metals in contact with different solutions, is to make a cell with two electrodes each dipping in a separate solution. (i) One electrode consists of the metal to be tested held by platinum-tipped forceps electrically connected with a galvanometer, and dipping in the required solution. (ii) The other is the so-called **normal electrode.** In Ostwald's non-polarizable normal electrode (1) mercury is electrically connected with the galvanometer by means of a glass-coated platinum wire, (2) the surface of the mercury is connected with a layer of mercurous chloride about 5 cm. thick, and (3) a solution containing a normal solution of potassium chloride. This gives an electromotive force of −0·560 volt, or a positive current tends to flow through the solution to the mercury which becomes positively electrified, while the solution itself becomes negatively electrified. When the solutions about the two electrodes are in contact, the slight e.m.f. due to the contact of the two liquids is neglected and the e.m.f. of the whole combination is the algebraic sum of the e.m.f.'s action at the two electrodes. The e.m.f. of the given metal in contact with the given solution is obtained by subtracting 0·560 volt from the observed e.m.f. of the combination. The e.m.f. of the combination is observed in terms of the deflection of a calibrated galvanometer, or by the compensation or zero method of J. C. Poggendorff described in laboratory manuals.

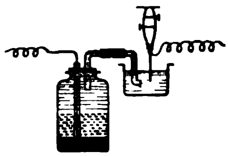


FIG. 4.

W. Nernst (1889) [2] has carried the idea of contact difference of potential still further. He assumes that if a metal rod be immersed in a liquid, it tends to dissolve. The supposed tendency of a metal to dissolve in any liquid is called the **solution pressure** of the metal. The supposed action is likened to the tendency of liquid to vaporize as indicated by the *vapour pressure* of the liquid at any given temperature. Still further, just as a liquid continues to evaporate at a free surface until the number of molecules leaving the surface of the liquid in any given time is equal to the number of molecules returning to the liquid, so W. Nernst suggests that a metal, when placed in contact with water or other liquid, tends to send charged ions into the solution and itself to assume an equivalent charge of opposite sign. A force has been invented to drive the ions into the solution, and it is called the **electrolytic solution pressure.** The force is supposed to vary with the nature of the metal, the solution, and the temperature. The solution pressure must be greatest with the metals at the cæsium end, and least with the metals at the osmium end of the electrochemical series. Conversely, the tendency of positive metal ions in solution to reprecipitate on the negative electrode must be least at the cæsium end of the series and greatest at the osmium end. The ionic hypothesis assumes that this back or **deposition pressure** represents the osmotic pressure of the ions. The ionization of the metal, so to speak, is supposed to continue until the concentration of the metallic ions in the liquid has attained a certain value when a state of equilibrium ensues. The number of ions passing into the solution is then equal to the number reprecipitated on the surface of the metal. Direct proof of the presence of iron ions in purified water, which has been in contact with the highly purified iron, is wanting. The evidence is indirect, or rather hypothetical.

When zinc is immersed in dilute hydrochloric acid, the supposed H$^{\cdot}$-ions which come in contact with the zinc plate lose their charge, and positively charged zinc ions pass into solution. If a stick of metallic zinc be dipped in a saturated solution of zinc sulphate, the solution and deposition or osmotic pressures are balanced, and no action occurs; but if a stick of metallic zinc be placed in a dilute, say normal, solution of zinc sulphate, the solution pressure is greater than the deposition or osmotic pressure, and positively charged zinc ions pass from the zinc rod into the solution. In consequence, the zinc acquires a negative charge, and the solution a positive charge, in agreement with the fact that zinc usually acquires a negative charge when immersed in a solution of its own salt. Similar remarks apply to aluminium, iron, etc. Conversely, if the solution pressure be less than the deposition or osmotic pressure of the ions, as appears to be the case with a stick of metallic copper immersed in a solution of copper sulphate, copper ions will be deposited on the metal, and the solution will acquire a negative charge while the metal acquires a positive charge. This also appears to be the case with the metals of silver, mercury, etc.

Let P denote the electrolytic solution pressure of the metal, and p the osmotic pressure of the metallic ions in the solution. It is presumed that the osmotic pressure of the metallic ions will oppose the tendency of the metallic ions to pass into solution. When the opposing forces are balanced, no action will take place—as will occur with zinc in a saturated solution of zinc sulphate.

In a normal solution of zinc sulphate, if P be *greater* than p, bivalent zinc ions will pass from the zinc rod into the solution, the solution will become positively, and the metal negatively charged. The attraction of opposite charges will cause positive ions to collect about the surface separating metal and solution, and thus form a Helmholtz's double layer. When the osmotic pressure p of the metallic ions in the solution has been augmented by the separation of ions from the metal itself until it is equal to the electrolytic solution pressure, the opposing forces will be balanced; there will be no further increase in the number of metal ions in the solution, and a definite electromotive force will be established—metal negative, solution positive. Thus zinc, aluminium, and iron are generally negative when immersed in solutions of their own salts. If the electrolytic solution pressure P be *less* than the osmotic pressure p such as occurs when copper is placed in a solution of copper sulphate, positively charged copper ions will separate from the solution and be precipitated on the metal and the rod of metal will become positively, and the solution negatively charged. An Helmholtz's double layer will be formed as the negative ions remaining in the solution collect about the surface separating solution and metal. Equilibrium will be established when $P=p$, and an electromotive force will appear at the boundary double layer in a reverse direction to that established when P was greater than p. Gold, silver, mercury, and copper are illustrations of metals usually positive when immersed in solutions of their own salts.

The electrical effect, or the contact difference of potential, produced when the different metals are immersed in a normal solution of their sulphates has been measured. B. Neumann's results are indicated in Table III. The number $+0{\cdot}524$ opposite zinc means that if metallic zinc be immersed in a normal solution of zinc sulphate, the solution will acquire a positive charge, and the metal a negative charge; and the difference of potential between the solution and the metal will be 0·524 volt. With metallic copper and a solution of copper sulphate, the solution will be charged negatively, and the copper positively, such that the difference of potential between the solution and the metal will be 0·515 volt.

TABLE III.

Metals.	Sulphate.	Chloride.	Nitrate.	Acetate.
Magnesium	+1·239	+1·231	+1·060	+1·240
Aluminium	+1·040	+1·015	+0·775	—
Manganese	+0·815	+0·824	+0·560	—
Zinc	+0·524	+0·503	+0·473	+0·522
Cadmium	+0·162	+0·174	+0·122	—
Thallium	+0·114	+0·151	+0·112	—
Iron	+0·093	+0·087	—	—
Cobalt	−0·019	−0·015	−0·078	−0·004
Nickel	−0·022	−0·020	−0·060	—
Lead	—	−0·095	−0·115	−0·079
Hydrogen	−0·238	−0·249	—	−0·150
Bismuth	−0·490	−0·315	−0·500	—
Arsenic	—	−0·550	—	—
Antimony	—	−0·376	—	—
Tin	—	−0·085	—	—
Copper	−0·515	—	−0·615	−0·580
Mercury	−0·980	—	−1·028	—
Silver	−0·974	—	−1·055	−0·991
Palladium	—	−1·066	—	—
Platinum	—	−1·140	—	—
Gold	—	−1·356	—	—

If a normal solution of copper sulphate be separated by a porous partition, Fig. 5, from a normal solution of zinc sulphate, and if a rod of copper immersed in the copper sulphate be connected by a wire with a rod of zinc immersed in the zinc sulphate (Fig. 5), the zinc pole on the right of the diagram acquires a negative charge *ex hypothesi* on account of the departure of positively charged ions from its surface, and the copper pole on the left acquires a positive charge on account of the departure of negatively charged copper ions from its surface. In consequence, an electrical current will flow through the connecting wire from the positively to the negatively charged pole and pass in the converse direction through the liquid. This action continues until all the zinc is dissolved or all the copper precipitated. The relative solution pressures of the two metals decide the magnitude of the resultant electromotive force of the current, and this is the difference of the two effects. The resultant electromotive force for the zinc : copper couple just described is $+0{\cdot}524 - (-0{\cdot}515) = 0{\cdot}524 + 0{\cdot}515 = 1{\cdot}039$ volts. The combination just described represents the so-called **Daniell's cell** (1836),[3] which resembled in principle the unpractical cell described by E. Becquerel in 1829. In reality, J. F. Daniell's cell contains the zinc rod with the sulphuric acid or zinc sulphate solution in a porous pot, and the copper plate with the copper sulphate solution in the surrounding jar, as illustrated by the drawing of an uncharged cell in Fig. 6. The reactions are symbolized

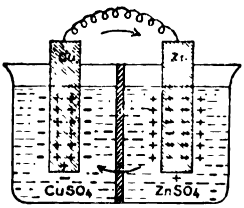


FIG. 5.—Daniell's Cell (Diagrammatic).

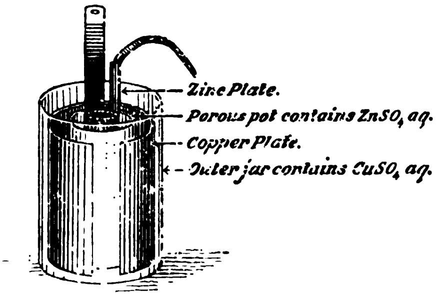


FIG. 6.—Daniell's Cell.

molecularly in the following manner: At the positive zinc plate, $Zn+H_2SO_4=ZnSO_4+H_2$. Instead of the hydrogen atoms being liberated on the negative copper plate, they are exchanged for copper in the copper sulphate solution: $H_2+CuSO_4=H_2SO_4+Cu$, and the copper is deposited on the copper plate. The net result of this round of changes is that the copper plate grows while the zinc plate lessens; and zinc sulphate increases, copper sulphate decreases. If a solution of zinc sulphate is used in Daniell's cell, the copper is exchanged for the zinc: $Zn+CuSO_4=ZnSO_4+Cu$. There are many other modifications of Daniell's cell, and numerous other types of cell with different " poles " and different solutions.

