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THE FOUNDATIONS OF CHEMICAL THEORY

By R. M. CAVEN, D.Sc. F.I.C.

Systematic Qualitative Analysis. For Students of Inorganic Chemistry.

A Short System of Qualitative Analysis. For Students of Inorganic Chemistry.

Quantitative Chemical Analysis and Inorganic Preparations. In two Parts.

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The Foundations of Chemical Theory. The Elements of Physical and General Chemistry.

By R. M. CAVEN, D.Sc. and G. D. LANDER, D.Sc.

Systematic Inorganic Chemistry, from the Standpoint of the Periodic Law. A Textbook for Advanced Students.

BLACKIE & SON, Ltd., LONDON, GLASGOW, BOMBAY

THE FOUNDATIONS OF CHEMICAL THEORY

The Elements of Physical and General Chemistry

BY

R. M. CAVEN

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SECOND EDITION

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PREFACE

Modern chemistry presents a multitudinous array of facts. It could not be otherwise, since the science undertakes to describe more than eighty separate elements and the compounds they form, one with another.

The exhibition of these facts, as set forth in a comprehensive textbook, whether of organic or inorganic chemistry, may well dazzle and bewilder the student, who will scarcely be likely to appreciate the beauty of the science, or the glamour of the human achievement of which it is the monument, if he is required laboriously to appropriate the facts without judicious selection and arrangement.

Indeed, the complaint is often made by students that chemistry requires too much memory-work, and is therefore not so inspiring a science as physics, which deals all the while with fundamental principles, and properties of matter.

Yet the facts of chemistry are the facts of nature, and nature is not chaotic. Consequently these accumulated facts present to the mind of man a powerful challenge. They must be systematized.

Chemical theory, however, is worthy of the facts which form the subject-matter of the science, for it includes some of the greatest generalizations of any science. The atomic and molecular theories, the theories of molecular structure, the periodic law, the conceptions embraced in modern physical chemistry, which constitute, *par excellence*, the science on its intellectual side, are among the noblest achievements of the human mind.

Every student of chemistry must become acquainted in some degree with chemical theory. The question therefore arises how this theory may best be communicated. Ought it to be intermingled dexterously with chemical facts—with the descriptive part, so much easier to understand and more difficult to remember;

or ought a special course of instruction in the theory of the science to be devised, apart from the descriptive lectures?

The exigencies of teaching generally lead to the following solution: that the student learns enough theory during his second year or intermediate course to serve him for the time being, and that in the later course for his degree he attends lectures in physical chemistry, which take for granted a solid foundation of elementary theory.

A degree course in physical chemistry is a serious affair, and in the hands of a specialist is likely to make a severe strain on the mental resources of a student. To profit by such a course a student should be very sure of his foundations.

The purport of this book may therefore now be stated. As its title indicates, it is an endeavour to disclose the foundations of the science, and make them plain and real to the average student.

The author hopes that the general reader, who wishes to know what modern chemistry really means, will find within these pages the information he desires; and that the student to whom chemical science offers an open field of glowing possibilities will find the chapters of this book a not unwelcome guide in his earlier excursions.

Briefly, it is suggested that the book may be read by the student during or at the end of his second year's course, for the purpose of knitting together his chemical knowledge in view of the more advanced studies which lie before him later.

The writer has utilized facts and methods of presentation contained in former books of which he is joint or sole author; and he desires to acknowledge his indebtedness to various other works, particularly to the introductory volume of *A Textbook of Inorganic Chemistry*, by Dr. J. Newton Friend. He also wishes to thank Dr. E. B. R. Prideaux for kindly reading the manuscript of the book.

Royal Technical College,
Glasgow, *October, 1920.*

PREFACE TO NEW EDITION

When this book was published five years ago it was deemed wise to omit from it any reference to new ideas in chemistry connected with the constitution of the atom, and all that is entailed in recent knowledge concerning the structure of matter. So far as he is aware, the author was not criticized for the omission of teaching which at that time seemed appropriate for advanced but not for elementary students of chemistry.

It was not long, however, before the author himself began to regret this omission, and to look forward to the time when the call for a new edition might enable him to include some of the new teaching which now undoubtedly forms an important part of the Foundations of Chemical Theory.

How to incorporate the new knowledge with the old—how safely to pour new wine into old wine-skins—was a difficult problem. Indeed it is a problem which at the present time is encountered by every teacher of chemistry who desires to keep his science up-to-date. The danger is that old doctrine may be utterly forsaken for new, and that instability and confusion may in consequence be introduced into chemistry. A wise conservatism is to be commended with regard to all new teaching in science—*festina lente* must be our motto. Moreover, the historic method of study is always wise. Therefore this method has been adopted in dealing with the new material. The earlier chapters have been revised in the light of what was to follow, and so have been made a pathway of approach, clear of stumbling-blocks, to the new territory.

Thus we have the older atomic and molecular theories, the older views of valency and chemical constitution, and the periodic

law according to Mendeléeff, as a preparation for the modern view of the atom, and the modern view of the molecule.

So it is respectfully suggested that teachers will find this a safe and helpful way of leading their students into possession of the new domain.

The author wishes to tender his grateful thanks to Dr. J. A. Cranston for the help he has given in reading and criticizing the new matter for this edition.

R. M. C.

Royal Technical College,
Glasgow, *October, 1925.*

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THE FOUNDATIONS OF CHEMICAL THEORY

PART I—ATOMS AND MOLECULES

CHAPTER I

THE OLDER ATOMIC AND MOLECULAR THEORIES

1. The Composition of Matter

The term *matter* at first suggests to the unsophisticated mind such qualities as bulk, shape, colour, hardness, weight. It is quickly recognized, however, that some of these qualities belong only to some kinds of matter, and are absent from others. Consider, for example, a log of wood floating on water. It will be admitted that the wood but not the water possesses hardness, though both possess weight; that the log but not the water has a permanent shape, though both have bulk. Above the water is the air, and the air is something, for it blows in a man's face, and raises ripples on water. By a proper instrument it can be shown that air possesses weight. So air is matter, though it is without form, permanent bulk, apparent colour, or hardness.

At the conclusions suggested by these thoughts the Ancients arrived after their own fashion. Their fundamental classification of natural things included the three categories: earth, water, air, together with a fourth—fire. These four were the *elements*, according to Aristotle, but their names really stood for qualities rather than separate species of matter. For instance, *earth* meant dryness and coldness, *water* wetness and coldness, and so on. Nevertheless, the first three terms at least suggest an outlook on the world which was essentially true, since they stand for the three fundamental forms of matter: *solid, liquid, gas.*

This conclusion as to the threefold constitution of the world is reached by an *extensive* outlook upon nature; an *intensive*, an introspective view, such as the following illustration furnishes, leads to another conclusion.

Sea-water is distinguished from fresh water by its saltness, that is, by its special taste. What proportion of salt water mixed with fresh water could be so distinguished depends upon the sensitiveness of the human palate; but such a test would assuredly fail when the salt water was highly diluted. The addition of silver nitrate to the much diluted salt water would, however, serve to detect the presence of salt after the test of taste had failed, because of the turbidity or opalescence which the silver nitrate produces with even very small quantities of chlorides in solution. Would this test fail in its turn when the utmost delicacy was required, or would it detect the minutest quantity of salt? It might fail by reason of defective human vision, were it not that an instrument has been made on purpose to detect the slightest cloudiness in a liquid; but it must fail at last for quite another reason. For the test depends on the insolubility of silver chloride in water; but silver chloride is not quite insoluble in water, and on this account will not be precipitated when the salt solution is excessively dilute.

So salt may perhaps be present in, and diffused through, water in quantity too minute to be detected by any test whatsoever. How far, then, may the dilution be carried; will salt still be present after infinite dilution? Or, more generally, is matter infinitely divisible? This is the question which arises directly out of an experiment which any novice in chemistry can perform. The same question presented itself to the alert minds of the ancient peoples of the East; not, it is true, by reason of experimental investigation, but because of meditation on the nature of the material world. Thus the question was: Is matter infinitely divisible or not? To believe the latter is the easier and more satisfying philosophy; this was the philosophy of Plato and Democritus. So matter was supposed to consist ultimately of hard, indivisible, and indestructible particles separated by vacuous interspaces; that is, of *atoms*.

Of the two theories of the Ancients, to which the Greeks gave finished expression—the theory of *Elements* and the theory of *Atoms*—the former passed through strange vicissitudes, which

need not here be traced; whilst the latter remained latent until modern times, when it was found to be in accord with the conclusions derived by Dalton from experimental data.

2. The Elements

A theory of the elements should precede a theory of atoms. So, dismissing the ancient theory of the elements, it may be said quite briefly that an element, as generally understood, is an ultimate species of matter; or, to adopt the more usual and explicit definition:

An element is a substance which hitherto has not been resolved into two or more dissimilar kinds of matter.

We owe this idea of an element first of all to Boyle (1678); it was Lavoisier (1789), however, who realized its provisional nature; and, indeed, some of Lavoisier's elements, such as lime and the alkalis, are now proved to be compounds. If this definition merely marked the present state of progressive human achievement it would not be a scientific definition. An assurance is necessary that some kind of finality has been or may be reached in the decomposition of substances; that at least the "elements" are equally elementary; this assurance may be given with every confidence. That the elements are absolutely undecomposable has, however, never been a settled belief of the chemist; on the contrary, he has held the opinion from time to time that they are derived from, and so are resolvable into, a common primordial substance. The phenomena of radioactivity now furnish evidence of the spontaneous and perpetual disintegration, into simpler forms of matter, of the atoms of certain of the elements; and new theories of matter which are now taking firm root in chemistry represent the atom as a complex structure; further, the fact has now been established that the elements are not truly homogeneous, but consist of atoms of differing relative weights, which, however, are indistinguishable and inseparable by ordinary chemical means.

These considerations, however, do not affect the chemist's working theory of the elements. He knows that the nearly ninety different kinds of matter into which he has resolved the many substances found in nature, and out of which he can elaborate a vast number of compounds to which nature has no counterpart, pass unchanged through the crucible of his everyday operations. So he habitually regards the catalogue of the elements that hangs in his

laboratory as a permanent record, not only of human skill, but of Nature's handiwork as well.

3. The Atomic Theory

The atoms of Greek philosophy were indestructible; indeed, the indestructibility of matter has probably always been an axiom of science, notwithstanding the surprising and fantastic changes matter was supposed to undergo in the hands of the alchemists of the Middle Ages. This principle was first clearly illustrated, however, by Lavoisier in his application of quantitative methods to chemistry, and was subsequently demonstrated, within the limits of the most accurate experimental research, by Stas, Landolt, and others.[1] In 1770 Lavoisier gave an account of experiments he had performed to test the supposition that water is transformed into earth by boiling. A weighed quantity of water was boiled for 101 days in a weighed and sealed glass vessel; and at the end of that time it was found that while "earth" appeared in the vessel the water weighed the same as at first, and the weight of the "earth" was equal to the loss in weight which the glass vessel had incurred. Thus it was shown that the "earth" came from the glass and not from the water, and that water is not transformed into earth by boiling. In these experiments the use of the balance played an essential part; but this was a novelty in chemistry. The scientific achievements of such men as Boyle, Black, Cavendish, Priestley, Scheele, notwithstanding their great value, were chiefly of a qualitative nature. Henceforth, however, chemistry was concerned with weighing things, and a new era began.

It was now but a step to the quantitative analysis of chemical substances. Lavoisier took this step in his investigation of mercuric oxide, or the calx of mercury, which Priestley and Scheele had decomposed into mercury and oxygen. Soon there arose an important question, the answer to which could be found only by quantitative analysis. This was the question: Is a chemical compound necessarily constant in composition, or may its composition vary within certain limits according to the way in which it is prepared?

It may appear to be a truism that the same compound must

[1] For an account of these researches see *The Study of Chemical Composition*, by I. Freund.

always have the same composition, so that it is better to state the problem in this way: Can the products of different chemical reactions, designed to produce the same compound, really differ slightly in composition? Berthollet was of opinion that they could; that the composition of a compound might vary within certain limits according to the way in which it was prepared; indeed, that the conditions of its genesis are the overruling factors of its composition. Barium sulphate was cited as an example. All known specimens of this compound were found to be identical in composition, but this identity was due, not to any inherent property of the constituent elements of the compound, but to the fact that by uniting in such proportions these elements produced a compound of maximum insolubility in water. It was fair to suppose, therefore, that if the salt could be precipitated from some other medium than water it would have a different composition accommodated to a new requirement of maximum insolubility. Such an idea was gravely erroneous, and was quite foreign to the principles on which the atomic theory was soon to be founded. Yet the idea appeared to have experimental support; and, indeed, it contained the germ of an important truth. In support of his belief, Berthollet showed that when nitric acid reacted with mercury or with tin the composition of the nitrate of mercury or oxide of tin produced varied within certain limits according to the concentration of the acid employed. Proust, on the other hand, maintained that "between pole and pole compounds are identical in composition; their appearance may vary owing to their manner of aggregation, but their properties never". After a controversy carried on with Berthollet over a period of eight years (1800–8), Proust fully established his proposition, and showed that the variable products obtained by Berthollet were variable mixtures of invariable compounds. Thus was established the first law of chemical combination—*the law of definite or fixed proportions*:

The same chemical compound always contains the same elements united together in the same proportions; or the proportions between the constituent elements of a chemical compound bear an unalterable relation to each other, and to the proportion of compound formed.

This was the first foundation of the atomic theory.

Nevertheless, it was a pity that the truth in Berthollet's view was entirely overlooked in the victory of Proust: the truth that

the proportions or concentrations in which reacting substances are present may determine the proportions subsisting between the products of a reaction, although the proportions in which elements or compounds actually react to form these products are quite beyond the influence of external and variable conditions. Thus, in the case of the action of nitric acid on mercury, studied by Berthollet, the concentration of the acid determines whether mercurous or mercuric nitrate or a mixture of these two salts is produced, although it can have no influence on the unalterable chemical composition of either of the two salts.

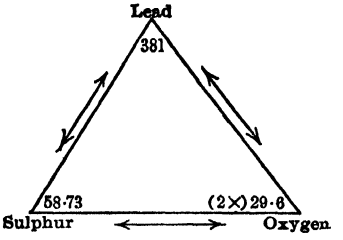
The existence of two nitrates of mercury is, however, a noteworthy fact, which appears the more striking when it is discovered that in one compound the proportion of mercury to nitrate is exactly twice what it is in the other. Further examples of this phenomenon were observed by Dalton, who showed that the proportion of hydrogen to a fixed quantity of carbon is twice as great in methane as in ethylene, and of oxygen to a fixed quantity of carbon, twice as great in carbonic acid gas as in carbonic oxide.

Other examples of compounds showing analogous relations are two of the oxides of lead, one of which contains twice as much oxygen compared with lead as the other, and the five oxides of nitrogen, in which the quantities of oxygen combined with a fixed amount of nitrogen are as 1 : 2 : 3 : 4 : 5. Here was an important generalization, which was formulated by Dalton as the *law of multiple proportions*:

When one element combines with another in more than one proportion, these proportions bear a simple relation to one another.

The foregoing facts furnish material enough for the atomic theory. It is usual, however, to add to the laws of definite and multiple proportions a third law, the law of reciprocal proportions, which, however, follows logically from the other two laws.