The *quantity* of electricity (coulombs) produced by Daniell's cell depends upon the amount of zinc consumed (Faraday's law); and the *rate* at which electricity is developed (ampères) depends upon the rate at which the zinc is consumed in the cell. The *difference of potential* or the electrical pressure cannot exceed 1·039 volts for the given solutions. The product of the number of coulombs into the number of volts gives the amount of electrical energy expressed in joules. If the term *ampère* be employed to represent a current equivalent to one coulomb per second, the product of the number of ampères into the number of volts gives the amount of electrical energy produced in one second by the cell, expressed in watts—a joule of electrical energy per second represents one watt.

EXAMPLES.—(1) The electrolysis of 36·5 grams of hydrochloric acid requires 96,540 coulombs of electricity at 1·31 volts. Hence the electrical energy needed for this work is $96{,}540\times1{\cdot}31=126{,}567$ units, or, defining a **joule** as the unit of electrical energy consumed by a current of one coulomb working against a resistance of one ohm (joules = volts × coulombs), the electric energy needed to decompose 36·5 grams of hydrochloric acid is 126,567 joules.

(2) A current of 100 volts and 1·5 amps. passes through a system, hence $100\times1{\cdot}5=150$ watts of energy are consumed per second.

The relation between the electromotive force and the osmotic pressure.—The qualitative sketch of Nernst's hypothesis can be described in a quantitative form. If a substance with an electrolytic solution pressure P be converted into ions with an equivalent osmotic pressure P_1, the opposing forces are balanced, and no work is done. On the other hand, if a metal with an electrolytic solution pressure P be converted into ions having an osmotic pressure p, the maximum work which can be performed during the transfer is analogous with the work performed when ions are transferred from an osmotic pressure P to an osmotic pressure p. If one gram-molecule be involved, the osmotic work will be $RT\log(P/p)$. One gram-ion carrying nC equivalents of electricity (n denotes valency) at a potential of E volts, can perform nEC units of electrical work. Assuming that the osmotic work and electrical work are equivalent, $nEC=RT\log(P/p)$, when $R=2$ cals., one volt-coulomb$=0{\cdot}24$ cal. Hence, in place of nEC we can write $nE\times96500\times0{\cdot}24=2T\log(P/p)$, and remembering that natural logarithms are converted into common logarithms by multiplying by 2·3026,

$$E=0{\cdot}000198\frac{T}{n}\log_{10}\frac{P}{p}\text{ volts}$$

This equation represents the electromotive force or potential difference developed, at the absolute temperature T, when an n-valent metal with an electrolytic solution pressure P is immersed in a solution in which the corresponding ion has an osmotic pressure p.

EXAMPLES.—(1) Let one zinc rod dip in a normal and another in a decinormal solution of zinc chloride, Fig. 7, assume that ionization is complete in both solutions. What is the resulting electromotive force of the cell? Ansr. $E=0{\cdot}0287$ volt.

(2) What is the electrolytic solution pressure of zinc in normal zinc sulphate solutions at 17° when the contact difference of potential is 0·524 volts? Here $n=2$; $E=0{\cdot}524$; p denotes the osmotic pressure of zinc ions when a gram-molecule of the salt is completely ionized in a litre of solution, $P=22{\cdot}4$ atm. Hence, $0{\cdot}524=0{\cdot}000198\times\frac{1}{2}\times290(\log P-\log22{\cdot}4)$, or $P=2{\cdot}7\times10^{19}$ atm.

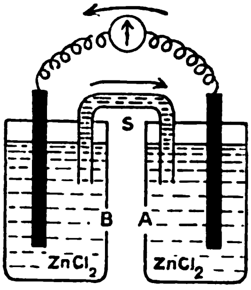
The electrolytic solution pressures cannot be measured directly, but they can be computed from the observed differences of potential as in the preceding example. The computed values for magnesium, zinc, iron, hydrogen, and silver expressed in atmospheres, are :

Magnesium.	Zinc.	Iron.	Hydrogen.	Silver.	Palladium.
10×10^{43}	$2{\cdot}7\times10^{19}$	$1{\cdot}2\times10^{4}$	$9{\cdot}9\times10^{-4}$	$2{\cdot}3\times10^{-17}$	$1{\cdot}5\times10^{-36}$

It is difficult to understand what these numbers mean. The number for zinc appears extraordinarily large; it is nearly equal to a weight of 180000,000000,000000 tons or $1{\cdot}8\times10^{17}$—the earth itself is estimated at 6000,000000,000000,000000, or 6×10^{21} tons. Nothing like these pressures have been directly observed; they are said to represent "the striving of the metal to overcome the opposing osmotic pressure of the metal ions already in solution in order that the atom of the metal may be ionized." We cannot employ the tabulated electrolytic solution pressures to calculate contact differences of potential E along with observed values of p and n in the expression $EC=RT \log (P/p)$, and compare the results with observed values of E in order to show the validity of the formula, because that would be reasoning in a circle.

Concentration cells.—Although the difference of potential of a given cell, say a Daniell's cell, is not affected by variations in the size or shape of the poles, or upon the quantity of liquid in the cells, the difference of potential is altered by changing the concentration of the solutions. In general the difference of potential between a metal and a solution of one of its salts is greater with increasing dilution. A tenth normal solution of zinc sulphate, for instance, will give a difference of potential of 0·551 volt, whereas with a normal solution a potential difference of 0·524 volt is obtained as indicated above.

If two rods of zinc be separately placed in a N-solution of zinc sulphate, the difference of potential in both "tends" to drive an electric current from the metal to the solution with a pressure of 0·524 volt.. If both rods be joined by a wire, no electric current will flow because the two equal forces are oppositely directed. On the other hand, if the zinc rods be dipped in solutions of a *different* concentration, the two contact differences of potential will be different, and an electric current will flow from the concentrated solution to the dilute solution outside the cell as indicated in Fig. 7. Here a normal solution of zinc chloride is supposed to be placed in one vessel, *A*, and a decinormal solution of zinc chloride in the other vessel, *B*. Zinc rods connected by a copper wire and galvanometer are dipped into the solutions, as illustrated in the diagram, and the two cells are connected by a syphon tube *S*. The difference of potential of the zinc in the normal solution is +0·524, and in the more dilute solution +0·551 volt. Hence an electric current tends to pass from the metal to the dilute solution with a force of +0·551 volt, and from the metal to the concentrated solution with a force of 0·524. The resultant pressure is therefore 0·551−0·524=0·027, and this represents the electromotive force of the combination. Cells in which the electromotive force is generated by the difference potential of two plates immersed in solutions of the same salt at different concentrations are called **concentration cells.** The chemical action which occurs in the two cells tends to bring the two solutions to the same concentration.



Dilute *Concentrated*

Fig. 7.—Concentration Cell.

The action is made clear by the following experiment: A layer of a concentrated solution of stannous chloride in hydrochloric acid, about 10 cm. deep, is placed at the bottom of a cylinder, and above this a layer of a dilute solution. A rod of metallic tin is fixed through a hole in the cork so that it is suspended axially in the liquid in the cylinder. The rod of tin thus represents both electrodes and connecting wire of a concentration cell. Tin is dissolved by the more dilute solution, and precipitated from the more concentrated solution. After the system has stood a couple of days, the rod of tin near the surface of the more dilute solution will be reduced in thickness. Cadmium and cadmium chloride can be used; zinc does not work so well; nickel gives negative results, probably because the surface of the metal becomes polarized; antimony and bismuth also give negative results, probably because they are not attacked by dilute hydrochloric acid.[4]

There is another interesting feature about a concentration cell. If an external electromotive force be applied so as to force an electric current to pass in a reverse direction to that which the combination normally furnishes when it is employed in a voltaic cell, the chemical actions will be reversed, and the difference in the concentration of the two solutions will be augmented. Such combinations are called **reversible cells** in contradistinction to **irreversible cells** in which the original condition cannot be restored by sending a current through the cell in a reverse direction to the current normally delivered by the cell. The $Zn|H_2SO_{4aq}|Pt$ cell is an irreversible cell; Daniell's cell, Fig. 6, and the concentration cell, Fig. 7, are reversible cells. If two metal rods are arranged so that one dips in a solution of concentration C_1 and the other rod in another solution of concentration C_2; and if the two solutions are separated by a porous partition and the rods be connected electrically, the electromotive force of the combination will be:

$$E=\frac{RT}{nE_0}\left(\log\frac{P}{p_1}-\log\frac{P}{p_2}\right);\quad \text{or } E=\frac{RT}{nE_0}\log\frac{p_1}{p_2}$$

where p_1 and p_2 respectively denote the osmotic pressures of the solutions of concentrations C_1 and C_2 respectively and P is the solution pressure of the metal. If the metal be nickel, and the solutions be nickel nitrate, $R=8{\cdot}31$ electrical units; $E_0=96{,}540$ coulombs; $n=2$; and at 18°, $T=273+18=291$; if, further, common logarithms are used, then, remembering that the osmotic pressures of dilute solutions are proportional to their concentrations,

$$E=0{\cdot}0288\log\frac{C_1}{C_2}$$

If one solution contains 0·1 gram-molecule of nickel nitrate and the other, 0·05 gram-molecule, the calculated electromotive force of the combination on the assumption that ionization is complete is $E=0{\cdot}0288\times0{\cdot}301=0{\cdot}0087$ volt; the observed value is 0·010 volt.

G. Meyer[5] showed that measurements of the e.m.f. of the combination

Concentrated amalgam | Solution of a salt of the solute metal | Dilute amalgam

enabled the molecular weight of the metal dissolved in the mercury to be computed when there is no combination between the mercury and the metal. Expressing the preceding equation in the form:

$$E=0{\cdot}002\frac{T}{n}\log\frac{C_1}{C_2}$$

divide n by the number of electrical units which go with an atom of the metal in question and the number of atoms in a molecule, and hence the molecular weight of the metal can be computed.