It was shown by Richter, about 1780, that the ratio between the quantities of two acids which neutralize a fixed amount of alkali is the same whatever the alkali may be; and by Berzelius, in 1810–2, that 381 parts of lead combine separately with 58·73 parts of sulphur and 29·6 parts of oxygen, whilst 58·73 parts of sulphur combine in turn with 57·45 parts of oxygen. Now, $57{\cdot}45 = 29{\cdot}6 \times 2$ within the limits of the experimental error of the time; and these facts may be expressed diagrammatically thus:



So is illustrated the *law of reciprocal proportions*:

The proportions of two elements which separately combine with a fixed proportion of a third element are also the proportions of these elements which combine with each other, or else—in accordance with the law of multiple proportions—they bear a simple ratio to these proportions.

This law has within it, especially in the way in which it was illustrated by Richter, the idea of chemical equivalents; and so it may be stated in this axiomatic way:

Quantities of substances which are chemically equivalent to the same quantity of a third substance, are chemically equivalent to one another.

Thus it appears that, granted the validity of the idea of chemical equivalents, which will be examined later, the law of reciprocal proportions requires no experimental justification.

Although we owe the essence of the modern atomic theory to Dalton alone, the precise way in which the theory took shape in the mind of its author has been rather problematical. At the close of a paper on the absorption of gases by water, Dalton wrote as follows:

"An inquiry into the relative weights of the ultimate particles of bodies is a subject, as far as I know, entirely new. I have lately been prosecuting this inquiry with remarkable success."

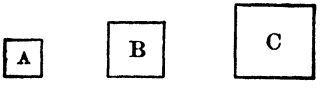
No hint is given in the context of the way in which the atomic values, which follow, were estimated, nor of the precise reason why such values were believed to exist. The idea that matter consists of discrete particles was, however, in the air. Apart from the ancient theory of atoms, a theory of particles had been held more or less firmly by F. Bacon, Boyle, Higgins, and others; whilst Newton made the following explicit statement:

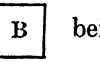
"It seems probable to me, that God in the beginning formed matter

in solid, massy, hard, impenetrable, movable particles, of such sizes and figures, and with such other properties, and in such proportion to space, as most conduced 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 very 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 traced only in the various separations and new associations and motions of these permanent particles."

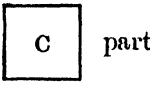
It would almost appear from such a pronouncement that Newton and not Dalton was the author of the atomic theory. Yet this statement is not a chemical theory: it is a cosmic theory intimately related to Newton's great discovery of universal gravitation. Dalton, however, was greatly indebted to Newton and the idea of ubiquitous particles which the theory of gravitation involved; and it appears that he conveyed this idea into chemistry and employed it to explain the laws of chemical combination.

To understand the atomic theory, therefore, is simply to understand how the theory of particles fits the chemical laws. This is quite easy.

Let there be three elements, A, B, C, and let the areas of the squares: 

represent the combining weights of these elements on any arbitrary scale, 

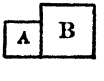
being the quantity of B which is found to combine separately with

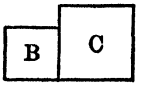
parts of A and 

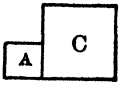
parts of C, according to the law of definite proportions; whilst

parts of C also combine with

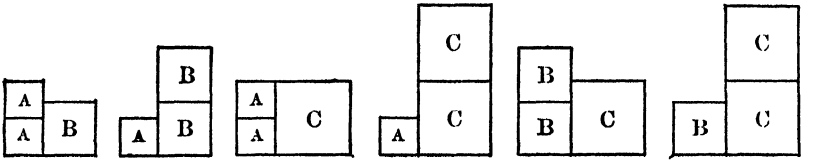
parts of A, according to the law of reciprocal proportions, so that the following compounds are formed:







Then, according to the law of multiple proportions, compounds such as these may be formed:



&c. How else can these experimental facts be interpreted than by the idea of "permanent particles"? The elements combine according to the laws of definite and multiple proportions because they combine atom by atom: 1 atom of A with 1 atom of B; 1 atom of A with 2 atoms of B; 2 atoms of A with 1 atom of B; and so on. That is Dalton's *atomic theory*, and the theory is expressed succinctly in the following statements:

1. All matter consists of discrete particles called atoms, which remain unbroken throughout chemical change.

2. Atoms of the same element are ordinarily supposed to be similar in all respects.

3. Chemical compounds are formed by the union of the atoms of different elements in simple numerical proportions.

4. The proportions in which elements combine to form compounds are determined by the atomic weights of the elements.

The transition from the laws to the theory is quickly made: it is taken, so to speak, in a stride; but the boundary line between them must not be obliterated. The laws of chemical combination are statements of experimental facts; the theory is an explanation of these facts which is very probably true, but it does not stand in the same category as the facts. In science, facts and theory must always be distinguished as clearly as possible.

When the atomic theory is accepted it at once appears that the combining weights of the elements represent the combining weights of their atoms. The atomic theory involves the atomic weights. No atomic theory previous to that of Dalton involved atomic weights; these were a novelty, and their introduction constitutes Dalton's great contribution to chemical science. The following atomic weights are selected from a list published by Dalton, the atomic weight of hydrogen being 1.

DALTON'S ATOMIC WEIGHTS

Hydrogen	1	An atom of water or steam, composed of 1 of oxygen + 1 of hydrogen ...	8
Azote	5		
Carbon or Charcoal ...	5		
Oxygen	7		
Phosphorus	9	An atom of ammonia, composed of 1 of azote + 1 of hydrogen	6
Sulphur	13		
Magnesia	20		
Lime	23		
Soda	28	An atom of carbonic oxide, composed of 1 of carbon + 1 of oxygen	12
Iron	38		
Potash	42		
Zinc...	56	An atom of carbonic acid, 1 carbon + 2 oxygen	19
Copper	56		
Silver	100		
Gold	140	An atom of sulphuric acid, 1 sulphur + 3 oxygen	34
Mercury	167		

If the student compares these atomic weights with those in use at the present day, he will see that they differ widely from the modern figures. Inaccuracies in Dalton's values are to be expected, but it is not experimental error which attributes, for example, an atomic weight of 7 to oxygen, instead of 16. As a matter of fact these combining weights are not atomic weights at all, but are approximately what we now recognize as equivalent weights.

For, in truth, Dalton had no means of determining atomic weights. The value 7 (or 8) for oxygen is derived from the analysis of water: 8 parts by weight of oxygen combine with 1 part by weight of hydrogen to form 9 parts by weight of water. Who shall say from this that the atomic weight of oxygen is 8? That depends on the number of atoms of each element which combine together to form a unit of water, a fact clearly recognized by Dalton.

Thus, we have the ratio O : H = 8 : 1 or 16 : 2 or 24 : 3, &c., and if 1 atom of oxygen combines with 1 atom of hydrogen, then the atomic weight of oxygen is 8; if 1 atom of oxygen combines with 2 of hydrogen, the atomic weight of oxygen is 16; if 1 combines with 3, it is 24; if 2 combine with 1, it is 4; and so on. There was, however, no evidence on which to base a decision between these alternatives. Just at this point Dalton made a regrettable mistake. Instead of recognizing the limitations of his experimental knowledge, he made the assumption

that since only one compound of hydrogen and oxygen was known, it necessarily had the simplest possible composition, and so was formed from 1 atom of each of its constituent elements. Consequently, the atomic weight of oxygen was thought to be 7 (or 8); and for a similar reason the atomic weight of nitrogen (azote) was supposed to be 5, and that of carbon also 5.

It is worth while to notice, however, that Dalton applied the term atom to the ultimate particles of substances known to be compounds as well as to those of elements; it is noteworthy also that his numerical values furnish examples of the law of multiple proportions; for instance, the composition of the two oxides of carbon.

Dalton's system of atomic symbols was ingenious: ◯ stood for oxygen, ⊙ for hydrogen, ◍ for carbon, &c.; whilst for compounds such formulæ as , which stands for sulphuric acid (SO_3), had to be constructed. In these formulæ, however, picturesqueness did not compensate for practical inconvenience; and the suggestion of Berzelius (1811), that initial letters should replace Dalton's hieroglyphics, found general acceptance.

4. The Molecular Theory

Dalton made no further advance along the road that he had traversed. His assumption that the simplest formulæ for a compound is the right one was a subterfuge which marked the end of the road. Advance must therefore be sought in another direction; and it is found in the study of gases; for gases are the simplest form of matter, and, if atoms exist, the properties of gases will best elucidate their existence.

In 1805 Gay-Lussac and Humboldt studied the volume proportions in which oxygen and hydrogen combine to form water; and announced that "100 volumes of oxygen required for complete saturation 199·89 volumes of hydrogen, for which 200 may be put without error". This is a single example of a law, *Gay-Lussac's law of volumes*, which is thus expressed:

The volumes in which gases combine are simply related to each other, and to the volume of the compound gas which is formed.

For example:

2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of steam.
1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrogen chloride.
3 volumes of hydrogen combine with 1 volume of nitrogen to form 2 volumes of ammonia.

A necessary corollary of this law is the statement that: *the densities*, i.e. the masses of unit volumes, *of the elementary gases are simply related to their combining weights.*

Thus, since 1 volume of hydrogen combines with 1 volume of chlorine, and also 1 grm. of hydrogen combines with about 35·5 grm. of chlorine, the density of chlorine compared with that of hydrogen as unity is about 35·5.

It further follows, if gases combine volume by volume, according to the law of Gay-Lussac, and also atom by atom, according to the theory of Dalton, that there is a simple connection between the volume and the atom; and, indeed, that *equal volumes of hydrogen and chlorine*, for example, *contain equal numbers of atoms.* This conclusion, which was quite valid so far as it went, was reached by Gay-Lussac, but was denied by Dalton, on account of a difficulty which arose when the volume of the product was considered.

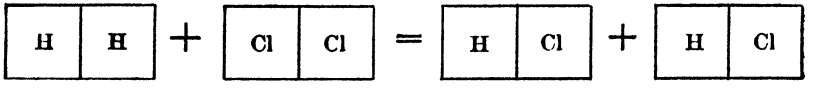
Now when two separate and different elementary atoms combine to form a compound atom, or whatever it may be called, it is one entity they form, not two. It is impossible, for instance, that 1 atom of hydrogen combining with 1 atom of chlorine can produce two compound atoms of hydrogen chloride. And yet 1 volume of hydrogen combining with 1 volume of chlorine forms 2 volumes of hydrogen chloride. That was a dilemma; and it was met by Dalton by a spirited denial of the law of Gay-Lussac. "The truth is", said Dalton, "that gases do not combine in simple proportions by volume; when they appear to do so, it is due to an error in our experiments"!

Now, Dalton was wrong; and yet what other solution can be found, unless indeed the "atoms" are torn in pieces in the process of chemical synthesis, and the pieces are afterwards joined together again in a different way?

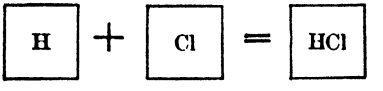
That is precisely the solution of the difficulty suggested by

Avogadro, in his celebrated hypothesis. In this hypothesis, which will now be expounded, two orders of particles were distinguished, which we now call *atoms* and *molecules*. Atoms are indivisible in ordinary chemical changes; molecules are aggregates of atoms — with a few exceptions — which maintain their integrity in ordinary physical changes, but suffer disruption in the course of chemical change, so that their constituent atoms may be rearranged to form fresh molecules.

Now, when hydrogen chloride is formed from its elements the volume of the product is twice the volume of the hydrogen or of the chlorine; therefore it is sufficient to assume that the molecules of hydrogen and chlorine consist of pairs of atoms, which break into single atoms, and recombine, thus:

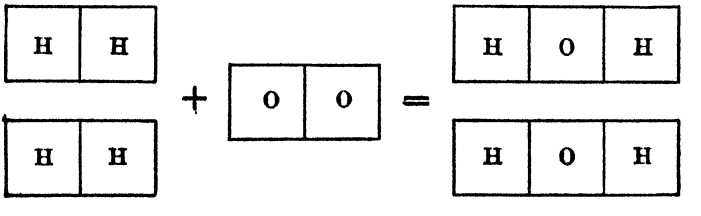


so that 1 volume of hydrogen plus 1 volume of chlorine gives 2 volumes of hydrogen chloride, instead of 1 volume, according to the scheme:

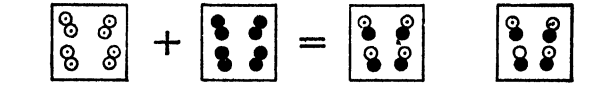


It might be objected, however, that if the molecules of hydrogen chloride are intrinsically twice the size of the atoms of hydrogen and chlorine, out of which they are formed, the volume of the compound gas might be expected in any case to be twice that of either of the simple gases. Such an objection, however, is invalid, since the actual size of the molecules of a gas is very small compared with the molecular interspaces, and consequently the question of a molecule of hydrogen chloride being intrinsically larger than an atom of hydrogen or of chlorine does not arise.

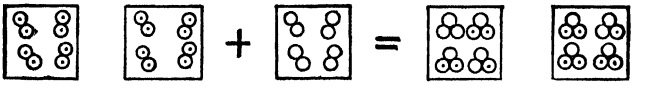
The formation of 2 molecules of steam from 2 molecules of hydrogen and 1 molecule of oxygen is thus represented:



The above processes of combination may be set forth in terms of volumes, by using Dalton's symbols, thus:



1 vol. hydrogen. 1 vol. chlorine. 2 vols. hydrogen chloride.



2 vols. hydrogen 1 vol. oxygen. 2 vols. steam.

Or by means of chemical equations:

$$H_2 + Cl_2 = 2\,HCl.$$
$$2\,H_2 + O_2 = 2\,H_2O.$$

Thus the molecular formula H_2O for water makes its appearance. The proof of this formula is contained in the preceding argument, which may be thus epitomized:

Hydrogen and chlorine gases consist of diatomic molecules, since the volume of hydrogen chloride they produce is twice the volume of either single gas.

Similarly, oxygen gas consists of diatomic molecules, since the volume of the steam is twice the volume of the oxygen it contains. The only formula for steam which agrees with the diatomicity of hydrogen and oxygen, as well as with the volumetric composition of steam, is H_2O. That the density of steam (H = 1) is 9 furnishes no additional evidence, since it is deducible from the densities of hydrogen and oxygen, and the volume of the steam. That the atomic weight of oxygen is 16 follows from the fact that its density is 16, and that, like hydrogen, it is diatomic. The argument would, however, be invalidated if it were shown that these gases are not diatomic, that in the molecules H_x and O_x, x is greater than 2. Underlying the whole of this argument is *Avogadro's hypothesis*, which is stated thus:

Equal volumes of all gases and vapours, under the same conditions of temperature and pressure, contain equal numbers of molecules.

But why *hypothesis*? This statement is not a law, any more than Dalton's atomic theory is a law. When first put forward it was properly regarded as a hypothesis, which, indeed, suffered much at the hands of its friends. Now, however, it is firmly established, and is of fundamental importance. It ought, therefore,

to be dignified with the name of *theory*. Henceforward we shall speak of *Avogadro's theory*.

It will be seen that this theory is in accord with Gay-Lussac's *law of volumes*, and satisfactorily explains the phenomena of the combination of gases. Thus, 1 volume of hydrogen combines with 1 volume of chlorine to form 2 volumes of hydrogen chloride, because 1 molecule of hydrogen reacts with 1 molecule of chlorine to form 2 molecules of hydrogen chloride. The language of volumes may be exchanged for the language of molecules; that is the significance of Avogadro's theory.