Mercury precipitates silver from a solution of silver nitrate, and silver precipitates mercury from a solution of mercurous nitrate. G. M. Smith (1904) has also found the following pairs of elements can be reciprocally precipitated: Zn—Cu; Ca—Cu; Fe—Hg; Fe—Ag; Hg—Ag; Hg—Pt; Hg—Au; Ag—Au. Again, potassium from a solution of potassium chloride can replace sodium from its amalgam, and conversely sodium can displace potassium from its amalgam; potassium and barium, and sodium and barium are reciprocally replaceable in spite of the fact that potassium is more electropositive than sodium, and sodium more than barium. M. Berthelot called the phenomenon an anomaly, and supposed it to be a consequence of the greater loss of energy suffered by potassium in comparison with sodium when the respective amalgams are formed. According to Nernst's theory, when one metal M_1 is immersed in the salt of another metal M_2, if M_2 is to be precipitated by M_1,

$$\frac{RT}{n_1}\log\frac{P_1}{p_1} > \frac{RT}{n_2}\log\frac{P_2}{p_2}; \text{ or } \sqrt[n_1]{\frac{P_1}{p_1}} > \sqrt[n_2]{\frac{P_2}{p_2}}$$

where the subscripts refer to the corresponding metals; P_1, P_2 are the electrolytic solution pressures; p_1, p_2 the osmotic pressures of the univalent ions; and n_1, n_2 the valencies of the metals in question. Hence the conditions which are favourable for the precipitation of M_2 are (i) a high osmotic pressure, that is, a high concentration of the ions of the second metal; and (ii) a high solution pressure, that is, a low osmotic counter pressure or low concentration of the ions of this metal. It is therefore to be anticipated that two metals might be reciprocally replaceable—all depends on the relative magnitudes of the above terms under different conditions.

There is a difference of potential at the surface of contact between two solutions. If two solutions of, say, hydrochloric acid of different concentration be in contact, the more concentrated solution will diffuse into the other; and, according to the ion theory, the hydrogen and chlorine ions can travel independently at different rates—the positively charged hydrogen ion being the faster will be in the van, the negatively charged chlorine ions will lag behind, and accordingly a difference of potential will be established. The electrostatic attractions set up by the two sets of oppositely charged ions will prevent their separating very far, but it will be sufficient to cause a layer of positively charged ions to accumulate near the surface of the more dilute solution, and a layer of negatively charged ions near the surface of the more concentrated solution. If a salt had been chosen such that the negatively charged ions moved the faster, the charges on the dilute and concentrated solution surfaces would have been reversed, for the more dilute solution must be charged by the more quickly moving ions.

Let $v^{\cdot}$ and v' respectively denote the relative velocities of the ions—assumed to be univalent. Suppose that the cation moves the faster, and that a unit charge of electricity—96,450 coulombs—is carried from the dilute to the concentrated solution. The total current, $v^{\cdot}+v'$, is shared between both ions, so that $v^{\cdot}/(v^{\cdot}+v')$ represents the cation's share, and $v'/(v^{\cdot}+v')$ the anion's share; or $v^{\cdot}/(v^{\cdot}+v')$gram-ions of the cation will have gone from the concentrated to the dilute solution, and $v'/(v^{\cdot}+v')$ gram-ions of the anion will have gone in the opposite direction. If p_1 denotes the osmotic pressure of the cations in the dilute solution it will also represent the osmotic pressure of the anion in the same solution; similarly, let p_2 denote the osmotic pressure of the anions, and of necessity, also, of the cations in the dilute solution. This means that $v^{\cdot}/(v^{\cdot}+v')$ gram-ions of the cation pass from the higher osmotic pressure p_2 to the lower osmotic pressure p_1. Hence the energy converted into electric energy by the cations, and the maximum work done upon the anions moving in the opposite direction from the higher to the lower pressure, will be respectively

$$\text{Work done by cations} = \frac{v'}{v^{\cdot}+v'}RT\log\frac{p_2}{p_1}$$

$$\text{Work done on anions} = \frac{v^{\cdot}}{v^{\cdot}+v'}RT\log\frac{p_2}{p}$$

The available electrical energy EC obtained will be the difference between these two quantities. This difference simplifies, as before, into

$$E = 0{\cdot}000198T\frac{v^{\cdot}-v'}{v^{\cdot}+v'}\log\frac{p_2}{p_1}\text{ volts}$$

More generally, (i) if the cation has a valency m and the anion a valency n; (ii) if the ratio of the concentrations of the two solutions C_1/C_2 be substituted, as before, for the ratio of the osmotic pressure p_1/p_2; and (iii) if the degree of ionization of the solution be x,

$$E=\frac{0\cdot000198\times T}{x}\cdot\frac{\frac{v^{\cdot}}{m}-\frac{v'}{n}}{v^{\cdot}+v'}\log\frac{C_2}{C_1}\text{ volts}$$

an expression which represents the contact difference of potential of two concentrations of the same solute at the absolute temperature T. This expression represents the contact difference of potential between two concentrations of an electrolyte. Obviously, if the velocities of the two ions were equal, $v^{\cdot}=v'$; and if the solutions have the same concentrations $p_1=p_2$; in either case the electromotive force would be zero.

EXAMPLE.—Calculate the electromotive force of the cell Ag|$\frac{1}{100}N$·AgNO$_3$|$\frac{1}{10}N$·AgNO$_3$|Ag at 17°, when the degree of ionization of the solution is 0·935 and the velocity of the cation is 52 and of the anion 58. There are three contacts to consider, and the electromotive force E will be the algebraic sum of the contact differences of potential of the two silver electrodes with their respective solutions, and of the two solutions with one another.

$$E=\frac{0\cdot000198T}{n}\log\frac{C_2}{C_1}+\frac{v^{\cdot}-v'}{v^{\cdot}+v'}\log\frac{C_2}{C_1}\text{ volt}$$

Here $C_2=100$, $n=m=1$, $v^{\cdot}=52$, $v'=58$, $T=290$, it follows that $E=(0\cdot000198\times290\times0\cdot935\times2\times58\times2\cdot3026)/(52+58)=0\cdot058$ volt. The observed value is 0·055 volt.

W. Nernst's method of calculating the e.m.f., E, of a concentration cell from the transport numbers $v^{\cdot}$ and v' and the ratio of the concentrations:

$$E=0\cdot0002\frac{2v'}{v^{\cdot}+v'}\cdot\frac{T}{n}\log\frac{C_2}{C_1}$$

is approximately correct for dilute solutions, but for concentrated solutions, and solutions in non-aqueous solvents of low-ionizing power, there are discrepancies attributed to incomplete ionization; and in that case, the ratio of the ionic concentrations calculated from the conductivities are substituted for the ratio of the concentrations. The prediction of the e.m.f. of a cell is dependent on the applicability of the ionic hypothesis to the solutions. Anomalies are harmonized by introducing hypotheses respecting the association of solute or solvent, or the combination of solvent and solute. H. von Helmholtz (1878) calculated the e.m.f. of a concentration cell from the vapour pressures of the two solutions, and the result is the same as that obtained by W. Nernst's method when the liquid : liquid potential difference is negligible.

L. Hermann has shown that when a current is passed from a dilute solution of a salt to one more concentrated, acid is liberated at the boundary layer, and if the current is sent in the opposite direction an alkali is set free at the same place. G. S. Walpole[6] showed that with all the neutral salts he examined, acid is always liberated when the current passes from the more dilute to the more concentrated solution, and an alkali when the current passes from the concentrated to the more dilute solution. The quantities of acid or alkali liberated bear no relation to the quantity of electricity passing through the circuit; but when the other conditions are the same, the same quantity of acid or alkali is liberated whatever neutral salt be used. G. S. Walpole calculated the effect which would be produced on the assumption that the phenomenon is due to the difference in the velocities of the hydrogen and hydroxyl ions on opposite sides of the boundary layer, and obtained numbers in agreement with the observed data.

When a substance in solution passes from a lower to a higher state of oxidation the change may be regarded as an increase in the number of electric charges on the ions in question; for instance, the oxidation of ferrous to ferric iron is represented, $Fe^{\cdot\cdot} \rightarrow Fe^{\cdot\cdot\cdot}$; and the oxidation of stannous to stannic tin, $Sn^{\cdot\cdot} \rightarrow Sn^{\cdot\cdot\cdot\cdot}$. Conversely, with the reverse changes, the reduction of stannic to stannous tin, $Sn^{\cdot\cdot\cdot\cdot} \rightarrow Sn^{\cdot\cdot}$, or of ferric to ferrous iron, $Fe^{\cdot\cdot\cdot} \rightarrow Fe^{\cdot\cdot}$. The tendency of an ion to pass from one state of oxidation to another can be expressed in terms of an electromotive force. A cell is filled with unattackable electrodes, say, with platinum electrodes immersed respectively in solutions of a ferric and a ferrous salt, and a current is passed from an accumulator in the direction of the arrow: $Pt^{+}|FeCl_2 \rightarrow FeCl_3|Pt^{-}$, the ferrous ions on the one side will be oxidized to ferric ions, and the ferric ions on the other side will be reduced to ferrous ions. If the accumulator is now removed and the circuit closed, ferric ions at one electrode will be reduced because they will give up positive charges to the one electrode, and, as a result, the other electrode will be charged positively and it will oxidize the ferrous ions in the vicinity to ferric ions. This action will continue until the ratio of the ferrous and ferric ions about the two electrodes is the same. If C_i denotes the concentration of the ferric ions and C_0 that of the ferrous ions, $K = C_i/C_0$; Nernst's equation assumes the form:

$$E = E_0 + \frac{RT}{nC} \log \frac{C_i}{C_0}$$

where E_0 is a constant representing the observed potential difference at the electrodes when the concentrations of the -ous and -ic ions are equal—say one gram-molecule per litre—so that $\log (C_i/C_0) = \log 1 =$ zero; n is the difference in the valency of the two ions—*e.g.* in the case of iron, $n=1$, and in the case of tin, $n=2$; the other symbols have their usual meaning; E is sometimes called the oxidation or reduction potential of a solution because it can be taken as a measure of its oxidizing or reducing power.

EXAMPLES.—(1) The potential difference between solutions of thallic nitrate and thallium were measured, and the mean value for E_0 for thallium solutions was 1·191 volts. What is the reduction potential $Tl^{\cdot\cdot\cdot} \rightarrow Tl^{\cdot}$ for solutions containing 0·0505 gram-molecule of thallic nitrate, $Tl(NO_3)_3$ and 0·00108 gram-molecule thallious nitrate $TlNO_3$? Here $E = E_0 + 0{\cdot}029 \log 46{\cdot}7$, or $E = -1{\cdot}233$ volts.

(2) The observed value of E_0 for solutions of uranyl and uranous sulphates is 0·615 at 27·5°, what is the electromotive force with solutions respectively containing 48·4 and 51·6 per cent. of uranyl and uranous sulphate?

Sacrificial metals.—If metallic zinc dissolving in, say, dilute sulphuric acid, be in contact with a piece of copper or platinum the rate of dissolution of the zinc is augmented. The combination Zn : Pt is called a **couple**, and it really forms a small galvanic cell with zinc, and, say, platinum electrodes connected together by metallic contact. Much of the hydrogen is evolved from the surface of the platinum. We have seen that any metal in the electrochemical series can be made one plate of a cell against a metal lower down in the series. Zinc, for instance, can be made the positive plate against a negative plate of iron, tin, lead, etc.; and iron the positive plate against a negative plate of tin, lead, etc. The further apart the elements in the series, the greater the electromotive force of the combination. *Tin-plate* is iron or steel coated with a thin layer of tin. If a little moisture be precipitated on the surface in contact with both the iron and the tin, the moisture, with its dissolved carbonic acid, dissolves the iron, and produces salts of iron; these ultimately form rust (*q.v.*). The iron is covered with a layer of tin to protect it from rust, but if there be a flaw in the protecting surface of tin so as to expose the underlying iron, rusting takes place more rapidly than if the iron had not been tinned at all. The tin remains untarnished. Zinc is also used as a protecting layer over the surface of thin iron plates—*galvanized iron.* The voltaic action developed when the protecting layer is damaged is much less than when tin is used. These facts can be illustrated by fitting up a cell like Fig. 8 with iron and tin plates, and another cell with iron and zinc plates. Water saturated with carbon dioxide is used in both cells. A feeble electric current will flow from the tin to the iron outside the cell in one case, and from the iron to the zinc in the other as illustrated graphically in the adjoining diagram. *In the iron : tin cell, iron dissolves and rusting occurs ; while in the iron : zinc cell, the zinc dissolves and no rusting occurs as long as the circuit is closed.* These results might also have been predicted from our study of Table I.

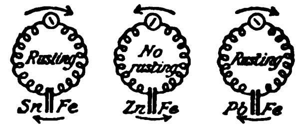


FIG. 8.

An iron : lead cell behaves like an iron : tin cell. Iron railings are often fixed in a bed of lead ; the iron corrodes first and the lead remains intact. H. Davy (1824)[7] once proposed to prevent the corrosion of the copper sheathing of ships by fixing pieces of metallic zinc here and there on the sheathing. The zinc was corroded and the copper preserved. When the zinc was all consumed, the copper ceased to poison the barnacles, and the bottom fouled as if the wood had not been sheeted with copper. In all these cases it has been fancifully said that one metal is sacrificed to ensure the safety of the other ; and all the cases quoted are examples of galvanic couples : Fe : Sn ; Zn : Fe ; Fe : Pb ; and Zn : Cu.

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§ 4. The Ionic Hypothesis and Chemical Reactions

The knowledge of nature as it is—not as we imagine it to be—constitutes true science.— PARACELSUS.

There are some fervid enthusiasts who claim that " all chemical reactions are reactions between ions ; molecules as such do not react at all." This statement is not quite in harmony with known facts. The same might be said of the assumption that " chemical activity is proportional to the number of available ions." L. Kahlenberg (1902),[1] J. L. Sammis (1906), and C. B. Gates (1911) have brought forward a large number of exceptions to these statements that it appears necessary to modify the hypothesis very materially before it can be accepted as an accurate description of the facts. Some chemical reactions proceed very rapidly in solutions which are considered to be virtually non-conductors of electricity, and which, *ex hypothesi*, are almost free from ions. For instance, dry hydrogen chloride precipitates metal chlorides from benzene solutions of the oleates of copper, cobalt, and nickel ; dry hydrogen sulphide precipitates sulphides from benzene solutions of the same salts and of arsenic chloride. All this in spite of the fact that these solutions do not conduct electricity appreciably. Again, dry ammonia does not unite with dry hydrogen chloride, but union does take place if a trace of non-conducting benzene vapour be present. One metal can displace another from a non-conducting solution in a non-aqueous medium. Thus, metallic lead, zinc, tin, silver, iron, etc., will precipitate metallic copper from solutions of various salts in carbon disulphide, carbon tetrachloride, ether, alcohol, etc. Hence, L. Kahlenberg claimed that in spite of the ionic hypothesis, chemical reactions do take place in non-conducting solutions, and these reactions are similar in result and speed to those which occur in conducting aqueous solutions.

H. C. Allen and H. P. Cady and H. O. Lichtenwalter have re-examined the experimental work on this subject, and they claim that the benzene and toluene *solutions* of the salts showed some conductivity which increased when dry hydrogen chloride was introduced. The solutions of the salts also showed polarization which indicated that they possessed properties similar to those of an ordinary electrolyte. It is thus possible that these reactions may be due to ionization. although an alternative explanation is suggested in the assumption that the reactions with hydrogen chloride and the salts of the unsaturated acids take place in two stages: (1) the formation of additive products with hydrogen chloride, and (2) the decomposition of the additive products into metal chloride and organic acid.

G. Senter showed that when an electrolyte enters into chemical reactions, the non-ionized molecules as well as the ions may simultaneously take part in the change, and later, S. F. Acree and J. M. Johnson came to the same conclusion. It was also assumed in the earlier form of the ionic theory that the $H^{\cdot}$-ions are catalytically active, but this did not explain the catalytic activity of neutral salts. A. Lapworth suggests that the difficulty could be overcome by assuming that the non-ionized molecules of the acid are also catalytically active, and this hypothesis is now generally accepted as a result of the work of H. Goldschmidt, G. Bredig and W. S. Millar, H. C. S. Snethlage, S. Arrhenius, H. S. Taylor, H. M. Dawson and T. W. Crann, etc.[2]

These facts leave the uncomfortable feeling that the ionic hypothesis is rather an encumbrance on the theory of chemical reactions; and with slight modifications of phraseology, A. L. Lavoisier's indictment of the phlogiston hypothesis could be applied to the ionic theory of chemical action. The ionic hypothesis cannot ignore these observations if it is to win a permanent place among the conquests of science. As O. D. Chwolson (1910) has emphasized that there is as yet no solidly established theory of solutions which will take into account all the known phenomena, and on which reliance can be safely placed. Hence, advocates of the ionic hypothesis revert to the ordinary language of the molecular theory where the ionic hypothesis fails.

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§ 5. Polarization—Back Electromotive Force

The source of chemical energy in the galvanic cell is certainly the chemical action, a correction being applied for any reversible heat which the cell absorbs from or gives up to its surroundings.—W. C. D. WHETHAM.

Just as an ordinary steam boiler is a device for transforming the chemical energy of burning coal into mechanical energy, so can the voltaic cell be regarded as an engine for converting chemical into electrical energy. In one of the simplest cases, where the cell Zn : H_2SO_4 : Pt is working, hydrogen is evolved mainly from the surface of the platinum. The chemical action is vigorous at first, but gradually diminishes in intensity, and finally nearly stops altogether. The curve, Fig. 9, shows the electromotive force of such a cell after different intervals of time when it is working with a resistance of about ten ohms in the external circuit. The rapid drop from an initial electromotive force of 1·3 volts to about half a volt in five minutes, is indicated by the rapid descent of the curve. After five minutes the electromotive force remained fairly constant at about 0·4 volt—that is, nearly 66 per cent. below the initial value. The effect is easily illustrated by connecting an electric bell with such a cell. The bell rings loudly at first, but gradually weakens, and finally stops. If the platinum plate be then removed, the surface will be found covered with a layer of bubbles of hydrogen gas, which have remained on the surface of the plate instead of passing away. If the circuit is broken, the bubbles of gas gradually dissipate from the platinum plate, and the cell then resumes its former electromotive force when the circuit is closed. This temporary reduction in the electromotive force of a cell is said to be due to the **polarization** of the cell. Polarization may be defined as the electrochemical fatigue which is caused either by a modification of one or both of the plates, or by the exhaustion of the solution about the surfaces of the electrodes during the working of the cell.

Whatever changes occur in the body of the electrolyte during electrolysis no energy is consumed in the process, but at the junctions of electrodes and electrolytes temporary or permanent changes may occur which produce the counter or negative electromotive force called polarization. If the change is transient and disappears when the current is stopped, it is *temporary polarization* in contrast with the so-called *permanent polarization* which arises from a more or less permanent alteration of the surface of the electrodes, and is utilized in the so-called *secondary batteries* or *accumulators*. All the so-called polarization phenomena are secondary effects of the change in the character of an electrochemical system produced by the progressive exhaustion of one or more of the components. As a result of polarization, the normal current furnished by a cell may appear to be weakened owing to the setting up of counter electromotive force; or to the increased resistance of a cell produced by changes in the concentration of the electrolyte or the decomposition of layers of gas on the electrodes. There are three general methods available for counteracting the ill effects of polarization; or for depolarizing a cell:

(1) *Mechanical.*—The electrolyte or liquid about the electrodes is kept agitated so that the gas layer may be brushed off, or the negative electrode may have a roughened surface so that the bubbles of gas can more easily escape from points on the surface.

In **A. Smee's cell** (1840) [1] the platinum plate is replaced by a silver plate covered with finely divided platinum. The idea is to make the hydrogen bubbles collect at the points of the roughened surface from which they escape more freely than from a plain smooth plate. The voltage drop with Smee's cell, however, is comparatively large.