That equal volumes of different gases contain equal numbers of atoms is true only when the molecules of these gases contain equal numbers of atoms. It is a statement of limited truth, and of no permanent importance. The same may be said of the statement that the densities of elementary gases are in the same ratio as their atomic weights. The important fact is that *the densities of all gases are in the same ratio as their molecular weights*; and further, that since the molecular weight of hydrogen is 2, and its density, which is taken as the standard, is 1, therefore *the molecular weights of all gases are twice their densities*. Thus, the molecular weight of a gas or vapour is revealed by its density, as the following approximate figures show:

Elementary Gas or Vapour.	Density.	Molecular Weight.	Atomic Weight.	Molecular Formula.
Hydrogen	1	2	1	H_2
Oxygen	16	32	16	O_2
Nitrogen	14	28	14	N_2
Chlorine	35·5	71	35·5	Cl_2
Ozone	24	48	16	O_3
Phosphorus	62	124	31	P_4
Mercury	100	200	200	Hg
Sulphur	128	256	32	S_8

It may be remarked, incidentally, that the magnitude of the atomic weight of an element cannot be deduced from its gas or vapour density unless the number of atoms contained within the molecule of the element, i.e. its *atomicity*, is known independently. As a rule, however, the atomic weight of the element is known independently, and then the atomicity is deduced from the density.

The breadth of Avogadro's generalization was not realized in the time of its originator; and, owing to the persistence of the volume-atom theory of Gay-Lussac, and its unwarrantable extension by Berzelius,[1] there was much confusion on the subject until Cannizzaro, in 1858, reinstated Avogadro's theory on a permanent basis.

It should be added that Avogadro's theory applies strictly only to an ideal gas. When a gas deviates from Boyle's law it deviates to the same extent from Avogadro's theory.

A useful fact to remember in connection with gas densities is that a litre of hydrogen at 0° C and 760 mm. pressure, i.e. normal temperature and pressure (N.T.P.), weighs almost exactly 0·09 grm., or that 1 grm. measures 11·125 litres. Thus a gram-molecule (i.e. the molecular weight in grams) of hydrogen at N.T.P. measures 22·25 litres; and from Avogadro's theory it follows that the volume of a gram-molecule of any gas or vapour, reduced to normal temperature and pressure, is 22·25 litres. To determine the weight in grams of 22·25 litres of any gas or vapour, reduced to 0° and 760 mm., is therefore to discover its molecular weight

SUMMARY

AN ELEMENT is a substance which hitherto has not been resolved chemically into two or more dissimilar kinds of matter.

LAWS OF CHEMICAL COMBINATION.—1. *Law of definite or fixed proportions.*—The same chemical compound always contains the same elements united together in the same proportions; *or*, the proportions between the constituent elements of a chemical compound are always the same.

2. *Law of Multiple Proportions.*—When one element combines with another in more than one proportion, these proportions bear a simple ratio to one another.

3. *Law of Reciprocal Proportions.*—The proportions of two elements which separately combine with a fixed proportion of a third element are also the proportions of these elements which combine with each other, or else—in accordance with the law of multiple proportions—they bear a simple ratio to these proportions.

[1] The practice of referring all gaseous molecules to 2 volumes, which was a pernicious outcome of the theorizing of Berzelius, appears now, fortunately, to be dying out. Why, indeed, should every molecule be regarded as a microcosm of 2 volumes, as if it could necessarily be dichotomized?

THE ATOMIC THEORY. — 1. All matter consists of discrete particles called atoms, which remain unbroken throughout chemical change.

2. Atoms of the same element are ordinarily supposed to be similar in all respects.

3. Chemical compounds are formed by the union of the atoms of different elements in simple numerical proportions.

4. The proportions in which elements combine to form compounds are determined by the atomic weights of the elements.

GAY-LUSSAC'S LAW OF VOLUMES.—The volumes in which gases combine are simply related to each other, and to the volume of the compound gas which is formed.

Corollary.—The densities of the elementary gases are simply related to their combining weights.[1]

AVOGADRO'S THEORY.—Equal volumes of all gases and vapours under the same conditions of temperature and pressure contain equal numbers of molecules.

Corollary.—Since the molecule of hydrogen contains 2 atoms, the molecular weight of any gas or vapour is twice its density compared with that of hydrogen as unity.

A litre of hydrogen at N.T.P. weighs 0·09 grm., and 1 gram-molecule of hydrogen (2 grm.) measures 22·25 litres. It follows from Avogadro's theory that this is also the volume at N.T.P. of 1 gram-molecule of any gas or vapour.

AN ATOM of an element is the smallest particle of matter which takes part in a chemical change; it is the unit of chemical exchange.

A MOLECULE is the smallest particle of matter which exists independently; it is the physical unit. The molecule of an element contains similar, that of a compound dissimilar atoms.

The number of atoms contained within the molecule of an element is called the *atomicity* of the element.

[1]The term "combining weight" has sometimes signified equivalent weight, and sometimes atomic weight. Since the term is ambiguous, a use is found for it during the development of the molecular theory when non-committal language is employed. Afterwards the term should be dropped.

CHAPTER II

EQUIVALENT, ATOMIC, AND MOLECULAR WEIGHTS

1. Equivalent and Atomic Weights

It was shown in the last chapter that Dalton's "atomic weights" were really equivalent weights, and that the equivalent weight of an element, when not identical with its atomic weight, is a sub-multiple of the latter. Thus, whilst the equivalent weight of oxygen referred to that of hydrogen as unity is approximately 8, the atomic weight of this element, referred to the same standard, is approximately 16. In general

$$\text{Atomic weight} = n \times \text{equivalent weight},$$

where n is a small whole number, which indicates the *valency* of the element. Valency, or atomic value, is a new idea, necessary to connect together the ideas of atomic weight and equivalent weight. It will be more fully developed later.

It will now be useful to define equivalent and atomic weights.

EQUIVALENT WEIGHT.—**The equivalent weight of an element is that weight of it which combines with, or displaces from combination, unit weight of a standard element.**

ATOMIC WEIGHT.—**The atomic weight of an element is the ratio between the weight of its atom and that of the atom of a standard element.**

When these definitions are considered, it appears that the equivalent weight of an element is an experimental value, independent of theory, whilst the atomic weight is connected with the atomic theory.

It further appears that since equivalent and atomic weights are ratios, they are not really weights at all, nor masses, but pure numbers. That the atomic weight of an element is not the weight of one of its atoms appears plainly enough when it is considered that the standard of atomic weights has varied from time to time.

Further, since equivalent weights are values to be determined experimentally, their determination may well form the starting-point in the estimation of atomic weights. As a matter of fact the accuracy with which the atomic weight of an element is known depends as a rule on the accuracy with which the quantitative observation of some chemical transformation has been carried out, so as to determine its equivalent weight.

In some cases, however, atomic weights have been estimated accurately by the determination of gas density.

For determining equivalents, comparison between reacting quantities may be made by *combination* as well as by *displacement*, because an element combines with, as well as displaces, what is equivalent to itself. Thus, if there are two elements, A and B, the chemical equivalent of B referred to A as standard is found by estimating the amount of B which combines with a known weight of A, as well as by causing B to displace A, or A to displace B from combination with another element or group of elements.

When the equivalent weight of an element is known, it is necessary to determine the value of n in the above equation before the atomic weight can be fixed. What multiple of the equivalent weight the atomic weight may be, has to be decided by reference to one or more of several distinct principles, which lie chiefly in the domain of physical chemistry, and will shortly be discussed in detail.

Standard for Equivalent and Atomic Weights.

The question of a standard needs first to be considered; and, since hydrogen has the least atomic weight of all the elements, and as small an atomic value (valency) as any element, it is natural to choose hydrogen as the standard both of atomic and equivalent weights, and so to make its equivalent and its atomic weight both equal to 1.

Now, although hydrogen combines with non-metals, and a few metals, and is displaced from its combination in acids by some metals, its chemical activity is too limited to permit its use as a general standard of comparison. Oxygen, however, with very few exceptions, combines with all the elements, metals and non-metals alike; on this account it was called by Berzelius the "pole of chemistry". As a matter of practical experience, therefore, equivalent and atomic weights are more often estimated with

reference to oxygen than to hydrogen; the hydrogen equivalent may then be calculated from the oxygen equivalent by multiplying the latter by the equivalent weight of oxygen, and thence the corresponding atomic weight may be found.

Now, although Dalton (1808) chose hydrogen = 1 as the atomic weight standard, oxygen was soon adopted in preference, so that Wollaston (1814) used oxygen = 10, Thomson (1825) oxygen = 1, Berzelius (1830) oxygen = 100, and Stas (1860–5) oxygen = 16.

Until recently the two standards H = 1 and O = 16 were in use, but the latter is now the standard adopted by the International Union of Pure and Applied Chemistry. Although unity as the standard is sacrificed by this procedure, the O = 16 has at least two advantages over the H = 1 standard.

It was pointed out by Stas that the standard atomic weight should, as far as possible, be directly connected with the atomic weight to be determined, and this is the case when oxygen rather than hydrogen furnishes the standard. Otherwise the ratio H : O is involved in the calculation when the data are derived from the composition of an oxide; and whilst this ratio has been determined with great accuracy to be 1 : 15·88, any future modification of the ratio would involve the recalculation of all atomic weights dependent upon it. If, however, the ratio is written 1·008 : 16, the atomic weight of oxygen being fixed at 16, any future alteration will involve only the atomic weight of hydrogen. The advantage of this is plain.

Another advantage of the modern system is the fact that when O = 16 several other important atomic weights approximate very closely to whole numbers; e.g. C = 12·00, N = 14·01, Na = 22·997. The reason for this approximation will appear later when modern views of the atom are considered.

It is unlikely that any further modification of the standard will now be made, but an unfortunate confusion even now remains in the minds of those who have employed several standards. For example, the atomic weight of chlorine has been variously given as 35·37, 35·18, 35·46; and these differences are due not to different estimations of the atomic weight of this element but to the adoption of three different standards for oxygen, viz. O = 15·96 (Dumas), 15·88, and 16·00.

2. Determination of Equivalent Weights

The following are the more important methods ordinarily employed in the laboratory to determine the equivalent weights of elements.

i. The measurement of the volume of hydrogen displaced from dilute sulphuric or hydrochloric acid by a weighed amount of a metal.

ii. The conversion of a weighed quantity of a metal into its oxide which is weighed, or the reduction of a weighed quantity of oxide to metal.

iii. The displacement of a metal from a solution of one of its salts by a weighed quantity of a more chemically powerful metal.

iv. The separation of elements at the electrodes during the passage of an electric current through a series of electrolytes. This method yields the electro-chemical equivalent of an element: but this value is numerically identical with the chemical equivalent

i. The chemical equivalent of magnesium, zinc, or aluminium may be easily determined by dissolving a weighed quantity of the metal in the dilute acid contained in a piece of apparatus designed for collecting the evolved hydrogen. The gas is measured over water at atmospheric temperature and pressure; it will consequently be moist, and the pressure of water vapour at the observed temperature must be subtracted from the atmospheric pressure, before the volume of the gas is corrected to normal temperature and pressure

The weight of metal divided by the weight of the evolved hydrogen gives the hydrogen equivalent of the metal. This must be multiplied by 1·008 if the equivalent on the modern atomic weight basis is desired; though in view of the likely experimental error such a correction is superfluous.

The experiment may easily be carried out on the lecture-table or by students. The following result has been obtained by a student

Weight of magnesium taken	= 0·033 grm.
Volume of moist hydrogen measured at 12° C. and 756 mm.	= 32·6 c. c.
Pressure of water vapour at 12°	= 10·5 mm.
Volume of dry hydrogen at N.T.P.	$= \frac{32{\cdot}6 \times (756 - 10{\cdot}5) \times 273}{760 \times (273 + 12)}$
	= 30·6 c. c.
Weight of hydrogen	= 30·6 × 0·00009 = 0·00275
Equivalent of magnesium	$= \frac{0{\cdot}033}{0{\cdot}00275} = \underline{12{\cdot}0.}$

ii. Magnesium may be converted quantitatively into oxide by the ignition of the metal in the air under suitable conditions, or by dissolving it in dilute nitric acid, evaporating the solution, and igniting the nitrate until brown fumes cease to be evolved. These methods are not without sources of error, but it may be shown that 0·30 grm. of magnesium yields almost exactly 0·50 grm. of oxide, so that the equivalent weight of magnesium is

$$\frac{\cdot 3 \times 8}{\cdot 2} = 12.$$

The method of conversion into oxide through the nitrate is applicable to such metals as zinc and copper, which dissolve in nitric acid and yield stable oxides by the decomposition of their nitrates. The equivalent of tin may be determined by the conversion of the metal into hydrated dioxide by means of nitric acid, since the ignition of the product yields the pure dioxide.

It would be possible to determine the equivalent of carbon by burning a weighed quantity of the element in a stream of dry air or oxygen, and collecting and weighing the carbon dioxide formed; but the great difficulty of obtaining pure carbon free from hydrogen under ordinary conditions stands in the way of this determination.

For the determination of an equivalent by the reduction of an oxide to metal, copper furnishes the usual example, since the reduction is easily carried out by passing a stream of hydrogen over oxide of copper contained in a boat in a heated tube. Thus 1·00 grm. of black oxide of copper leaves a residue of 0·799 grm. of copper; whence the equivalent of copper in this oxide is

$$\frac{\cdot 799}{\cdot 201} \times 8 = 31 \cdot 8.$$

There is another oxide of copper, however, the red oxide, whose equivalent weight is $31 \cdot 8 \times 2 = 63 \cdot 6$. This fact is connected with the exhibition of a dual valency by copper, which again furnishes an example of the law of multiple proportions. This phenomenon will be further dealt with under the subject of valency.

iii. A well-known example of the displacement of a metal from the solution of one of its salts by another metal is the action of zinc upon a solution of copper sulphate, when the zinc is supposed to displace from combination its equivalent of copper which may be collected and weighed. This takes place almost quantitatively when a cold concentrated solution of copper sulphate is

employed; but the method is generally unreliable, because other reactions occur between the displacing metal and the solution simultaneously with the main reaction, and these vitiate the results. The method is not therefore to be recommended.

iv. When a suitable electric current is passed through acidified water contained in a "voltameter", hydrogen and oxygen are evolved in the proportion of two volumes of hydrogen to one volume of oxygen. Provided the densities of hydrogen and oxygen are known, and the conditions of temperature under which the gases were measured have been observed, the hydrogen equivalent of oxygen might be calculated from the volume relations

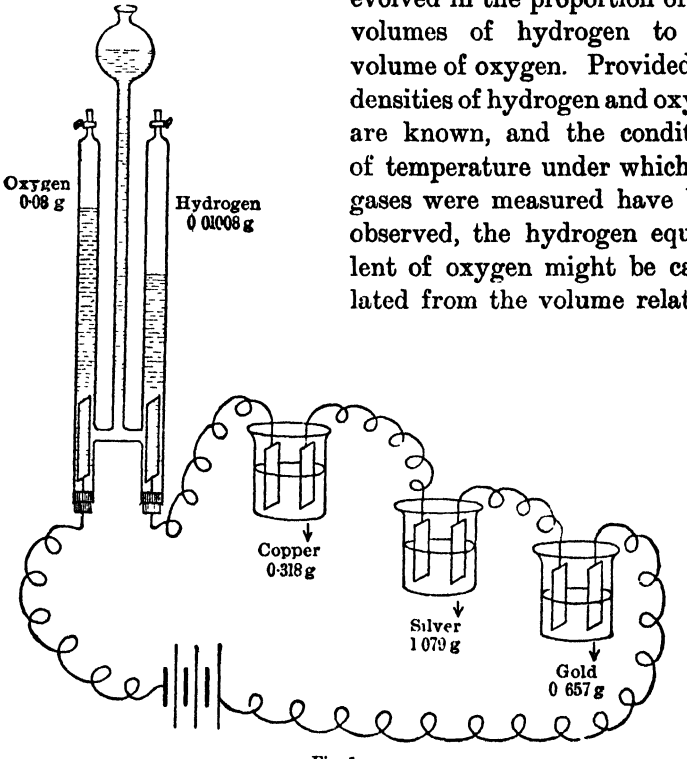


Fig 1

of the gases. The estimation would not, however, be very accurate, owing to several sources of experimental error.