(2) *Chemical.*—The negative plate is surrounded by a powerful oxidizing agent to oxidize any hydrogen which might be formed thereon. The chemical agent employed for this purpose is called a **depolarizer**—*e.g.* nitric acid, chromic acid, manganese dioxide, etc.

W. R. Grove's cell (1839) has a porous pot like Daniell's cell, but the porous pot contains a platinum plate and nitric acid; zinc and sulphuric acid are placed in the outer cell. The hydrogen produced by the action of sulphuric acid on the zinc, instead of accumulating on the platinum plate is oxidized by the nitric acid, and the latter is reduced say symbolically: $H_2+2HNO_3=2H_2O+2NO_2$. Owing to the high cost of platinum J. T. Cooper (1840) proposed to use carbon in place of platinum in Grove's cell, and this modification is generally known as **R. Bunsen's nitric acid cell** (1841).

In **R. Bunsen's dichromate cell** (1875) the zinc and carbon plates dip in a solution of sulphuric acid mixed with chromic acid or an alkali dichromate. The zinc plates are attacked by the solution when the cell is not in use, so that an arrangement is made whereby the zinc plates can be drawn out of the solution when the cell is not being worked. The object of the chromic acid is to "burn" up the hydrogen and prevent its accumulating on the negative carbon plate. The chromic acid is at the same time reduced to chromic oxide, Cr_2O_3. At the zinc plate, therefore: $Zn+H_2SO_4=ZnSO_4+H_2$, and then $3H_2+2CrO_3=Cr_2O_3+3H_2O$. The solution is acidified with sulphuric acid, and consequently the chromic acid forms chromic sulphate, $Cr_2(SO_4)_3$; potassium (or sodium) dichromate is the usual source of the chromic acid, so that chrome alum, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$, usually forms, and this can be partially separated from the zinc sulphate in dark purple crystals. The end stages of the reaction are therefore symbolized: $3Zn+K_2Cr_2O_7+7H_2SO_4+Aq=Aq+3ZnSO_4+K_2SO_4+Cr_2(SO_4)_3+7H_2O$.

In **G. Leclanché's cell** (1868) a zinc rod and carbon plate are clamped between two blocks of compressed manganese dioxide and granulated carbon. This combination is dipped in a concentrated solution of ammonium chloride. When the circuit is closed the ammonium chloride attacks the zinc: $Zn+2NH_4Cl=ZnCl_2+2NH_3+H_2$. The cell does not give a constant current very long, but if left for a short time the accumulated hydrogen is "burnt" by the manganese dioxide: $H_2+2MnO_2=Mn_2O_3+H_2O$, and the cell rapidly recovers. Millions of these cells must be in use where current is required only for a few moments—electric bells, etc.—and the circuit is usually open. There are a great many modifications.

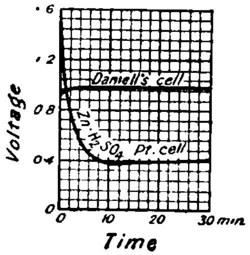

FIG. 9.—Voltage Drop of Voltaic Cells.

(3) *Electrochemical*.—The negative plate is immersed in a solution of a salt of the same metal—*e.g.* a copper plate in a solution of copper sulphate—as in Daniell's cell—is free from polarization because metallic copper is deposited upon the plate, presumably by the hydrogen which would otherwise accumulate on the copper plate. In Daniell's cell, the variation in the electromotive force of the working cell is chiefly due to changes in the concentration of the solution surrounding the battery plates. The electromotive force is therefore nearly constant. This is illustrated by the curve shown in Fig. 9, where a Daniell's cell is allowed to work for half an hour against a resistance of 10 ohms in the external circuit. A comparison of this curve with that of the $Zn|H_2SO_4|Pt$ cell emphasizes the constancy of the current delivered by the Daniell's cell. In Clarke's cell, mercury deposits and zinc dissolves; in Weston's cell, mercury deposits and cadmium dissolves.

Back electromotive force.—Again, if a current exceeding two volts be directed through an electrolytic cell containing dilute sulphuric acid, and fitted with two platinum plates and a galvanometer in circuit, bubbles of gas are disengaged at the two electrodes, oxygen at the anode, hydrogen at the cathode. The direction of the current is indicated by the deflection of the needle of the galvanometer. Now let the battery be cut out of the circuit, and the electrodes immediately joined directly with the galvanometer. The deflection of the needle shows that a feeble current passes in an *opposite* direction to that which occurred when the battery was in circuit. Here, then, when an electric current is passed through a liquid, a counter-e.m.f. is set up, relieving the stress set up by the original current. An examination of the plates of the polarized electrolytic cell shows that gaseous films are present. Obviously, therefore, after a current has passed through such a cell for a short time, the plates—originally quite similar—are no longer alike. The plates are polarized with different gases. The gases adhere to the surface and penetrate the interior of the plates. The plates then behave as if they were made of two different materials. Contact differences of potential are established. We have in fact a voltaic cell, $O_2|H_2SO_4|H_2$, which furnishes a current flowing in an opposite direction to the original current. The cell acts as a kind of "accumulator" of electrical energy until the gases absorbed by the plates are used up. This does not take long. The polarization of the plates of an electrolytic cell thus makes them behave like two different

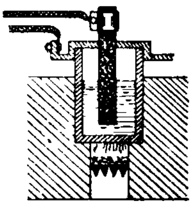

FIG. 10.

metals which exert a *back electromotive force* opposing the electromotive force of the battery. By Ohm's law, the current C (amps.), the resistance R (ohms), and the electromotive force E(volts) of a cell are related $C=E/R$; and if e denotes the back e.m.f. $C=(E-e)/R$.

A high-class steam engine will barely convert 13 per cent. of latent energy of the fuel into useful work; while a high-grade gas engine might convert up to about 35 per cent. of the available energy of the fuel into useful work. There is therefore need for a more efficient and more direct means of converting the chemical energy of the fuel into mechanical energy. Hence, one of the most important of all technical problems is to get the largest possible amount of available energy from the combustion of coal. In the ordinary zinc-platinum cell, 90 per cent. of the available energy of the zinc is converted into electrical current. Zinc is far too costly a fuel for use on a large scale, and hence chemists and physicists have sought a method of obtaining electricity directly from the combustion of carbon or coal. In the so-called *combustion cells*,[2] carbon or some other cheap fuel is transformed into electrical energy by consuming the oxygen of the air at one electrode, and some kind of fuel at the other electrode. A. C. and A. E. Becquerel (1855) tried fusing potassium nitrate in an iron crucible as one electrode and a carbon electrode dipped in the fused nitre as the other electrode. The process was far too costly, and so far, all attempts to dissolve carbon so as to convert the energy of oxidation into electric current have had no real success. In all the proposed cells yet made, including the carbon monoxide cell of W. Borchers and the coke cell of W. W. Jacques, the source of the electric current has been traced not to the primary oxidation of the carbon, but either to a secondary reaction or to a thermoelectric action similar to the development of an electric current when the junction of two dissimilar metals is in a closed circuit.

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§ 6. Decomposition Voltages

> During the electrolysis of a mixture of electrolytes those substances are set free which absorb in becoming free the least intrinsic energy, or the lowest voltage.—J. T. Sprague.

Suppose a current of half a volt be sent through the electrolytic cell, containing normal sulphuric acid and fitted with platinum plates in circuit with a galvanometer. The current passes through the cell for an instant as indicated by the "throw" of the galvanometer needle, and then the quick drop to nearly zero. The hydrogen and oxygen developed on the plate sets up a back electromotive force of nearly ½ volt which very nearly stops the current. A minute steady current—**residual current**—does flow through the system, but this is only just sufficient to maintain the polarization, since if no current at all passes through, the plates would gradually depolarize owing to the dissipation of the gases from the plates. If the current be now raised to 1 volt, a similar state of things prevails. The amount of oxygen and hydrogen adhering to the plates increases; and the increased polarization raises the back electromotive force to very nearly one volt. The residual current passing through the cell is slightly larger than before. This is required to maintain the polarization. If the current is now raised to 1·7 volts, the electrodes become saturated with hydrogen and oxygen gases. Polarization reaches a maximum value, and the back electromotive force also attains its maximum value. Hence any further increase in the applied electromotive force is available for electrolysis, 1·7 volts is the minimum needed for steady electrolysis. If 2 volts are passed through the system, there is a back electromotive force of about 1·7 volts, and the "excess" or "residual" current, 0·3 volt, is the effective electromotive force available for the production of current, and the steady evolution of gases from the electrodes.

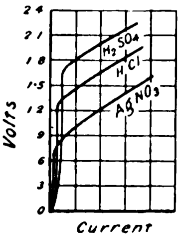

FIG. 11.—Effect of an increasing E.M.F. on some Electrolytes.

The facts here described can be exhibited very concisely by plotting the applied electromotive forces as ordinates and quantities of electricity passing through the system as abscissæ. Fig. 11 shows the results with normal solutions of sulphuric acid, hydrochloric acids, and silver nitrate. The "residual" current flowing through the cell with normal sulphuric acid rises very slowly with increasing voltages until the driving force reaches 1·67 volts. There is then a sudden change in the direction of the curve. Increasing electromotive forces now augment the quantity of electricity passing through the system, and also the amount of electrolysis. Normal hydrochloric acid gives a similar break at 1·31 volts; and silver nitrate, one at 0·70 volt.

The minimum electromotive force required to cause steady electrolysis in any solution is called the **decomposition voltage** or **discharge potential.** The decomposition voltages for a few acids, bases, and salts are shown in Table IV.

TABLE IV.—DISCHARGE POTENTIALS OF SOME ELECTROLYTES.

Salts.		Acids.		Bases.	
N-solutions.	Decomposition voltages.	*N*-solutions.	Decomposition voltages.	*N*-solutions.	Decomposition voltages.
Zinc sulphate	2·35	Sulphuric acid	1·69	Sodium hydroxide	1·69
Nickel sulphate	2·09	Hydrochloric acid	1·31	Potassium hydroxide	1·67
Lead nitrate	1·52	Nitric acid	1·69	Ammonium hydroxide	1·74
Silver nitrate	0·70	Phosphoric acid	1·70		

While the values for the metallic salts vary from metal to metal, the acids and bases have a decomposition voltage approaching 1·7 volts, and the products of the electrolysis are oxygen and hydrogen. Those acids which have a lower decomposition voltage usually give off other products on electrolysis, and attain the final value—1·7 volts—on further dilution. Thus hydrogen and chlorine are evolved when the strength of the hydrochloric acid exceeds $2N$-HCl, and the decomposition voltage of the $2N$ acid is 1·26 volts. The voltage steadily rises with increasing dilution until, with $\frac{1}{32}N$-HCl, the decomposition voltage is 1·69, and hydrogen and oxygen are the products of electrolysis. Not only do the numbers vary with concentration, within certain limits, as exemplified in the case of hydrochloric acid, but also with the nature of the electrodes. The decomposition voltage of normal sulphuric acid, for example, with polished platinum electrodes is 1·67 volts, whereas with platinum electrodes covered with platinum black, the decomposition voltage is 1·07 volts.

The contact potential between metallic zinc and a normal solution of a zinc salt, —0·493 volt, shows that when a zinc ion is deposited on a zinc electrode it conveys a positive charge to the electrode and so lessens the negative charge there present. The system is only in equilibrium when the zinc electrode is negatively charged to a potential of −0·493 volt. If, therefore, zinc is to be deposited in an electrolytic cell, this difference of potential must be counterbalanced by the current. Hence contact differences of potential may also be regarded as decomposition voltages.

The discharge potentials of a few anions and cations are indicated in Table IV, which may be compared with Tables II and III. The numbers refer to normal solutions. The prefix refers to the electrical state of the electrode in the presence of a normal solution of its ions, say, 32·5 grams of zinc per litre. Some of the numbers have not been measured directly. For instance, the number of zinc sulphate has been obtained by extrapolation, since, according to the conductivity measurements, only 23 per cent. of zinc sulphate is ionized in normal solutions.

TABLE V.—DISCHARGE POTENTIALS OF SOME ANIONS AND CATIONS.

Cations.	Charge on metal points.	Anions.	Charge in volts.
$Zn^{\cdot\cdot}$	−0·493	I'	+0·797
$Fe^{\cdot\cdot}$	−0·063	Br'	+1·270
$Ni^{\cdot\cdot}$	+0·049	O'' (in acid)	+1·396
$Sn^{\cdot\cdot}$	+0·085	Cl'	+1·694
$Pb^{\cdot\cdot}$	+0·129	OH' (in acid)	+1·96
$H^{\cdot}$	+0·277	OH' (in bases)	+1·16
$Cu^{\cdot\cdot}$	+0·606	NO_3'	+1·75
$Hg^{\cdot\cdot}$	+1·027	SO_4''	+1·9
$Ag^{\cdot\cdot}$	+1·048	HSO_4'	+2

Just as different electrical pressures (e.m.f.) are needed to produce in different solutions equivalent amounts of chemical change, so different chemical reactions in a voltaic cell generate different amounts of electrical energy, and produce currents with different electromotive forces. During electrolysis a difference of electrical pressure must be continuously supplied because the current is consumed, so to speak, by the separation of chemically equivalent quantities of matter (Faraday's law). In a voltaic cell electrical energy is produced, so to speak, from the chemical energy of the dissolving zinc. The question **whether or not a given supply of electrical energy can start electrolysis is determined by the intensity pressure, or voltage of the current.** The total supply of available electrical energy does not matter. Although a given quantity or electricity, say 96,540 coulombs, will separate chemically equivalent quantities of different electrolytes, these 96,540 coulombs must be supplied at definite pressures before electrolysis can take place. In other words, just as different compounds decompose at different temperatures, and this quite independent of the total quantity of available heat, so electrical energy at different voltages is needed for the decomposition of different electrolytes.

Current density.—If the cathode be small in comparison with the anode, the solution about the former will be very much more quickly exhausted than if a larger cathode had been used. The decomposition voltage of the substance will rise in a proportional manner. Hence, the larger the cathode the lower the "average" electromotive force needed for the decomposition of the pure metal. It is convenient to call the quantity of electricity flowing through the unit surface area, the current density at the electrode, in other words, "the number of ampères per unit surface." "Unit surface" is usually taken in the laboratory to be one square decimetre. The symbol $ND_{100}=\frac{1}{2}$ means that a current of 0·5 amp. flows for every 100 sq. cm. of electrode surface.

EXAMPLE.—What was the current density at each electrode of an electrolytic cell when 4 sq. cm. of each electrode was immersed in the electrolyte, and a current of 4·25 amperes was passed through the system for one hour? One square decimetre = 100 sq. cm. Hence, 1·0625 amps. passed per sq. cm.; or 106·25 amps. per sq. decimetre. The current density at the anode was therefore 106·25 amps., or $ND_{100} = 106\cdot25$.

Current density is one of the most important factors in electrolysis, since it determines the character and nature of the products obtained at the different electrodes. Thus, by using a large current density and a concentrated solution of sulphuric acid, hydrogen, oxygen, ozone, and free sulphur can be obtained, whereas under ordinary laboratory conditions the last substance does not appear.[1]

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§ 7. Gas Cells

The term gas cell is applied to cells devised in 1839 by W. R. Grove[1] in which gases are dissolved in inert electrodes, which are then treated as if they were electrodes consisting of the gases alone—one gas may be hydrogen and the other oxygen or chlorine, or even hydrogen at a different pressure. In the first case, water is produced; in the second, hydrogen chloride; in the third, hydrogen passes from the electrode, where it is at the greater pressure to that where it is at the less. Such a cell with platinum electrodes is shown in Fig. 12. The e.m.f. of the cell is very irregular; a day or two after the preparation it approximates 1·08 volts in nearly all electrolytes, although higher voltages have been observed by F. G. Smale, T. N. M. Wilsmore, and E. Bose. Some days later the voltage falls below the value just indicated. According to theory, the potential difference between the two poles should be constant, 1·231(±0·001) volts (17°) in all electrolytes. In his review of the potential of the oxygen electrode, E. P. Schoch has pointed out that the value 1·08 volts cannot be due to the maximum e.m.f. of the gases, *i.e.* the potential with which the action of the poles is reversible. If the cell be reversed, by discharging oxygen at the poles by electrolysis, the gases are not evolved at a potential slightly greater than 1·231 volts; instead, a potential difference exceeding 1·5 volts must be applied before any current greater than those due to diffusion, convection, etc., will pass, and the evolution of gases occur.

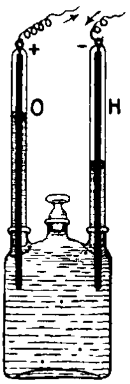

FIG. 12.—W. R. Grove's Oxygen-Hydrogen Gas Cell.

The hydrogen electrode is quite reversible in its action, and its potential is independent of the metal used in its production, and can be obtained in all kinds of electrolytes, all the observed irregularities must be due to the oxygen electrode. The work of F. Förster, E. Müller, R. Lorenz, L. Wöhler, and R. Ruer has shown that the irregularities with the oxygen electrode are due to the oxidation of the electrode.

The discharge potential of an ion is determined by the opposing potential of the electrode; thus, to discharge oxygen or hydrogen at an electrode devoid of any electrochemical activity requires but a small e.m.f., but if the respective electrodes be charged with these gases the e.m.f. required is over one volt. If the products of the electrolysis react with the electrodes, then the discharge potential is determined by the nature of the film formed at the surface of the electrode. Thus, the discharge potential of chlorine at an inert electrode, say, graphite, is quite different from its value at a silver electrode because silver chloride is formed; similarly, oxygen gas is liberated at a lower potential at platinum than at a lead electrode, because in the latter case lead dioxide is formed; R. Luther and F. J. Brisbee found the discharge-voltage of chlorine from hydrochloric acid at a polished platinum electrode is higher than is required for the discharge of chlorine from platinum electrodes, possibly because of the formation of a film of some product on the surface of the electrode; and E. P. Schoch found evidence of the formation of a hydride on the surface of iron or nickel electrodes. In cases of this kind, the main process is irreversible because the extra potential entails a loss of free energy. Hence, the term discharge potential may have two meanings, one refers to the reversible, the other to the irreversible process; it usually has the former meaning.

G. Preuner showed that with the gas cell Pt|H|H_2O|O_2|Pt, when the pressures of the gases at the electrodes are each one atmosphere, and the hydrogen electrode the partial pressure of the hydrogen in saturated water vapour are respectively reduced to p_1 and p_2, the e.m.f. E is

$$E=\frac{RT}{2}\log\frac{1}{p_1}+\frac{RT}{4}\log\frac{1}{p_2}\text{; or } E=\frac{RT}{4}\log\frac{1}{p_1^2p_2}$$

W. Nernst and H. von Wartenberg calculate at 290° K., $p_1=0{\cdot}0191\times1{\cdot}80\times10^{-27}$ atm. and $p_2=\frac{1}{2}p_1$; hence, $E=1{\cdot}2322$ volts (17°); in agreement with this value, J. N. Brönsted and G. N. Lewis respectively obtain 1·224 and 1·234 volts. The difference between these theoretical values and the observed lower value 1·15 is attributed to the observations being made on what virtually amounts to a platinum oxide, not platinum electrode. T. N. M. Wilsmore calculated $dE/dT=-0{\cdot}00121$; F. J. Smale found $-0{\cdot}00142$.

When a gradually rising e.m.f. is applied to platinized electrodes in dilute sulphuric acid or sodium hydroxide, only small currents of the order of diffusion currents pass, the potential of the anode rises rapidly until it passes 1·50 volts, when bubbles of oxygen appear; the anode potential still rises but less rapidly than before. If it were a reversible electrode, which had turned its reversible point at 1·50 volts, the current voltage curve would not have risen but continued nearly parallel to the current axis. The polarization potential also increases steadily with time so long as the current is continuous, but there is no indication of a definite maximum for a particular current density. This polarization is due to a specific surface attraction between the platinum and the gas, as H. G. Möller showed to be the case with hydrogen, because (i) the range of potential extending to nearly three volts is too great, and (ii), as F. Förster showed, the platinum is able to function at a low or high potential which would require the assumption of an arbitrary change in the absorption power of the gas. The effect is also incompatible with the difference of potential being caused by a resistance film. In this manner, E. P. Schoch argues that the potential rise requires that the active substance formed on the anode have a physical form which can change its concentration continuously. Again, if a single solid were formed, the potential would remain practically constant; and it is assumed that the material which is formed should be dissolved by the remainder of the electrode so that it exhibits an increase of potential corresponding with the increased concentration.