If, however, the same current passes in succession through several salt solutions—for example, copper sulphate, silver nitrate, gold chloride solutions—it will liberate at the cathodes or negative electrodes amounts of the metals chemically equivalent to the hydrogen which is liberated in the voltameter. Thus, whilst 0·01008 grm. of hydrogen gas is being evolved, and 0·08 grm. of oxygen, 0·318 grm. of copper, 1·079 grm. of silver, and 0·657 grm.

of gold will be deposited in the successive electrolytic cells. The necessary arrangement is shown in fig. 1. Thus the equivalent weights of these metals are determined.

3. Determination of Atomic Weights

It has been suggested in the previous pages that two distinct considerations have to be taken into account in the problem of atomic weight determination. These are:

i. An exact estimation of the chemical equivalent of the element must be made, generally by carrying out some suitable chemical transformation, occasionally by other means.

ii. A decision must be arrived at as to the order of magnitude of the atomic weight, so as to discover the small whole number by which the equivalent weight must be multiplied to give the atomic weight.

The order in which the two parts of the problem are here placed is that which would naturally occur to the mind. Nevertheless it is not the order of historic sequence in relation to modern atomic weights. The approximate magnitude of the atomic weights of all the elements has long since been settled and is not discussed in modern research upon atomic weights; but the determination of the exact values of all these atomic weights is a laborious task which is not yet completed.

The methods for determining chemical equivalents which have been described above are suitable for demonstration purposes, but not all of them are equally useful in the actual determination of atomic weights. Illustrations of the methods that have been employed in accurate atomic-weight determinations will be given in the sequel.

The principles which have led to decisions upon the order of magnitude of the atomic weights of the elements will now be dealt with.

It has already been seen that Dalton was in need of some guiding principle to enable him to fix the magnitude of his atomic weights; and that such a principle came to light in the discovery by Gay-Lussac of the law of gaseous volumes, and the proper interpretation of this law by Avogadro. Thus, by means of Avogadro's theory it was shown that the atomic weight of oxygen is very probably 16 and not 8; but clearly this theory is limited in

its application, since it can only be of use in the case of gaseous or gasifiable substances. Here may be mentioned the method of *chemical displacement*, which is of some value in deciding the magnitude of atomic weights.

In 1819 two other and quite distinct principles became available in the *law of specific heats* of Dulong and Petit, and the *law of isomorphism* discovered by Mitscherlich. These laws are especially valuable in furnishing guidance as to the magnitude of atomic weights, because they are applicable to solid elements and their solid compounds.

The former of these two laws is the more important, and has the wider application. Finally, the *periodic law*, established by Mendeléeff in 1869, has been of distinct value in several ways in fixing the approximate magnitude of atomic weights.

So the five guiding principles that aid in settling the order of magnitude of atomic weights are:

i. Avogadro's theory.
ii. Chemical displacement.
iii. Dulong and Petit's law of specific heats.
iv. Mitscherlich's law of isomorphism.
v. Mendeléeff's periodic law.

i. The Method of Avogadro's Theory.

It will be remembered that according to Avogadro's theory the molecular weights, not the atomic weights, of gases and vapours are proportional to their densities. It follows, therefore, that the relative magnitudes of molecular weights, and not of atomic weights, are directly deducible from Avogadro's theory. So the question arises how far a knowledge of the relative weights of molecules can be of use in fixing the relative weights of any of their constituent atoms. Such knowledge may be employed in two ways.

Consider the following volatile hydrocarbons:

	Methane.	Ethylene.	Propane.	Benzene.	Naphthalene.
Approximate Density (O = 16)	8	14	22	39	64
Approximate Molecular Weight	16	28	44	78	128
Molecular Proportion of Carbon	12	24	36	72	120

Approximate estimations of gas or vapour density yield approximate molecular weights; whilst quantitative analysis shows the proportion of carbon within the molecular proportion of each compound. Now, it is evident that all these hydrocarbons, except the first, contain more than 1 atom of carbon in their molecules. The molecule of methane might indeed contain more than 1 atom, though the fact than no submultiple of 12 appears in the proportions of carbon in the other molecules is evidence, so far as it goes, that the figure 12 represents an indivisible unit, or in other words that 12 is approximately the atomic weight of carbon. And since by the examination of the very large number of hydrocarbons that exist, every molecular proportion has been found to contain 12, or a multiple of 12 parts of carbon, the probability that 12 is the atomic weight of carbon reaches a practical certainty.

The principle thus illustrated may be put in the following words:

The least proportion of an element found within the molecular proportion of any of its volatile compounds is likely to be the atomic weight of the element; and if the number of compounds which have been examined is large, the value indicated is very probably the atomic weight.

The question may be asked, however, whether atomic weights can be determined exactly by the method of Avogadro's theory, i.e. by the determination of gas density, and the answer is in the affirmative, provided an *ideal* gas density can be determined and the molecular composition of the gas is known.

The density of a gas is determined by weighing a large glass globe of about 10 litres capacity, first evacuated, and then filled with the gas, at known temperature and pressure, corrections being applied for the air displaced by the globe, and for the slight shrinkage which the glass undergoes when the globe is evacuated. Thus it has been found, as the mean result of the experiments of Rayleigh, Morley, and Leduc, that 1 litre of oxygen at 0° and 760 mm. at the latitude of Paris weighs 1·42895 grm., whilst 1 litre of hydrogen, under similar conditions, according to the experiments of Morley and Leduc, weighs 0·08985 grm.

To conclude, however, that the atomic weights of oxygen and hydrogen are in the ratio $\frac{1{\cdot}42895}{0{\cdot}08985}$, although we know that the molecules of both gases are diatomic, would be erroneous, because it would be to assume that the gases are ideal gases which behave in perfect accord with the gas laws (q.v.), and so with Avogadro's

theory. Such, however, is not the case, and the deviation of these gases from the ideal must be discovered, and allowed for. This may best be done, in the present case, by determining the effect of the deviation upon the volume relations in which oxygen and hydrogen combine to form water.

Now it has been estimated that 2·00268 litres of hydrogen combine with 1 litre of oxygen, at 0° and 760 mm. at the latitude of Paris. This complex ratio is due, not to any discrepancy between the simple proportions in which the molecules of these two gases interact, but to the fact that equal volumes do not contain quite equal numbers of molecules because oxygen is a little more compressible than hydrogen. But since the densities relate to equal volumes it may be concluded that

$$2{\cdot}00268 \times 0{\cdot}08985 \text{ grm.}$$

of hydrogen combine with 1·42895 grm. of oxygen, and therefore that the hydrogen equivalent of oxygen is

$$\frac{1{\cdot}42895}{2{\cdot}00268 \times 0{\cdot}08985} = 7{\cdot}9412;$$

and its atomic weight 15·88 when H = 1; so that H = 1·0076 when O = 16. A similar method may be applied to determine the atomic weight of a constituent element of a compound gas. Thus, by the calculation of the ideal densities of carbon monoxide, carbon dioxide, methane, and acetylene, by applying a correction for compressibility to the estimated densities, several observers have accurately determined the molecular weights of these gases, and thence the atomic weight of carbon.

Methods of Determining Vapour Density.

The determination of gas density always consists in weighing a certain volume of the gas; but for determining the vapour density of a volatile liquid or solid, an alternative procedure may be adopted: the volume of the vapour produced by a weighed quantity of the liquid or solid may be measured under known conditions.

There are three well-recognized methods of vapour density determination: the methods of *Dumas*, *Hofmann*, and *Victor Meyer*. In the first of these three methods the weight of a known volume of the vapour is ascertained; in the two latter the volume of a weighed quantity of the substance is measured. The method of Victor Meyer is the easiest and most often employed.

(*a*) *Dumas's Method of Vapour-density Determination*

A glass globe of the shape shown in fig. 2, and capable of holding from 50 to 100 c. c. or more, is weighed, and then filled with the vapour of the substance in the following manner.

A few cubic centimetres of the liquid are introduced into the globe, which is then immersed in a bath of another liquid whose temperature is kept constant, and from 20° to 30° above the boiling-point of the liquid in the globe. As the latter liquid boils it displaces the air from the globe, and vapour issues from the neck as long as any liquid remains within the globe. When the stream of vapour ceases, the globe is filled with the vapour at atmospheric pressure, and at the temperature of the bath in which it is immersed. The neck is then sealed by means of a blowpipe; and the temperature of the bath. and the pressure of the atmosphere at the time of sealing are recorded. After being cleansed, the sealed globe is weighed, and the temperature and pressure of the air in the vicinity of the balance are also observed.

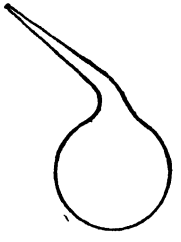


Fig 2

Since the true weight of the sealed globe with its contents is equal to its apparent weight plus the weight of the air which it displaces whilst it is being weighed, the weight of this air must be calculated and added to the apparent weight. For this calculation, as well as to ascertain the volume of the vapour at the time of sealing, the cubical capacity of the globe must be determined. This is done by breaking off the end of the neck of the globe under water, which should then enter and fill the globe. The quantity of water in the globe is determined by another weighing, the weight of the air displaced being in this case negligible; then the weight of the water in grams shows the volume of the globe in cubic centimetres with sufficient accuracy.

From these data the weight of the known volume of the vapour contained by the globe at the temperature and pressure at which it was sealed is calculated. The volume is then reduced to N.T.P., and the weight of hydrogen or air corresponding to it is calculated. The ratio of the weight of the vapour to that of the hydrogen is the vapour density of the substance.

EXAMPLE.—Calculate the density of ether vapour from the following data:

Weight of open globe in air	= 22·549 grm.
Temperature of bath at time of sealing	= 60° C.
Atmospheric pressure at times of sealing and weighing	= 760 mm.
Apparent weight of sealed globe + vapour in air	= 22·662 grm.
Temperature of air at time of weighing	= 15°
Capacity of globe, indicated by weight of water it can contain	= 75 c. c.
Weight of 1 c. c. of air at 0° C. and 760 mm.	= 0·001293 grm.
Weight of 1 c. c. of hydrogen at 0° C. and 760 mm.	= 0·0000899 grm.

Calculation

Weight of air displaced when sealed globe is weighed

$$= \frac{0{\cdot}001293 \times 75 \times 273}{288} = 0{\cdot}092 \text{ grm.}$$

Weight of vapour in globe $= 22{\cdot}662 + 0{\cdot}092 - 22{\cdot}549 = 0{\cdot}205$ grm.

Weight of an equal volume of hydrogen at 60°C. and 760 mm.

$$= \frac{0{\cdot}0000899 \times 75 \times 273}{333} = 0{\cdot}00553 \text{ grm.}$$

So density of ether $((C_2H_5)_2O)$ vapour $= \frac{0{\cdot}205}{0{\cdot}00553} = \underline{37{\cdot}1}.$

(*b*) *Hofmann's Method of Vapour-density Determination*

A weighed quantity (about 0·05 grm.) of the liquid contained in a small, drawn-out bulb or stoppered bottle is introduced into the Toricellian vacuum of a graduated barometer tube surrounded by the vapour of a liquid boiling at a suitable temperature, which may be below the boiling-point of the liquid whose vapour density is being determined. As the liquid is vaporized it depresses the mercury in the barometer tube; and when the volume has become constant it is read off, and the temperature of the vapour jacket is observed. The pressure of the vapour is equal to atmospheric pressure less the height of the mercury in the tube above its level in the vessel in which the tube stands. Strictly speaking, the height of

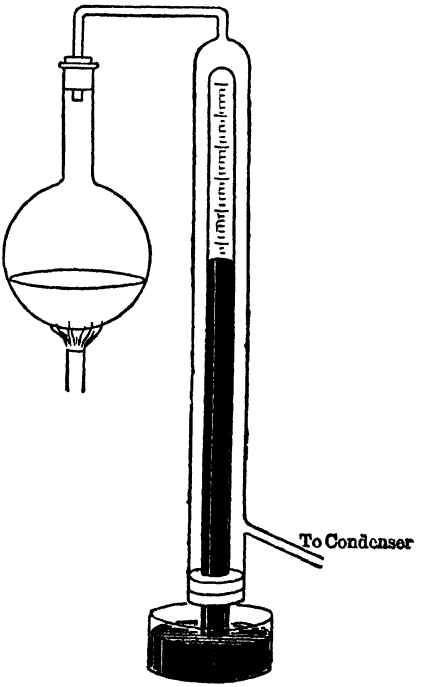


Fig. 3

the mercury column should be corrected for expansion by heat; but this need not be considered. From these data the vapour density of the liquid can be calculated; as the following example shows:

Weight of stannic chloride (B.P. 114°)[1] taken	= 0·0445 grm.
Volume of vapour	= 16·2 c. c.
Temperature of vapour jacket	= 99°
Barometric pressure	= 752 mm.
Height of mercury column	= 512 mm.
Whence pressure of vapour	= 240 mm.
Volume of vapour reduced to N.T.P.	$= \frac{16 \cdot 2 \times 273 \times 240}{372 \times 760} = 3 \cdot 75$ c. c.
Weight of 3·75 c.c. of hydrogen at N.T.P.	= 3·75 × 0·00009 grm.
	= 0·0003375 grm.
Vapour density of stannic chloride ($SnCl_4$)	$= \frac{0 \cdot 0445}{0 \cdot 0003375} = \underline{131 \cdot 8}$.

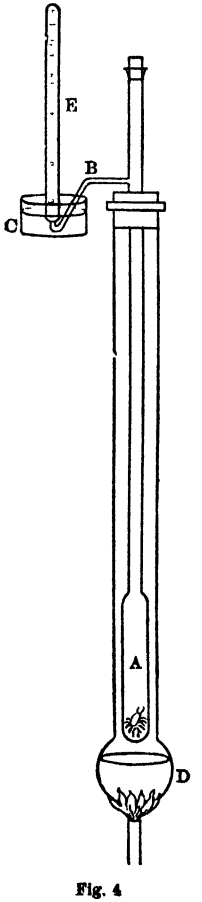


Fig. 4

(c) *Victor Meyer's Method of Vapour-density Determination*

In this method a weighed quantity of the substance is made to evaporate into a space surrounded with the vapour of a boiling liquid whose boiling-point is at least 25° higher than that of the substance. The volume of the vapour is not directly measured, but the air displaced by it is collected and measured at atmospheric temperature and pressure; while all the displacing vapour remains in the locality of its production. The weight of an equal volume of hydrogen is then calculated, and the weight of substance taken divided by this weight of hydrogen gives the vapour density of the substance, since the vapour of the substance, if it could be obtained at atmospheric temperature and pressure without condensation, would occupy the same volume as the air. The tube A (fig. 4) is closed at the lower end, and is furnished with a bent delivery tube B which dips under water in the dish C. The upper end of A is closed by a rubber stopper. The lower part of the tube is heated by the vapour of a liquid, e.g. water, boiling in the outer jacket D, and, owing to expansion, air escapes by the side

[1] Since the compound is vaporized into a vacuum the temperature of its vapour may be lower than the B.P. of the compound.

tube through the water. When no more bubbles of air are seen, the graduated tube E is placed over the end of B, and a little tube or loosely-stoppered bottle, containing a weighed quantity of the substance under investigation, is dropped to the bottom of A, being received on a pad of asbestos or glass wool, which prevents fracture. For the introduction of the little vessel containing the substance the rubber stopper is removed, and quickly replaced, or the vessel may be held by a mechanical contrivance at the top of the tube A, where the air is nearly cold,[1] and then allowed to fall at the right moment, without opening the tube.

EXAMPLE.—0·144 grm. of chloroform displaced 28·6 cu. cm. of moist air measured at 14° and 756 mm. pressure. Pressure of water vapour at 14° = 12 mm.

$$\text{Vol. of air at N.T.P.} = \frac{28{\cdot}6 \times 273 \times (756 - 12)}{287 \times 760} = 26{\cdot}6 \text{ c. c.}$$

$$\text{Weight of an equal vol. of hydrogen} = 26{\cdot}6 \times 0{\cdot}0000899 \text{ grm.} = 0{\cdot}00239 \text{ grm.}$$

$$\text{Vapour density of chloroform } CHCl_3 = \frac{0{\cdot}144}{0{\cdot}00239} = \underline{60{\cdot}3.}$$

The method of Victor Meyer is more easily carried out than either of the other methods. It employs very little of the substance and is sufficiently accurate for most purposes. Consequently, it is the method usually employed.

[1] It might be supposed that since the air is colder in the upper part of the tube, which extends beyond the vapour jacket, than in the lower part, which is within it, too much air will be displaced, and a high result obtained. This, however, is not the case, because of the contraction of the air that rises in the body of the tube to take the place of the air driven out. The following proof of this statement has been given by Dr. E. B. R. Prideaux.

First, suppose temperature constant in the V. Meyer tube, so that the heated vapour immediately displaces its own volume of heated air, which is then cooled. Let T = abs. temperature of vapour and air when first expelled, and T_0 abs. temperature of cooled air leaving the end of delivery tube under water; let V = vol. of vapour formed and therefore of air expelled, and V_0 vol. of air collected. Then $V_0 = \frac{T_0 V}{T}$.

Second, let there be two temperatures T and T_1 within the tube, with corresponding volumes of equal masses of air V and V_1.

Then let V be expelled into the T_1 region, and thereby become V_1, so that $V_1 = \frac{T_1 V}{T}$. V_1, not V, will now displace its own volume of air, which will be cooled so as to become, say, V_2 at the end of the delivery tube. Then $V_2 = \frac{T_0 V_1}{T_1} = \frac{T_0 T_1 V}{T_1 T} = \frac{T_0 V}{T} = V_0$; and similarly with any number of temperature zones.

Thus a temperature gradient within the V. Meyer tube does not affect the volume of air displaced from the end of the delivery tube.

ii. The Method of Chemical Displacement.

Somewhat related to the above principle is another by which the molecular formula of a compound may be determined, and so the atomic weight of a constituent element.

Consider methane. The hydrogen in this compound can be displaced by chlorine in four distinct stages, the following substitution products being formed: methyl chloride, methylene chloride, chloroform, and carbon tetrachloride. The carbon, however, cannot be displaced fractionally. From these facts the inference is drawn that the molecule of methane contains 4 atoms of hydrogen and only 1 atom of carbon; but if methane is CH_4, Dalton's problem of the number of atoms in the molecule is solved, and the atomic weight of carbon is 12.

A similar argument may be applied to water. The composition of sodium hydroxide proves that half the hydrogen of the water molecule has been displaced by sodium. By no means, however, can any fraction of the oxygen of the water molecule be displaced. Thence it is concluded that water is H_2O, and that the atomic weight of oxygen is 16.

The principle of this method of fixing the magnitude of atomic weights may be stated thus:

When $\frac{1}{n}$th of the proportion of a constituent element in a chemical compound can be displaced by another element, a molecule of the compound contains at least n atoms of that element.

iii. The Method of Dulong and Petit's Law.

The specific heat of a substance is the ratio of the amount of heat required to raise unit weight of it through one degree of temperature to the amount of heat required to raise unit weight of a standard substance through the same temperature interval. The standard substance is water.

In 1819 Dulong and Petit published the specific heats of thirteen elements, and showed that the product of specific heat into atomic weight is approximately a constant quantity, the average of which, on our modern atomic weight basis, is 6·4. In the following table, containing the elements studied by Dulong and Petit, modern values are given throughout.

Element.	Specific Heat.	Atomic Weight.	Atomic Weight × Specific Heat = Atomic Heat.
Bismuth	0·0305	208·0	6·34
Lead	0·0315	207·2	6·53
Gold	0·03035	197·2	5·99
Platinum	0·03147	195·2	6·14
Tin	0·0559	119·0	6·65
Silver	0·0559	107·88	6·03
Zinc	0·0939	65·37	6·14
Tellurium	0·0475	127·5	6·06
Copper...	0·09232	63·57	5·81
Nickel	0·10842	58·68	6·16
Iron	0·10983	55·84	6·13
Cobalt	0·10303	58·97	6·08
Sulphur	0·1712	32·07	5·49

The *law of Dulong and Petit* may therefore be stated thus:

The specific heats of the solid elements are in the inverse ratio of their atomic weights.

The product of specific heat and atomic weight, which is approximately a constant, is called the *atomic heat* because it is the heat capacity of a quantity of an element proportional to its atomic weight. Thus, for example, 55·84 parts by weight of iron require the same amount of heat to raise them through one degree of temperature as, say, 208·0 parts of bismuth. But these quantities of the elements contain equal numbers of atoms. So, in the words of Dulong and Petit, "the atoms of all substances have exactly the same capacity for heat".

In order to reach this result, however, Dulong and Petit made some drastic changes in the accepted atomic weight values, which aroused the opposition of Berzelius, their author. Thus, taking the atomic weight of sulphur as a true magnitude, they halved the atomic weights of the metals in relation thereto. This procedure was, however, justified, even in the opinion of Berzelius, after Mitscherlich, his pupil, had arrived at similar conclusions by an application of the law of isomorphism.

Now, since

$$\text{Specific heat} \times \text{atomic weight} = 6{\cdot}4 \text{ (approx.)}$$

or

$$\text{atomic weight} = \frac{6{\cdot}4}{\text{specific heat}} \text{ (approx.)},$$

here is a valuable method for fixing the magnitude of the atomic

weight of an element. All that it is necessary to do is to determine the specific heat of the element, and divide 6·4 by this value.

It must be clearly understood, however, that the value thus obtained is only approximate, for the atomic heat value, 6·4, is only approximate, since it is a mean value, even if the specific heat is accurately known. The method serves to indicate what multiple of an accurately determined equivalent weight is the atomic weight. To divide 6·4 by the given specific heat of an element, and report the quotient as its atomic weight, is a gross error.

The following illustration will make plain the use of Dulong and Petit's law: Marignac[1] found that 100 grm. of lead yielded 134·201 grm. of the chloride. The specific heat of the metal is 0·0315; find its atomic weight; Cl = 35·46.

The equivalent weight of lead is found from the proportion:

Wt. of chlorine : wt. of lead :: equivalent Cl : equivalent Pb,
so 34·201 : 100 :: 35·46 : 103·68.

The approximate atomic weight of lead. as indicated by its specific heat, is: $\frac{6 \cdot 4}{0 \cdot 0315} = 203 \cdot 2.$

Therefore the atomic weight of lead is twice its equivalent weight;

so $\underline{\text{Pb}} = 103 \cdot 68 \times 2 = \underline{207 \cdot 36}.$

Dulong and Petit's law applies strictly only to solid elements, generally metals, whose atomic weights exceed 30. The specific heats of other solid elements vary with temperature, but become approximately constant at high temperatures, when they give an atomic heat value of about 5·5.

iv. The Method of the Law of Isomorphism.

Isomorphism is similarity of crystalline form. It was supposed by the earlier mineralogists that identity of crystalline form generally indicated identity of chemical composition; but it was shown by Mitscherlich in 1819 that compounds of analogous as well as identical composition crystallize in similar forms belonging to the same crystal systems. Thus di-sodium hydrogen phosphate and di-sodium hydrogen arsenate, which are now represented by the formulæ $Na_2HPO_4 \cdot 12H_2O$ and $Na_2HAsO_4 \cdot 12H_2O$, were found to be isomorphous. Careful measurements of the crystal angles of isomorphous salts show that these angles are not quite equal

[1] Marignac, *Œuvres Complètes*, 1846, I, 186.

but the following criteria of isomorphism have been established: (i) great similarity of crystalline form, (ii) analogous composition, (iii) power to form mixed crystals by simultaneous crystallization, (iv) power of crystal overgrowth, so that a crystal of one compound may form the matrix on which the growth of the crystal may be continued by the deposition of another substance.

With regard to the second criterion, it must be noted that isomorphism is sometimes observed in pairs of compounds which are not chemically analogous, but have the same numbers of atoms within their molecules. Thus calc-spar ($CaCO_3$) is isomorphous with Chili saltpetre ($NaNO_3$), and aragonite ($CaCO_3$) with nitre (KNO_3).

Mitscherlich stated the *law of isomorphism* as follows:

"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."

Nevertheless isomorphism such as that illustrated by the case of sodium phosphate and arsenate is the rule; that is to say, not only do the molecules of isomorphous compounds contain the same number of atoms similarly combined, but these atoms themselves are analogous, as, for instance, are phosphorus and arsenic. Indeed, isomorphism is taken to be a sign of chemical analogy.

Therefore, for practical purposes, the *law of isomorphism* may be stated more briefly:

The molecules of isomorphous substances contain equal numbers of atoms, which when not of identical are of analogous elements.

The consequence of this law, when applied to the case already mentioned, is that the atomic weights of phosphorus and arsenic can be directly compared, and if one atomic weight is known the other is derivable from the results of chemical analysis.

A simple numerical example is furnished by the following results of the analysis of the isomorphous salts potassium sulphate and potassium selenate, carried out by Mitscherlich:

K_2SO_4		K_2SeO_4	
100 parts contain		100 parts contain	127·01 parts contain
K	44·83	K 35·29	44·83
O	36·78	O 28·96	36·78
S	18·39	Se 35·75	45·40
	100·00	100·00	127·01

In the third column is shown the proportion of selenium in an amount of the selenate which contains the same amounts of potassium and oxygen as are shown in the percentage analysis of the sulphate. Whence it follows that 45·40 parts of selenium take the place of 18·39 parts of sulphur.

Now, the law of isomorphism declares that the ratio between these quantities is the ratio between the atomic weights of the two elements. Therefore, if the atomic weight of sulphur is 32·0 that of selenium is $\frac{32{\cdot}0 \times 45{\cdot}40}{18{\cdot}39} = \underline{79{\cdot}0.}$

The phenomena of isomorphism are somewhat confused by those of *dimorphism* and *polymorphism*. Thus calcium carbonate, as shown above, is *dimorphous* in calc-spar and aragonite; ammonium nitrate, NH_4NO_3, is *tetramorphous*, crystallizing in four distinct forms; arsenious and antimonious oxides, As_4O_6 and Sb_4O_6 are *isodimorphous*, that is to say, they are both similarly dimorphous.

Nevertheless, the phenomena of isomorphism have been of value, not only in confirming atomic-weight magnitudes derived from other considerations, but in correcting erroneous magnitudes.

For example, previous to the recognition of isomorphism, Berzelius regarded various metallic monoxides MO as dioxides MO_2; similarly, Fe_2O_3 was written FeO_3, Cr_2O_3 was CrO_3, and CrO_3 was CrO_6. But when this chemist recognized the isomorphism of chromates with sulphates he altered CrO_6 to CrO_3 to agree with SO_3, the oxide known to be present in sulphates. Consequently, the former CrO_3 became Cr_2O_3; and since chromic and ferric alums were isomorphous, what was formerly FeO_3 became Fe_2O_3, and so FeO_2 became FeO. But compounds of copper, nickel, cobalt, manganese, zinc, and magnesium are isomorphous with corresponding iron compounds, and so if FeO_2 should be FeO the corresponding dioxides of all these metals should really be monoxides.

This sweeping change would involve the halving of a number of accepted atomic weights; nevertheless, the change was made by Berzelius in accordance with the principles of isomorphism; and it was at once ratified by the law of specific heat, which required the same atomic weight magnitudes for the elements concerned.

The alums which conform to the general formula

$$M_2SO_4 \cdot X_2(SO_4)_3 \cdot 24\,H_2O$$

are amongst the best-known isomorphous compounds; and the

atomic weight of the element X can be determined by an analysis of its alum. For this purpose it is best to ignite the ammonium alum, which leaves a residue of the oxide X_2O_3.

Thus, if a grm. of the alum leaves b grm. of oxide, the value of X is calculated from the expression:

$$a : b = (NH_4)_2SO_4 \cdot X_2(SO_4)_3 \cdot 24\,H_2O : X_2O_3$$
$$= [132 + 2\,X + 288 + 432] : [2\,X + 48].$$

By this means Lecoq de Boisbaudran, who discovered gallium, found that 3·1044 grm. of its ammonium alum left on ignition a residue of 0·5885 grm. of the sesquioxide; whence Ga = 70·1.

v. The Method of the Periodic Law.

An adequate account of the periodic law is necessary to an appreciation of its value as a guide to the magnitudes of the atomic weights of the elements; but this must be deferred to a later chapter.

It will be sufficient to state here that a natural connection exists between the properties of an element and its atomic weight, and therefore that the order of magnitude of the atomic weight of an element may be judged from a study of the properties of the element and its compounds. Examples of this use of the periodic law will be given later.

The application of the foregoing methods of atomic-weight determination is well illustrated by the case of carbon.

4. The Atomic Weight of Carbon

The determination of the atomic weight of carbon has consisted of two parts:

i. The determination of the order of magnitude.

ii. The determination of the exact value.

i. Determination of the Order of Magnitude of the Atomic Weight.

Dalton and his contemporaries attributed the value 6 to the atomic weight of carbon, but this was really only an equivalent weight. The following is the evidence that the atomic weight is about 12:

(*a*) *Avogadro's Theory.*—Never fewer than 12 parts by weight of carbon are present in a molecular proportion of any of the gaseous or volatile compounds of this element.

(*b*) *Chemical Displacement.*—Use might be made of the argu-

ment that, for example, hydrogen is displaceable from methane in four equal fractions, but carbon not fractionally; whence it follows that the formula for methane is CH_4 and the atomic weight of carbon 12.

(*c*) *The Law of Specific Heat.*—Although Dulong and Petit's law does not apply strictly to an element whose atomic weight is less than 30, and the specific heats of diamond and graphite differ widely from each other at ordinary temperatures, at 600° the specific heats of these two allotropic forms of carbon, which vary with temperature, become almost constant and equal, and give an atomic heat of 5·5, if C = 12, a value which is comparable with the atomic heats of analogous elements.