When the polarized oxygen electrode is left at rest, the self-discharge results in a continuous decrease in the e.m.f. until a potential difference of 1·08 volts is attained, the potential retains this value for some time—steady state—and afterwards falls to still lower values. R. Lorenz found that, unlike the platinized platinum electrode investigated by F. Förster, a polished platinum electrode exhibits a large number of abrupt changes during its discharge. The halting stages, so to speak, occur at 1·3, 1·05, 0·94, 0·74, 0·64, 0·57, 0·43, 0·27, 0·12, 0·05, and 0·008 volts. This is supposed to correspond with the formation of definite oxides, with different potentials. Generally, however, the step-by-step discharge is not shown because the drop of potential during discharge is continuous. F. Förster showed that the self-discharge of an iridium anode is quite analogous to that of the platinum anode, but the drop is rather more rapid and it falls to 0·865 volt. The behaviour of lead is rendered familiar through the accumulator; and F. Streintz studied the different potentials exhibited by the hydrated lead oxides. The nickel oxide anode in alkaline solutions has been studied by F. Förster in connection with the nickel accumulator; J. Zedner, and F. Förster and V. Herold the iron electrode; E. Müller studied the copper anode in alkali lye; and R. Lorenz has shown that oxygen gas electrodes, with the metals lead, silver, nickel, copper, iron, and zinc, exhibit potentials analogous to those shown by their oxides. The two metals usually regarded as non-oxidizable by gaseous oxygen are therefore supposed to be oxidized, and to owe their potential to the presence of oxides. In general, therefore, (1) During the discharge of "oxygen yielding" anions all metal electrodes are oxidized. (2) The potential of the electrode is that of the oxide irrespective of any (adsorbed) oxygen gas also present. (3) The oxides specifically determine the potentials with which oxygen is evolved. (4) The amount of an oxide that must be actually present to give all characteristic effects may be less than is optically perceptible. (5) Oxygen gas does not appear to be directly electromotively active.

The oxides PtO, PtO_2, PtO_3, with several hydrated forms, were prepared by L. Wöhler, and R. Lorenz determined the potentials of the different oxides used as anodes as well as the potential at which the steady state occurs during the discharge of the platinum anode.

	Oxide potential.	Potential during steady state.
$PtO_2.4H_2O$	0·93	0·94
$PtO_2.3H_2O$	0·86	—
$PtO_2.2H_2O$	0·74	0·74
$PtO_2.H_2O$	0·63	0·64
PtO_2	0·53	0·57
$PtO.2H_2O$	0·45	0·43
$PtO.H_2O$	0·34	—
PtO	0·25	0·27

The value for PtO_3 has not been measured because it decomposes so rapidly, but it is supposed to lie above 0·43, and it is therefore thought to be the oxide to which all higher potentials are due. For potentials above one volt, R. Lorenz believes the different potentials are due to a number of distinct oxides or hydrates, while F. Förster attributes them to the formation of a solution of a higher oxide in the material of the electrode.

F. Förster and E. Müller believe that the evolution of oxygen from the oxygen electrode is a secondary effect, due to the formation and decomposition of a higher oxide; if this means that oxygen is not evolved except through such action, it is not in agreement with G. Schulze's observation that the formation of oxygen also occurs while other oxides are present which are not capable of such decomposition—*e.g.* alumina, magnesia, etc.

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§ 8. The Relation between Electrical and Thermal Energy

No chemical development will be satisfactory and permanent unless erected on a thoroughly physical basis.—O. J. LODGE (1885).

The total amount of electrical energy required for the liberation of chemically equivalent quantities of different electrolytes can be approximately determined by multiplying 96,540 coulombs (or one farad) of electricity by the voltage needed for electrolysis. Hence, the decomposition voltage is proportional to the energy needed for the decomposition of a gram equivalent of a given electrolyte, and the product of the quantity of electricity into its electromotive force not only representing the energy of a battery, but it also measures the chemical energy which was transmuted into electrical energy by the battery. As previously indicated, a **joule,** the unit of electrical energy, is numerically equivalent to the product of one volt into one coulomb. The amount of heat evolved when a given compound is decomposed can be measured and the minimum amount of electrical energy required to decompose a given compound must be at least equivalent to the amount of heat developed when the separate substances re-unite to form the original compound. Measurements show that a joule is equivalent to 0·24 calorie of thermal energy; and a calorie is equivalent to 4·2 joules. Hence, just as thermochemistry writes $Na+Cl=NaCl+97,900$ cals., so electrochemistry writes $Na+Cl=NaCl+411,000$ joules. As a first approximation, it may be assumed that the heat of formation of any given compound is a measure of the thermal equivalent of the electrical energy required to break up the compound by electrolysis.

From the first law of thermodynamics, the law of the equivalence of the different forms of energy, if the work W ergs done by an electric current be wholly expended in decomposing a substance, $W=JQ$, where Q cals. denotes the thermal equivalent of the electrical energy, and J is a numerical conversion factor required, to make the units of work and heat comparable. Here $J=42\times10^6$ because one calorie is nearly equivalent to 42×10^6 ergs or 4·2 joules. By definition, the work done in a circuit per unit of electricity conveyed is $W=EC$; and from the definition of electrochemical equivalent $m=eC$. Again, the heat q liberated during the formation of one gram of a compound from the radicles into which it has been decomposed by a current in $q=Q/m$ provided none of the energy remains in any form other than heat. Substituting these values of Q, m, and W in $W=JQ$, there remains $E=Jeq$, which is a symbolic form of the statement that the electromotive force required to decompose a substance into given constituents is equal to the product of the heat of formation of a gram equivalent to the substance and the number of joules per calorie; or $E=4{\cdot}2eq$ joules.

EXAMPLE.—The heat of formation of sodium chloride is 97,900 calories: what is the equivalent electrical energy needed for the electrolysis of a gram equivalent of the fused salt, and what is the decomposition voltage required? Here, 97,900 calories are equivalent to $97,900\times4{\cdot}2=411,000$ joules. But 96,540 coulombs will liberate chemically equivalent quantities of sodium and chlorine, and 411,000 joules are needed for this purpose. Consequently, since electrical energy = volts × coulombs; 411,000 = volts × 96,540; or volts = 4·3. This means that in order to liberate 23 grams of sodium and 35·5 grams of chlorine from 58·5 grams of fused sodium chloride, 411,000 joules of electrical energy must be supplied at a minimum voltage electromotive force of 4·3 volts. The minimum voltages so calculated are usually a little higher than are needed in practice. It will be observed that this arithmetic is summarized in the formula: volts = 0·043 × Cals. Where Calories are employed to represent the heat developed in the reaction of an equivalent weight of a given compound expressed in grams, the equivalent of water is half the molecular weight in grams, the equivalent of aluminium chloride is one-third the molecular weight expressed in grams.

The computation of the electromotive force of various battery cells from the heat of combination of the "elements" of the cell has been of great value in technology. It is commonly assumed that the electrical energy which a battery can supply may be calculated directly from the thermochemical data. According to the old observation of Lord Kelvin (*ante* W. Thomson),[1] the electrical energy which can be obtained from a galvanic element is equivalent to the thermal value of the chemical processes producing the current when the current is not doing any special work in the circuit—**Kelvin's rule.** In illustration, the thermal value of the reaction in a Daniell's cell is $Zn+CuSO_4=Cu+ZnSO_4+50{\cdot}11$ Cals. That is to say, every gram-atom of zinc dissolved in the reaction is attended by the evolution of 50·11 units of heat. Every gram-atom of bivalent zinc carries in the cell $2\times 96{,}540=19{,}300$ coulombs of electricity. The electromotive force developed during the action is 1·096 volts. Hence the thermal equivalent of the electrical energy developed by the dissolution of one gram-atom of zinc in Daniell's cell is $0{\cdot}24\times 1{\cdot}096\times 2\times 96{,}540=50{,}000$ cals., provided the electrical energy produced is equal to the chemical energy used up. The difference between the thermal value of the chemical processes and the thermal value of the electrical energy derived from the cell is 50·11 and $50{\cdot}00=0{\cdot}11$ Cal. The two quantities differ by about one-fourth per cent.; the difference is within the range of experimental error, and Kelvin's rule, cited above, is valid. J. P. Joule immersed a cell in a calorimeter, and its outer circuit in another, and he found that the heat energy of the cell can be made to appear in the outer circuit. Further experiments showed that some cells directly heat and others directly cool themselves.

As a matter of fact, observation shows that cells sometimes furnish more, and sometimes less energy than corresponds with the thermal data, and the difference between the thermal values of the chemical process and the electrical energy exceeds the limits of experimental error; thus, with the $Pb : Pb(NO_3)_2 : AgNO_3 : Ag$ cell the difference is -16 per cent.; with Pb : lead acetate : copper acetate : Cu the difference is nearly $+15$ per cent. The assumption that the electrical energy derived from a cell is equivalent to the heat of the reaction of the components of the cell, is one of the half truths illustrated further by Berthelot's law of maximum work. The electrical energy is equivalent to the free energy, and that alone is a measure of the maximum work obtainable from a chemical reaction.