(*d*) *The Law of Isomorphism.*—The iodides of carbon and silicon are isomorphous; therefore they are similarly composed, and the atomic weights of carbon and silicon are in the ratio 12 : 28.

(*e*) *The Periodic Law.*—With an atomic weight of 12, carbon is appropriately placed in the periodic table between boron (10·82) and nitrogen (14·01); and is thus the first or "typical" element of the fourth group. If carbon forfeited its place owing to an alteration in the magnitude of its atomic weight, there is no vacant place in the periodic table which this element could fill, nor is any element known which could occupy the place of carbon.

ii. Determination of the Exact Value of the Atomic Weight.

There are two ways in which the atomic weight of carbon has been determined exactly:

(*a*) By estimating the densities of its gaseous compounds.

(*b*) By the combustion of carbon or the analysis of its compounds.

(*a*) It has already been pointed out that gas or vapour density is simply related to molecular weight only when Avogadro's theory is rigidly true. This, however, is never the case; but an "ideal" density can sometimes be calculated from carefully ascertained data. This has been done[1] for the three gases: carbon monoxide (CO), carbon dioxide (CO_2), and acetylene (C_2H_2).

	CO	CO_2	C_2H_2
Experimental density (O_2 = 1)	0·87495	1·38324	0·8194
"Ideal" density	0·87516	1·37516	0·81331
Molecular weight	28·005	44·005	26·026
Atomic weight of carbon ...	12·005	12·005	12·005

[1] Leduc, *Ann. Chem. Phys.*, 1898 [vii.], *15*, 5; 1910 [viii.], *19*, 441.

It appears from these figures that the method leaves nothing to be desired from the point of view of accuracy.

(*b*) The atomic weight of carbon has been determined by several chemists by burning diamond or carefully purified graphite, weighing the carbon dioxide produced, and then calculating the result from the proportion:

Weight of CO_2 : weight of C :: 32 + atomic weight C : atomic weight C.

The following are the results, as originally given, and as corrected by Scott:

	Uncorrected.	Corrected by Scott.[6]
Dumas and Stas[1]	11·9975	11·9938
Erdmann and Marchand[2]	12·0093	12·0054
Roscoe[3]	12·0029	11·9973
Friedel[4]	12·0112	12·0056
Van der Plaats[5]	12·0031	12·0017

The ignition of organic silver salts, such as the acetate and tartrate, which leave a residue of pure silver, serves as a means of estimating the atomic weight of carbon; or the silver may be estimated electrolytically, as was done by Hardin,[7] with the following results, obtained with silver acetate and benzoate respectively:

(1) $C_2H_3O_2Ag : Ag = 100 : 64·637$
whence atomic weight of carbon = 12·000.

(2) $C_7H_5O_2Ag : Ag = 100 : 47·125$
whence atomic weight of carbon = 12·001.

[Ag = 107·880, H = 1·00762, O = 16·00.]

The above results are selected from amongst others as typical; they serve to show the degree of accuracy which has been attained in the determination of the atomic weight of carbon. This value lies between 12·000 and 12·005, and may be taken to be 12·003.

5. Determination of Molecular Weights (in Solution)

The establishment of molecular weights by the determination of gas and vapour densities has been fully considered in the preceding pages. By the study, however, of the influence of dissolved

[1] Dumas, *Pogg. Annalen*, 1838, *44*, 110.
[2] Erdmann and Marchand, *J. prakt. Chem.*, 1841, *23*, 159.
[3] Roscoe, *Compt. rend.*, 1882, *94*, 1180.
[4] Friedel, *Bull. Soc. Chim.*, 1884 [ii.], *41*, 100.
[5] Van der Plaats, *Compt. rend.*, 1885, *100*, 52.
[6] Scott, *Trans. Chem. Soc.*, 1897, *71*, 550.
[7] Hardin, J., *Amer. Chem. Soc.*, 1896, *18*, 990.

substances on the solidifying- and boiling-points of liquids, the molecular weights of substances in solution in these liquids may be determined; and it will be appropriate to consider here these newer methods of molecular-weight determination.

It is well known that salt water freezes at a lower temperature than fresh water, and that sea ice when melted yields fresh water. Thus, when a dilute solution of salt in water is cooled, crystals of pure ice begin to separate from the solution at a temperature a little below 0°. Blagden, in 1788, showed that the depression of the freezing-point of water by a dissolved salt is directly proportional to the amount of salt present. The boiling-point of water, on the other hand, is raised by salt in solution, and the elevation of boiling-point is directly proportional to the amount of salt dissolved. In 1883–4 F. M. Raoult discovered that not only are the depression of freezing-point and rise of boiling-point of a solvent proportional to the number of molecules of a particular substance in solution, but that equimolecular proportions of different substances have the same influence on the freezing- and boiling-points.

Raoult's law, which applies equally to freezing- and to boiling-points of solvents, may be stated thus:

The depression of freezing-point and elevation of boiling-point of a solvent by a quantity of dissolved substance are directly proportional to the number of molecules of the substance in solution, and consequently inversely proportional to its molecular weight.

Or, otherwise:

Equimolecular solutions, with the same solvent, have the same freezing- and boiling-points.

Evidently these facts provide a means of comparing molecular weights, or of determining them if a substance of known molecular weight is chosen as a standard of comparison. It should be added that the extent to which a freezing- or boiling-point is affected depends also upon the solvent; consequently the first procedure is to determine the *freezing-* or *boiling-constant* (K) for a particular solvent by the use of a substance of known molecular weight. This constant is the number of degrees the freezing-point is lowered or boiling-point raised by 1 grm.-molecule of the substance dissolved in 100 grm. of the solvent.

For instance, 2 grm. of cane sugar dissolved in 100 grm. of water cause a depression of the freezing-point, $\Delta = 0{\cdot}11°$. Since

the molecular weight of cane sugar ($C_{12}H_{22}O_{11}$) is 342, the freezing-constant, K, for water, sometimes called the *molecular depression*, is

$$\frac{0{\cdot}11 \times 342}{2} = 19.$$

The same quantity of sugar dissolved in the same amount of water raises the boiling-point of the water 0·030°. Therefore the boiling-constant or *molecular elevation*, K, for water is:

$$\frac{0{\cdot}030 \times 342}{2} = 5{\cdot}2.$$

When the freezing- or boiling-constant K for a solvent is known, an unknown molecular weight is calculated from observed data as follows:

Let K = depression or rise caused by 1 grm.-mol. of a substance in 100 grm. of solvent (known constant).
„ S = weight of substance taken.
„ L = weight of solvent taken.
„ Δ = observed depression or rise.
„ M = required molecular weight.

Then, since the observed depression of freezing-point or rise of boiling-point is directly proportional to the amount of substance taken, and inversely proportional to the amount of solvent,

$$\Delta = \frac{K \times S \times 100}{M \times L} \quad \text{or} \quad M = \frac{100\ KS}{\Delta L}.$$

Practical Methods.

The prime necessity for the experimental determination of molecular weights of substances in solution is a thermometer which will indicate accurately hundredths of a degree. If this thermometer is to be used both for freezing- and boiling-points, it would appear necessary for it to have a long range in addition. Real temperatures, however, have not to be read; only temperature differences. Consequently a thermometer has been devised by Beckmann with a range of about six degrees, the scale being divided into hundredths of a degree, and furnished with a reservoir of mercury from which mercury can be added if low temperatures are to be recorded, and into which mercury can be driven when the instrument is to be used for higher temperatures. By the use of this device the same thermometer can be employed for temperatures near the freezing- as well as the boiling-point of water or other solvent.

The Cryoscopic Method.

The determination of molecular weights by the cryoscopic method, that is, by observing the depression of freezing-point, is carried out in the apparatus of Beckmann shown in the figure. The tube (A), furnished with a side limb for the introduction of the substance, is fitted with a cork through which the thermometer (T) and platinum stirrer (S) pass. The lower part of this tube is surrounded by a wider tube (B) which provides an air jacket between the tube (A) and the freezing-mixture contained in the outer vessel (C). This freezing-mixture, whose temperature should be about 5° below the freezing-point of the solvent employed, is also furnished with a stirrer (S^1). A weighed quantity of water, or other solvent, is placed in the tube (A) and then frozen. Owing to under-cooling the temperature indicated by the thermometer falls below the freezing-point, and then quickly rises again, and becomes stationary at that point as soon as ice separates. When the freezing-point of the solvent has been indicated on the arbitrary scale of the thermometer, a weighed quantity of the substance is introduced and the freezing-point of the solution determined. The amount of substance added should produce a depression of about 0·5°. The determination may be repeated after the addition of a further quantity of substance. The reading should, however, be taken when a minimum quantity of the pure solid solvent has separated, so that the concentration of the solution may not be appreciably increased. The following are important freezing-constants (K):

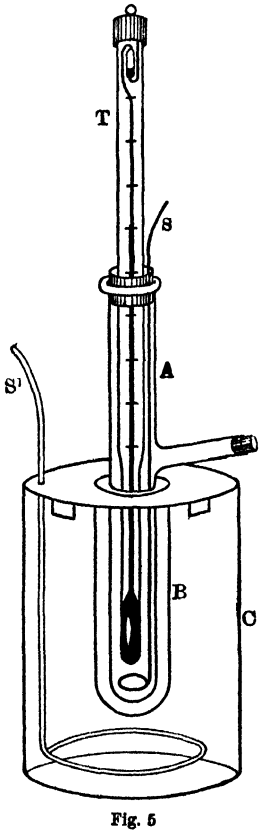


Fig. 5

Water 18·6; acetic acid 39; benzene 50; phenol 73.

EXAMPLE.—Successive quantities of 0·317, 0·394, and 0·5152 grm. of a substance were dissolved in 18·054 grm. of benzene, the depressions of freezing-point being 0·278°, 0·348°, and 0·452° respectively; what is the molecular weight of the substance? The

molecular lowering of the freezing-point of benzene (K) is 50. (Institute of Chemistry, July, 1902.)

$$M = \frac{100KS}{\Delta L}.$$

i. $M = \frac{100 \times 50 \times 0{\cdot}317}{0{\cdot}278 \times 18{\cdot}054} = 315{\cdot}8.$

ii. $M = \frac{100 \times 50 \times 0{\cdot}394}{0{\cdot}348 \times 18{\cdot}054} = 313{\cdot}6.$

iii. $M = \frac{100 \times 50 \times 0{\cdot}5152}{0{\cdot}452 \times 18{\cdot}054} = 315{\cdot}7.$

The Ebulliscopic Method—Beckmann's Apparatus.

The tube (A) (fig. 6) employed in the Beckmann apparatus for determining elevation of boiling-point resembles that in which freezing-point determinations are carried out; but, in addition to the side tube for the introduction of the substance, it is provided with another tube (B) fitted with a reflux condenser for the condensation of the vapour arising from the boiling liquid. In order to prevent super-heating of the liquid, and consequent irregular boiling, a short piece of stout platinum wire (C) is fused into the bottom of the tube, which also contains some small beads which surround the lower part of the thermometer bulb, and serve to break and distribute the bubbles of vapour as they rise. In addition to this, the boiling-tube is surrounded with a wider vessel (D) packed with some non-conducting material to prevent loss of heat by radiation, or sometimes

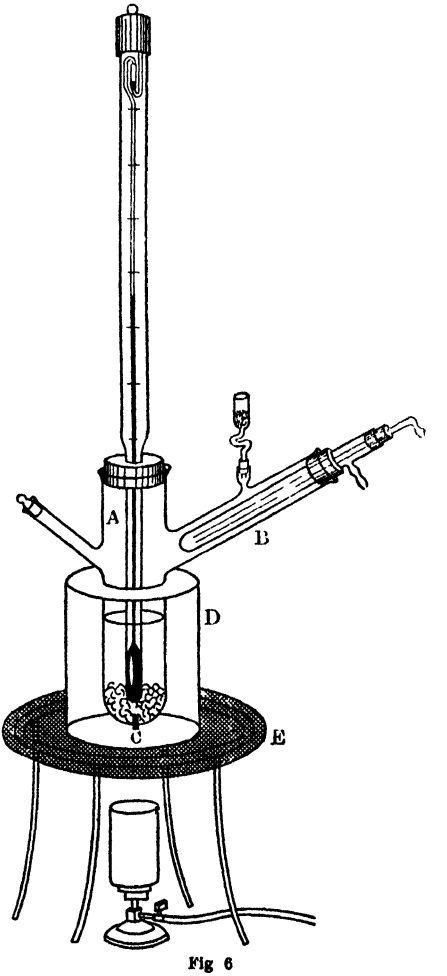


Fig 6

with a glass envelope containing the vapour of the boiling solvent The whole apparatus stands upon a sheet of asbestos (E), below which the burner for heating is placed.

In carrying out an experiment a weighed quantity of the solvent is heated until it boils briskly, and its temperature has become constant. If the condenser is acting efficiently the solvent should not lose in weight; but about 0·3 grm. should be subtracted from its weight to allow for the quantity required to wet the internal walls of the tube and condenser. After the boiling-point of the solvent has been recorded, the weighed quantity of the substance is introduced, and a reading again taken when the temperature has become constant. As in the case of freezing-point determinations, successive quantities of substance may be added to the same quantity of solvent, and corresponding readings taken. If much time elapses between the observations of the boiling-points of solvent and solution, it is necessary to read the barometer, and make a correction for change of atmospheric pressure during the interval.

The Modified Landsberger Apparatus.

A method of determining elevation of boiling-point, introduced by Sakurai,[1] modified by Landsberger,[2] Walker and Lumsden,[3] and others, and more recently by Turner and Pollard,[4] consists in raising the solvent to its boiling-point by passing into it the vapour of the same liquid boiling in another vessel. The vapour condenses, and its latent heat eventually causes the solvent to boil, although the boiling-point after the addition of the substance is above that of the pure solvent. As the amount of the solvent continuously increases by condensation of vapour, it is estimated by weighing or measuring after condensation has been arrested instead of before heating is begun.

By this method all possibility of superheating is avoided, and accurate results are rapidly obtained.

The construction of the apparatus is shown in fig. 7. The vessel (A), about 16 cm. high and 3 cm. in diameter, is fitted with a two-holed cork through which pass the thermometer (T) and the delivery tube (B) by which vapour is conveyed to the bottom of the vessel

[1] *Trans. Chem. Soc.*, 1892, *61*, 994. [2] *Ber.*, 1898, *31*, 461.
[3] *Trans. Chem. Soc.*, 1898, *73*, 502.
[4] *Trans. Chem. Soc.*, 1910, *97*, 1184, *Proc. Chem. Soc.*, 1913, *29*, 349.

from the liquid boiling in the flask (F). A small hole (C) in the upper part of the vessel allows uncondensed vapour to pass into the outer vessel (D), where it forms a vapour jacket and is then condensed, either here or by subsequent cooling after escaping by the side tube (E).

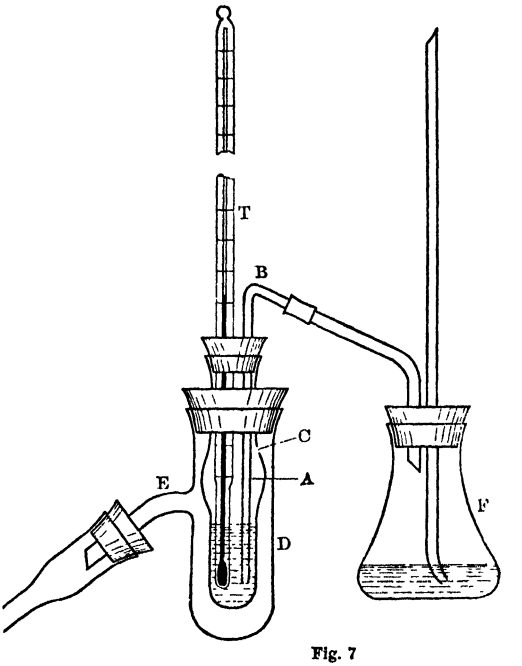


Fig. 7

The boiling-constants (K) of important liquids are: Water 5·2; ethyl alcohol 11·7; chloroform 39; benzene 27.

EXAMPLE. — Turner found that 1·150 grm. of diphenylamine $(C_6H_5)_2NH$, dissolved in 42·82 grm. of chloroform caused the boiling-point of the solvent to rise 0·618°. K = 39. Find the molecular weight of diphenylamine.

$$M = \frac{100\,KS}{\Delta L} = \frac{100 \times 39 \times 1{\cdot}150}{0{\cdot}618 \times 42{\cdot}82} = 169{\cdot}5.$$

Theory for $(C_6H_5)_2NH$ = 169·1.

6. Molecular Complexity

The methods and results of determining the molecular weights of gases and vapours and of substances in solution have been reviewed in the preceding pages; and it appears that the molecules of substances in solution are often of the same order of magnitude as those of the same substances in the state of vapour. For example, ferric chloride in a state of vapour at about 750° consists of molecules represented by the formula $FeCl_3$, and the elevation of the boiling-point of ether or alcohol by dissolved ferric chloride points to the same molecular formula. The reason for this identity of molecular state is to be found in the fact that the vaporous state

and the state of solution are analogous to each other, and that the process of vaporization of a solid or liquid, with the consequent distribution of its molecules through space, resembles the process of solution of the same substance, and the distribution of its molecules throughout the solvent.

Yet the molecular state of a dissolved substance depends sometimes upon the liquid in which it is dissolved. Hydrogen chloride, for example, forms molecules when dissolved in benzene and nitrobenzene which may be as much as five times as great as the gaseous molecule; its molecules are then said to be associated. With regard to liquids themselves, there is good reason to believe that their molecules are often associated. Consider water, for example. Water is the first of the series of four hydrides: H_2O, H_2S, H_2Se, H_2Te; three of these are gases; why, therefore, is water a liquid? Since the atomic weight of oxygen is the least of the atomic weights of the four elements combined with hydrogen in this series, and volatility diminishes from H_2S to H_2Te, water would be expected to be the most instead of the least volatile of the four hydrides. The reason water is a liquid at atmospheric temperature must be that it forms complex molecules $(H_2O)_n$. Steam even appears to contain a very small proportion of molecules, which are regarded as double, since its density is a little greater near the point of condensation than corresponds with the simple formula H_2O. Liquid water undoubtedly consists of associated molecules, e.g. $(H_2O)_2$ and $(H_2O)_3$, whilst ice is believed to be $(H_2O)_3$ only. It is noteworthy that hydrogen fluoride, which follows water in the periodic classification, also contains associated molecules, and has an anomalous boiling-point.

Regarding benzene, C_6H_6, there is evidence that near its point of condensation the saturated vapour begins to contain double molecules, $(C_6H_6)_2$, and that liquid benzene consists entirely of these molecules, until near its freezing-point, when $(C_6H_6)_4$ molecules begin to appear, and increase in number until solid separates, which consists wholly of $(C_6H_6)_4$ molecules.

It is remarkable that the association of various molecules is promoted by the entire absence of water. Thus benzene, which usually boils at 80°, was found by H. B. Baker[1] to boil at 106° after being dried over phosphoric oxide for eight years. This rise of boiling-point must, no doubt, be attributed to molecular association.

[1] *Chem. Soc. Trans.*, 1922, *121*, 570.

Concerning the molecular state of solids little or nothing has been known until recently; but the examination of the X-ray spectra produced by solids is throwing much light on their molecular structure. The nature of the problem presented by solids may be realized by considering a simple example. Carbon and silicon are related elements; yet carbon when it burns forms a gas and silicon a solid. Thus the molecules of CO_2 are not associated, but those of SiO_2 are, if indeed SiO_2 molecules can be said to exist at all. What is the reason for this difference? The difference may be expressed, though not explained, by saying that any field of influence outside the CO_2 molecule, by which other molecules of the same kind might be attracted, and associated, is very limited, or else the attractive force exerted therein is very small; whereas in the case of the SiO_2 molecule the external field of attractive force is considerable in extent or strength or both.

The difference between the two cases is referable to the difference between the carbon and silicon atoms, and must depend ultimately upon the different structures of these atoms. Meanwhile it may be stated that the "crystal unit", i.e. the smallest unit that takes part in crystal growth of silica, is $(SiO_2)_3$.

With regard to the formulæ to be applied to liquid and solid compounds there is much difficulty if real molecules are to be represented. Indeed it can hardly be asserted that molecules, NaCl, of common salt exist either in the solid state or in solution. It is not necessary, however, to have molecular formulæ in order to represent chemical reactions, since the simplest formulæ representing the inherent properties of compounds are sufficient for all ordinary purposes. The formula $CaCO_3$, for example, serves for chalk; it would be interesting to know what is the molecular or crystal unit of this compound, but such knowledge is not necessary for the representation of its common reactions.

In some cases, however, the smallest empirical formula would be untrue; e.g. hyponitrous acid is $H_2N_2O_2$ and not HNO; and benzene is C_6H_6 and not CH nor C_2H_2.

7. The Molecular Compositions of Compound Gases

The evidence on which the molecular formula H_2O for water is based has already been considered. There are a number of compound gases whose molecular formulæ may be established by the

application of the principles set forth in this chapter; and these will now be dealt with.

It has already been shown that the molecules of hydrogen, chlorine, and oxygen are diatomic. This follows, it will be remembered, from the fact that the hydrogen chloride formed from equal volumes of hydrogen and chlorine occupies twice the volume of each separate gas, and that steam occupies twice the volume of its constituent oxygen at the same temperature and pressure. By an extension of the principle here employed the number of atoms of a gaseous element within the molecule of a compound gas may always be determined.

Thus, since it can be shown that 2 volumes of ammonia gas yield when decomposed 3 volumes of hydrogen and 1 volume of nitrogen, it follows, provided the nitrogen molecule is diatomic, that ammonia must be represented by the formula NH_3; for the molecular change on the decomposition of ammonia is:

2 mols. ammonia yield 3 H_2 + N_2,
consequently 2 NH_3 = 3 H_2 + N_2.

The argument may be put in another way. Since the volume of the ammonia is to that of the hydrogen as 2 : 3, the atomic concentration of hydrogen in ammonia is to that in free hydrogen as 3 : 2; and since the volume of ammonia is to that of nitrogen as 2 : 1, the atomic concentration of nitrogen in ammonia is to that in free nitrogen as 1 : 2; whence the formula NH_3 follows.

In the case of a gas containing a solid element, such as sulphurous anhydride, the additional estimation of the density of the gas suffices to show how many atoms of the solid element it contains, provided the atomic weight of this element is known. Thus, (*a*) the gas produced by burning sulphur in oxygen measures the same volume as the oxygen; therefore the molecule of this gas contains 2 atoms of oxygen; (*b*) the density of the gas is 32, and its molecular weight consequently 64, whilst the weight of oxygen within its molecule is 32, and the atomic weight of sulphur is 32; therefore it follows that the molecule of the gas contains 1 atom of sulphur, and that its molecular formula is SO_2.

The following statements epitomize the evidence for the molecular formula of a number of the best-known gases:

Hydrogen Chloride.

That 1 volume hydrogen + 1 volume chlorine give 2 volumes

hydrogen chloride is fundamental to the molecular theory. The following facts suffice to prove this relation:

(*a*) Electrolysis of an aqueous solution of hydrogen chloride under suitable conditions yields equal volumes of hydrogen and chlorine.

(*b*) Sodium amalgam removes the chlorine from hydrogen chloride gas, and the remaining hydrogen occupies half the volume of the hydrogen chloride.

Water and Steam.

(*a*) Electrolysis of acidified water yields hydrogen and oxygen in the proportion of 2 volumes of the former to 1 of the latter,

(*b*) When a volume of electrolytic gas, i.e. a mixture of 2 volumes of hydrogen with 1 volume of oxygen is exploded in a eudiometer kept at a temperature above the boiling-point of water, the volume of the resulting steam is two-thirds the volume of the mixed gases. Therefore

2 vol hydrogen + 1 vol. oxygen yield 2 vol. steam.

Carbonic Anhydride.

When carbon is burnt in oxygen gas the volume of the gas remains unaltered. Therefore a molecule of the gaseous product contains 2 atoms of oxygen ($O_2 = 32$).

The density of carbonic anhydride is 22; therefore its molecular weight is 44. Within this molecular proportion are 32 parts (O_2) of oxygen, and therefore 12 of carbon. But 12 is the atomic weight of carbon. Therefore carbonic anhydride is CO_2, and is rightly called carbon dioxide.

Sulphurous Anhydride.

When sulphur is burnt in oxygen the volume of the gaseous product is the same as that of the oxygen. The density of sulphurous anhydride is 32, and its molecular weight 64. The atomic weight of sulphur is 32; therefore, by the same argument as applies to carbon dioxide, sulphurous anhydride is sulphur dioxide, SO_2.

Hydrogen Sulphide.

When hydrogen sulphide gas, confined over mercury, is decomposed by electric sparks, or when its sulphur is removed by means of tin heated in the gas and so converted into sulphide, the volume

of the remaining hydrogen is equal to the volume of the original hydrogen sulphide, whose formula is consequently H_2S_n. That $n = 1$ is proved by the fact that the gas density is 17 and molecular weight 34; for of this 32 parts must be sulphur, and 32 is the atomic weight of sulphur. Thus the formula for hydrogen sulphide is proved to be H_2S.

Nitrous Oxide.

Potassium, sodium, copper, and other metals remove the oxygen from nitrous oxide when heated in the gas, leaving nitrogen. There is some risk of nitrite being produced if the two former metals are heated too strongly in the gas, but strongly heated copper removes only the oxygen, and leaves all the nitrogen in a pure state. By this means it may be shown that nitrous oxide contains its own volume of nitrogen, and therefore that its molecule contains 2 atoms of this element. The density of nitrous oxide is 22, and its molecular weight is 44, and this weight contains 28 parts (N_2) of nitrogen, and therefore 16 parts of oxygen. Since 16 is the atomic weight of oxygen the molecule of nitrous oxide contains 1 atom of this element, and therefore the molecular formula for the gas is N_2O.

The same conclusion is reached by mixing nitrous oxide with its own volume of hydrogen and exploding the mixture. After condensation of the steam pure nitrogen remains equal in volume to the nitrous oxide. Thus it is shown, not only that nitrous oxide contains its own volume of nitrogen, but that the oxygen it contains would occupy half that volume, since it combines with a volume of hydrogen equal to that of the nitrous oxide. These facts are sufficient to establish the formula N_2O for nitrous oxide.

Nitric Oxide.

If potassium is heated in nitric oxide the vigorous combustion which takes place results in the formation of nitrite and nitrate; but a spiral of iron wire heated electrically removes all the oxygen from the gas without combining with the nitrogen, and the residual nitrogen then occupies half the volume of the original nitric oxide. This proves that a molecule of nitric oxide contains 1 atom of nitrogen (N = 14). The density of nitric oxide is 15, and, since its molecular weight is 30, the molecule contains 1 atom of oxygen (O = 16), and the molecular formula is NO.

Ammonia.

When ammonia solution is dropped into chlorine gas, hydrogen chloride is formed, and nitrogen set free. The experiment may be carried out in a long graduated tube, sealed at one end and provided at the other end with a cork furnished with a tap funnel. Ammonia solution is passed through the funnel into the chlorine, and the reaction is accompanied by a greenish flame and fumes of ammonium chloride. After the ammonia has been added in excess, dilute sulphuric acid is introduced to combine with the excess of ammonia, after which water is allowed to enter until the gas in the tube is at atmospheric pressure, when the flow of water ceases. Then it is found that the gas, which is nitrogen, fills one-third of the tube. Since hydrogen and chlorine combine in equal volumes to form hydrogen chloride, the hydrogen of the ammonia from which the hydrogen has been liberated would have occupied three times the volume of this nitrogen. This shows that ammonia, when decomposed, yields 1 volume of nitrogen to 3 of hydrogen; but since the volume of ammonia gas which is thus decomposed is unknown, all that this experiment reveals is that the molecule of ammonia is $(NH_3)_n$.

The relation between the volume of ammonia and the volumes of its decomposition products may be determined by confining a measured volume of the gas over mercury and passing electric sparks through it until expansion ceases. The gas will then have been decomposed into a mixture of hydrogen and nitrogen which will occupy twice the volume of the ammonia. That this mixture consists of 3 volumes of hydrogen and 1 volume of nitrogen may be shown by adding excess of oxygen and exploding the mixture.

Thus for example:

Volume of ammonia	= 10·0 c. c.
Volume of nitrogen + hydrogen after sparking	= 20·0 „
Volume after addition of oxygen	= 75·0 „
Volume after explosion	= 52·5 „

Thus 22·5 c. c. of gas have disappeared, of which 15·0 c. c. must have been hydrogen. So it follows that 10·0 c. c. of ammonia were decomposed by electric sparks into 15 c. c. of hydrogen and 5 c. c. of nitrogen; and, as shown before, this proves the molecular formula NH_3 for ammonia.

Phosphine.

The case of phosphine differs from that of ammonia because, when the gas is decomposed by electric sparks, the liberated phosphorus remains as a solid whose volume is negligible. Consequently, the proportion of phosphorus in the molecule must be discovered by density determination as in the case of sulphur dioxide, hydrogen sulphide, &c.

Two volumes of phosphine, decomposed by electric sparks, yield 3 volumes of hydrogen. Therefore a molecule of the gas contains 3 atoms of hydrogen.

The density of phosphine is 17, and its molecular weight 34. Consequently, the proportion of phosphorus within the molecular proportion of phosphine is 31. But 31 is the atomic weight of phosphorus. Therefore the molecule of phosphine contains 1 atom of phosphorus, and so its formula is PH_3.

Carbon Monoxide.

Carbon monoxide can be converted into carbon dioxide by exploding it with oxygen, when it is found that 2 volumes of the gas combine with 1 volume of oxygen to form 2 volumes of carbon dioxide; or, since the molecular formulæ CO_2 and O_2 are known, in the equation,

$$2\ C_xO_y + O_2 = 2\ CO_2,$$

x and y both $= 1$, so that the molecular formula CO is proved. This conclusion is confirmed by the density of the gas, which is 14, whence the molecular weight is 28; and C $= 12$, O $= 16$, so that CO $= 28$.

Methane, Ethylene, and other Hydrocarbons.

If a certain volume of a hydrocarbon is exploded with a known volume of oxygen used in excess, the resulting moist gas, measured at atmospheric temperature and pressure, consists of carbon dioxide mixed with unused oxygen. The volume of carbon dioxide formed is estimated by absorbing this gas in sodium hydroxide solution, and the total volume of oxygen used, part of which has produced carbon dioxide, and part water, is shown by the difference between the original and the remaining volume of oxygen. These data are sufficient to establish the molecular formula of the hydrocarbon.