If the cell in which the electrical energy is being produced rises in temperature, less electrical energy than is represented by Kelvin's rule will be obtained, because part of the chemical energy may also be converted into heat in working against the resistance of the cell; and a correction factor is required to allow for the energy dissipated in this way. Conversely, if a cell becomes cooler while it is working, more than the calculated quantity of electrical energy might be expected from the cell. Only when the working cell suffers no change of temperature is the electrical energy produced equal to the chemical energy expended. Similar remarks, *mutatis mutandis*, apply to the reverse action during electrolysis. In electrolyzing fused cryolite, for example, J. Hopkinson obtained but 60 per cent. of the amount of aluminium corresponding with the electrical energy expended. In addition, some energy may be expended during electrolysis in overcoming polarization, in secondary chemical reactions, etc. Suppose that the temperature changes ever so little, say dT, while the cell is working, there will be a corresponding change, dE, in the electromotive force of the cell; let q denote the amount of heat absorbed or evolved when a gram-equivalent of the electrolyte is decomposed. Let the cell be placed in a bath maintained at a constant temperature, the units of heat must be added to or given up by the cell if its temperature is kept constantly at T°. If S and T respectively denote the capacity and intensity factors of thermal energy, while C and E denote the corresponding factors of electrical energy, then $q=ST$, and $\epsilon=CE$, and when the two forms of energy are in equilibrium, $CE=ST$, and when T and E change as indicated above, $C(E+dE)=S(T+dT)$, or $CdE=S.dT$, and by substituting $q=ST$, we get

$$C.dE=Q\frac{dT}{T}, \quad \text{or} \quad q=CT\frac{dE}{dT} \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

This expression represents the change in the thermal value of the electrical energy of a cell at T° when the temperature changes dT during the working of the cell, and the electromotive force increases by dE per degree rise of temperature. The factor dE/dT is called the **temperature coefficient of a cell,** and it is usually evaluated by measuring the electromotive force of the cell at two different temperatures.

EXAMPLE.—The e.m.f. of a cell at 0° was 0·1483 volt; and at 43·3°, 0·1846 volt. Hence, the increase in the e.m.f. per degree is $(0{\cdot}1846-0{\cdot}1483)\div 43{\cdot}3=+0{\cdot}000838$ volt $=dE/dT$.

If one farad of electricity be passed through a reversible cell, and it is found necessary to apply q calories of heat in order to maintain the temperature constant, the electrical energy which would be furnished by the cell working in the opposite direction will be equivalent to the thermal value of the reaction, $Q+q$, or expressed in suitable units, electrical energy $=Q+q$. Substituting the value of q obtained in (1) above, and electrical energy $e=CE$, we get $CE=Q+CTdE/dT$, or

C = NF

$$e=Q+CT\frac{dE}{dT};\quad \text{and}\quad E=\frac{Q}{C}+T\frac{dE}{dT}$$

This is called the **Gibbs-Helmholtz equation**—after J. W. Gibbs (1878) and H. von Helmholtz (1882). The equation shows that in order to calculate the electromotive force E of a galvanic element, from Q, the thermal value of the chemical processes which occur during the working of the cell, it is necessary to know the temperature coefficient showing the variation of e.m.f. with temperature. By measuring the electromotive force E and the temperature coefficient dE/dT of a zinc-iodine combination, A. P. Laurie (1885)[2] was able to estimate the heat of combination of these two elements.

1. *If the temperature coefficient of a cell be negligibly small,* dE/dT may be taken as zero, and **Kelvin's equation** $E=Q/C$ remains. Hence, Kelvin's rule indicating the relation between the equality of the thermal and electrical energy of a cell is a limited equation which is valid only when the electromotive force of the cell does not change with variations of temperature. This is nearly the case with the Daniell's cell, and in consequence, the electromotive force calculated from the thermal value of the reactions in the cell is nearly equal to the observed value.

EXAMPLES.—(1) Assume the temperature coefficient of Daniell's cell is zero, and the heat of the reaction 50,110 cals.; then 50,110 calories equal $50{,}110\div 0{\cdot}24=209{,}900=Q$ joules; and $C=2\times 96{,}540$. Hence, $E=1{\cdot}087$ volts; the observed voltage is 1·096.

(2) According to F. Haber and S. Tolloczko (1904) the thermal value of reaction in the AgCl : CuCl cell is $\mathrm{Cu}+\mathrm{AgCl}=\mathrm{Ag}+\mathrm{CuCl}+3500$ cals., and at 200° the temperature coefficient of the cell is zero. Show that the calculated e.m.f. is accordingly 0·151 volt. (The observed value is 0·149 volt.)

2. *If the temperature coefficient of the cell* dE/dT *be negative,* the electromotive force will diminish with rising temperature, and the electrical energy derived from the cell will be less than that computed from the thermal energy. The cell will therefore become hot while it is working. This does not refer to heat due to the internal resistance of the cell. L. Clark's cell has a temperature coefficient of —0·0012345 volt per degree at about 18°.

EXAMPLES.—(1) Show that the e.m.f. of the oxyhydrogen cell is $1{\cdot}075+0{\cdot}0014\theta$ when $H_2+O=H_2O+67{,}520$ cals., and the temperature coefficient of the cell is $-0{\cdot}0014$ volt per degree.

(2) The reaction in a Clark's cell evolves 340,000 joules. Show that the temperature coefficient of the cell is $-0{\cdot}00114$ when the e.m.f. at 18° is 1·429.

(3) According to G. N. Lewis and C. A. Kraus (1910), the difference of potential of a cell with sodium and 0·206 per cent. sodium amalgam as electrodes in a solution of sodium iodide in ethylamine is 0·8456 volt at 25°, and the temperature coefficient $-0{\cdot}0000408$ volt per degree. Hence calculate the heat evolved during the solution of one equivalent of sodium in an excess of the 0·206 per cent. amalgam. Substitute in Helmholtz's equation, C is the Faraday equivalent $=96{,}540$ coulombs; $E=0{\cdot}8456$; $dE/dT=-0{\cdot}0000408$; $T=25+273$. The result furnishes $Q=82{,}850$ joules; and since one joule is equivalent to 4·186 cals., the thermal value of the process is nearly 19,800 cals.

3. *If the temperature coefficient of the cell dE/dT be positive,* the electromotive force of the cell will increase with rise of temperature and the electrical energy of the cell will be less than that computed from the thermal value of the chemical processes, and heat will be abstracted from the surrounding objects in order to maintain the temperature of the cell constant. Such a cell will become colder in action.

Examples.—(1) The slight discrepancy between the observed and calculated values of the electromotive force of Daniell's cell indicated in a preceding example is due to the small but measurable positive temperature coefficient of the cell, for $dE/dT = +0·000034$ vol. per degree at 15°. If this factor be introduced into the previous calculation for the cell working at about 15°, $T = 280°$ K., we must add $0·000034 \times 288$ to the 1·087 volts obtained in the previous computation. This furnishes 1·096 volts; the observed value is 1·092 volts.

(2) According to F. Haber and S. Tolloczko (1904), the thermal value of the reaction $Pb + 2AgCl = PbCl_2 + Ag + 24$ Cals. The temperature coefficient is +0·152 millivolt per degree at about 250°. What is the calculated e.m.f. of the lead chloride : silver chloride cell ?

The self-cooling of a working cell has been compared with the self-cooling of a freezing mixture, or of a jet of compressed gas.

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[2] A. P. Laurie, *Phil. Mag.*, (5), **21.** 409, 1886; *Journ. Chem. Soc.*, **49.** 700, 1886; F. Haber and S. Tolloczko, *Zeit. anorg. Chem.*, **41.** 407, 1904.

§ 9. Fractional Electrolysis—G. Magnus' Rule

During the electrolysis of a number of mixed electrolytes, there is a selective power at the electrodes which is based solely on the ratio of the voltage required to free the several ions.—J. T. Sprague.

When a solution containing salts of different metals is subjected to electrolysis, there is a certain voltage at which one and only one of the metals will be deposited on the cathode—**G. Magnus' rule** (1856). If a mixed solution of nickel and copper sulphates, for example, be subjected to electrolysis, copper alone is precipitated when the applied electromotive force has reached 1·29 volts ; the nickel is not precipitated, since its decomposition voltage is 1·95 volts. On the other hand, if a mixture of nickel and iron sulphates be similarly treated, a mixture of iron and nickel will be simultaneously deposited. The decomposition voltage of these salts are too close to allow an effective separation of the two elements by electrolysis. Hydrogen is also evolved during the electrolysis of these salts. This arises from the fact that the decomposition voltage of sulphuric acid—1·67 volts—renders it also susceptible to the influence of the same current as liberated nickel and iron.

Many useful methods of analysis are based upon these principles. In metallurgy, too, electrolytic processes for refining metals—nickel, copper, lead, tin, silver, gold, etc.—have been developed. For example, in copper refining, as we shall soon see, anodes made of crude copper are dipped in a solution of copper sulphate acidified with sulphuric acid ; the cathodes are sheets of pure copper. Zinc, iron, and copper from the anode pass into solution during electrolysis. The decomposition voltage is kept below that needed for the deposition of zinc and iron. In consequence, refined copper is deposited upon the cathode. Other impurities affecting the crude copper are but slightly soluble in the electrolyte, and are deposited about the anode as a thin mud—*anode mud.*

The effect of concentration on the decomposition voltage.—The decomposition voltage of an electrolyte is greater the more dilute the solution. The concentration of any given salt about the electrode naturally decreases during the process of electrolysis. Hence also the decomposition voltage for that particular salt in the mixed electrolyte also increases. When the concentration of the copper sulphate in a mixture of copper and nickel sulphates has become so small that the decomposition voltage of the dilute solution approaches that of nickel, any further electrolysis will bring down a mixture of both metals. There is, therefore, a limit to the process of electrolytic separation, just as there is a limit to the separation of substances in ordinary analysis. The limit in the former case is determined by the decomposition voltages of the respective metals; and in the latter case, the limit is determined by the solubility of the precipitates in the given menstruum. The limiting concentration can be approximately estimated from the rule: A decrease of one-tenth in the concentration of the electrolyte raises the decomposition voltage of any given ion $0·058/n$ volt, where n is the valency of the particular ion.

As the cation is deposited about the cathode, the loss in concentration is made up by diffusion from the surrounding electrolyte. To hasten diffusion, and prevent undue attenuation of the electrolyte in the vicinity of the cathode, stirring by rotating one of the electrodes is sometimes used.

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