For, consider the gaseous hydrocarbon C_xH_y. The result of its explosion with oxygen is represented by the equation

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 = xCO_2 + \frac{y}{2}H_2O.$$

The volume of steam formed and condensed is not measured; but when the volume of carbon dioxide, referred to that of the hydrocarbon as unity, which is x, has been ascertained, the value of y is found by subtracting this from the total volume of oxygen used, referred to the same standard, and multiplying the remainder by 4.

When x and y are found, the formula of the hydrocarbon is settled. Vapour density will confirm the formula, but is not necessary to establish it.

Methane.

When a mixture of 10 c. c. of methane with 30 c. c. of oxygen is exploded, the resulting gas, measured at the same temperature and pressure, is a mixture of 10 c. c. of carbon dioxide and 10 c. c. of oxygen.

Thus 1 volume methane requires for combustion 2 volumes oxygen, and yields 1 volume carbon dioxide.

So in the equation

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 = xCO_2 + \frac{y}{2}H_2O, \; x = 1 \text{ and } \frac{y}{4} = 1;$$

therefore the formula for methane is CH_4; or otherwise, because the volume of the carbon dioxide produced is equal to the volume of the methane, a molecule of the latter contains 1 atom of carbon; and, because the volume of the oxygen required to burn the hydrogen of methane is equal to the volume of the methane, the atomic concentration of hydrogen in the methane molecule is twice what it is in the free hydrogen molecule; i.e. there are 4 atoms of hydrogen in methane. Thus the molecular formula for methane is CH_4.

Ethylene.

When a mixture of 10 c. c. of ethylene with 40 c. c. of oxygen is exploded, the resulting gas, measured at the same temperature and pressure, is a mixture of 20 c. c. of carbon dioxide and 10 c. c. of oxygen.

Thus 1 volume ethylene requires for combustion 3 volumes oxygen and yields 2 volumes carbon dioxide.

So in the equation

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 = xCO_2 + \frac{y}{2}H_2O, \; x = 2 \text{ and } \frac{y}{4} = 1;$$

consequently the formula for ethylene is C_2H_4.

Or, to employ the alternative argument, since the volume of the carbon dioxide produced is twice the volume of the ethylene, a molecule of this hydrocarbon contains 2 atoms of carbon; and since the volume of oxygen required to burn the hydrogen of ethylene is equal to the volume of the ethylene, this hydrocarbon contains 4 atoms of hydrogen. Thus, again, the molecular formula for ethylene is C_2H_4.

In a similar way the molecular formula of any gaseous hydrocarbon may be established.

SUMMARY

EQUIVALENT WEIGHT.—The equivalent weight of an element is that weight of it which combines with, or displaces from combination, unit weight of a standard element.

ATOMIC WEIGHT.—The atomic weight of an element is the ratio between the weight of its atom and that of the atom of a standard element. The standard is: O = 16·00.

DETERMINATION OF ATOMIC WEIGHT:

(*a*) Exact estimation of chemical equivalent.
(*b*) Decision as to order of magnitude.

Guiding principles: i. Avogadro's theory.
ii. Chemical displacement.
iii. Law of specific heats.
iv. Law of isomorphism.
v. Periodic law.

PRINCIPLE OF CHEMICAL DISPLACEMENT.—When $1/n^{th}$ of the proportion of a constituent element in a chemical compound can be displaced by another element, a molecule of the compound contains at least n atoms of that element.

LAW OF SPECIFIC HEATS: DULONG AND PETIT'S LAW.—The specific heats of the solid elements are in the inverse ratio of

their atomic weights; *or* the atoms of the solid elements have the same capacity for heat.

$$\text{Specific heat} \times \text{atomic weight} = 6{\cdot}4 \text{ (approx.)}$$

$$\text{or} \quad \text{atomic weight} = \frac{6{\cdot}4}{\text{specific heat}}.$$

LAW OF ISOMORPHISM: MITSCHERLICH'S LAW.—The molecules of isomorphous substances contain equal numbers of atoms, which when not identical are analogous.

DETERMINATION OF MOLECULAR WEIGHTS: RAOULT'S LAW.—The depression of freezing-point, and elevation of boiling-point of a solvent caused by any dissolved substance are directly proportional to the number of molecules of the substance in solution, and consequently, inversely proportional to its molecular weight; *or* equimolecular solutions, with the same solvent, have the same freezing- and boiling-points.

CHAPTER III

OLDER VIEWS OF VALENCY AND CHEMICAL CONSTITUTION

In the preceding pages the experimental foundations of the atomic and molecular theories, as these were laid by the chemists and physicists of the nineteenth century, have been considered; and it has been found possible to exhibit and expound these without reference to modern conceptions of the atom; this is because the phenomena concerned have been superficial and have not dealt with the inter-relations of the atoms themselves in chemical compounds.

When, however, the subjects of valency and chemical constitution are approached the case is otherwise. It is impossible at the present time to consider these subjects adequately without bringing into view the atom as it appears in the light of to-day's knowledge. Moreover, the tide of this new knowledge is so powerful that much that was considered sound and stable has been broken by its flood; so that the first task of the chemical philosopher is to strengthen what remains of the harbour of his thought, whilst the flotsam disappears.

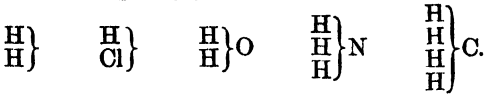
Consequently this chapter on "Older Views of Valency and Chemical Constitution" is historical; touching lightly the great subjects with which it deals, it brings chemical knowledge up to the boundary of the new domain, and leaves for a further chapter the task of exploration. It will be enough for the present purpose if what was temporary and must disappear can be distinguished from what is permanently useful. If this purpose is achieved, if impedimenta are dropped, and only useful tools and weapons are retained, there is hope that in the new field valuable possessions may be acquired.

It has already been seen, with regard to an element, that

$$\text{Atomic weight} = n \times \text{equivalent weight};$$

and that n is the *valency* or *atomic value* of the element.

The doctrine of valency, in the form in which it was held during the latter part of the nineteenth century, was a matter of slow development. It arose during the growth of organic chemistry, because of the need of a theory of structure in systematizing this branch of the science. Chemists developed the habit of referring various organic compounds to a few simple inorganic types, and this idea proved fertile, for it stimulated research, and led to important discoveries. These simple types were:



It cannot be said that the conception of valency was definitely contained in these types, yet it was not far off.

The chief exponent of the theory of types was Gerhardt; but it was E. Frankland who first introduced the idea of saturation capacity or valency. Frankland showed that whilst 1 atom of tin was capable of combining with two atoms of oxygen to form the dioxide SnO_2, a molecule of the compound tin diethyl, $Sn(C_2H_5)_2$, or $SnEt_2$, could combine with only 1 oxygen atom forming the compound $SnEt_2O$. Thus it appeared that the tin atom had a certain *saturation capacity*, that it could combine with not more than 2 atoms of oxygen or their equivalent; and that its power of combining with oxygen was diminished by the extent to which it was already combined with other atoms or groups of atoms.

The principle was further illustrated by Frankland by reference to such compounds as

$$NH_3,\ NI_3;$$
$$PH_3,\ PCl_3,$$

in which the atoms of nitrogen and phosphorus combined with 3 atoms of hydrogen or halogen; and by Kekulé, who showed that the carbon atom could combine with four other atoms, as in the compounds

$$CH_4,\ CH_3Cl,\ CHCl_3,\ CCl_4.$$

The phenomenon here illustrated is now called *valency*, about which the following statement may be made:

The valency of an element indicates the number of other atoms with which one of its atoms can directly combine.

An atom may be uni-, bi-, ter-, quadri-, quinque-, sex-, sept-, or even octa-valent;[1] equivalent terms are monad, dyad, triad,

[1] The Greek prefixes *mono-*, *di-*, *tri-*, &c., which, when attached to *valent*, make hybrid words, are now being abandoned.

tetrad, &c. In the compounds cited above the nitrogen and phosphorus atoms are tervalent, and the carbon atom is quadrivalent; whilst the hydrogen, chlorine, and iodine atoms are univalent. Hydrogen is never more than univalent, and therefore its atom is chosen as the standard of valency; chlorine is univalent with regard to hydrogen and metals, and, indeed, probably to all elements except oxygen; it may therefore replace hydrogen as a standard.

The following hydrides exhibit the valency of a number of elements:

Valency 1	2	3	4
FH	OH_2	NH_3	CH_4
ClH	SH_2	PH_3	SiH_4
BrH		AsH_3	
IH		SbH_3	

and the following halides[1] illustrate valency more extensively:

Valency 1	2	3	4	5	6	7	8
NaCl	OCl_2	BCl_3	CCl_4	PF_5	SF_6	—	OsF_8
KI	$ZnCl_2$	PCl_3	$SiCl_4$	AsF_5	TeF_6	—	
AgCl	$HgCl_2$	$AlCl_3$	$SnCl_4$	SbF_5	UF_6	—	

Oxygen is here shown to be bivalent. It is seldom other than this; and if oxygen is bivalent, the large number of oxides that exist may be classified to show valency, on the assumption that the valency of an element is equal to twice the number of oxygen atoms with which one of its atoms combines.

Valency 1	2	3	4	5	6	7	8
Na_2O	MgO	B_2O_3	CO_2	N_2O_5	SO_3	Cl_2O_7	OsO_4
K_2O	CaO	Al_2O_3	SiO_2	P_2O_5	CrO_3	(I_2O_7)	RuO_4
Ag_2O	ZnO	Fe_2O_3	PbO_2	Bi_2O_5.	UO_3	Mn_2O_7	

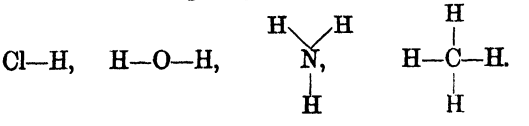
These oxides are in a different category from that of the foregoing hydrides and halides. In those the molecular formulæ have in all cases been established by vapour density or other measurements, and the valency of the element concerned is directly indicated by the number of attached hydrogen or halogen atoms. The formulæ for these oxides, however, are seldom truly molecular. Phosphoric oxide, for example, is $(P_2O_5)_2$ even as vapour, and the crystal unit of silica is $(SiO_2)_3$; but little, as a rule, can be said about the molecules of solids. Moreover, according to the above statement, valency as a property cannot strictly be judged from oxides at all, for these compounds do not exhibit, attached to a nuclear

[1] Halide = fluoride, chloride, bromide, or iodide.

atom, a number of peripheral atoms corresponding to its valency. Nevertheless, there is good reason to regard the valencies indicated by oxides such as those in the table to be correct.

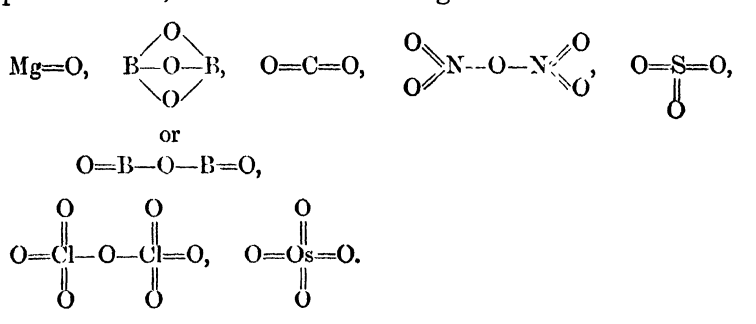
The establishment of the idea of valency was soon followed by a device by which the facts of atomic union were represented graphically.

Bonds were introduced by Couper to show the joining together of the atoms in the following way:



Thus *graphic* or *constitutional* formulæ were constructed, with bonds to show *units of valency*, or *units of affinity*, which they might be called, if they are thought of as standing for the forces by which the atoms are united.

Oxides containing bivalent oxygen have been represented by graphic formulæ, such as the following:

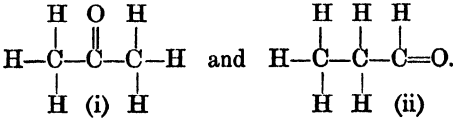


Formulæ such as these are chiefly of historic interest, for they have to be reconsidered carefully in the light of modern knowledge and theory concerning the atom. It will appear later that Couper's bonds ought not to be used indiscriminately or similarly for all these compounds; e.g. while they are appropriate in the case of carbon dioxide they are hardly proper in the case of magnesium oxide, since the mode of chemical union in this case seems to be different from that in the case of the gaseous oxide.

When bonds were first employed it was thought that the atoms in all compounds were united together in a similar way; and all that has been done in constructing these formulæ has been to arrange the atomic symbols in relation to one another so as to

represent known or supposed facts of chemical constitution, and then to join these symbols by bonds to represent the supposed acting valencies of each atom. How artificial such formulæ are is seen by comparing the two formulæ given for B_2O_3. Each satisfies the requirement that boron be tervalent and oxygen bivalent, yet both cannot truly represent the constitution of this oxide.

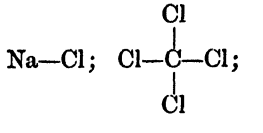
Is, then, the writing of graphic formulæ merely an interesting geometrical exercise based on the facts of valency alone? Consider, for example, a substance with the formula C_3H_6O. Since carbon is quadrivalent, oxygen bivalent, and hydrogen univalent, two graphic formulæ are possible for this substance:



Does it matter which formula is adopted? The answer is that two quite different substances are known, both of which are C_3H_6O; and one of which, acetone, certainly has the constitution (i), whilst the other, propaldehyde, as certainly possesses the constitution represented by (ii).

Thus *graphic* formulæ are *constitutional* formulæ, and only so far as they represent the ascertained constitution of compounds are they valid; therefore the construction of graphic formulæ for compounds which have not been definitely proved to have a certain constitution is to be deprecated.

A fundamental question connected with this subject was raised by comparing magnesium oxide with carbon dioxide. This question has lately assumed great prominence, and may be illustrated more clearly by considering the two chlorides NaCl and CCl_4. Until recently these compounds have been formulated thus:



there are, however, great differences between the two chlorides, both in physical and chemical properties, which suggest different modes of union of their constituent atoms. Sodium chloride is a solid whose separate atoms[1] of sodium and chlorine are arranged

[1] Or, more accurately, ions.

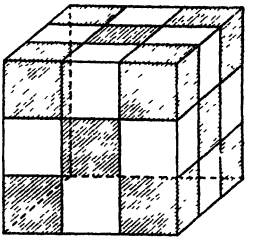
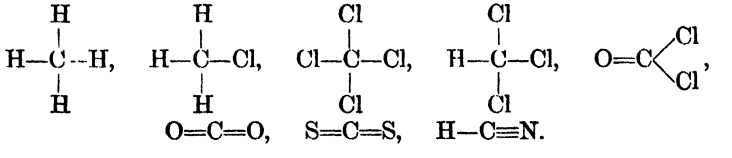


Fig. 8

like cubes[1] packed close together (fig. 8), until cubic crystals of various sizes are produced; whilst carbon tetrachloride consists of self-contained CCl_4 molecules which easily separate from one another, and exist apart in the state of vapour. Further, when sodium chloride dissolves in water its chlorine becomes reactive in a manner in which the chlorine of carbon tetrachloride never becomes reactive; i.e. it shows the reaction of chloride with silver nitrate which carbon tetrachloride fails to show. Can it reasonably be maintained that the same kind of bond unites chlorine with sodium as unites this element with carbon? It cannot; and consequently there appear to be two kinds of valency; the kind of valency which exists in carbon tetrachloride can be properly represented by "bonds", whilst the kind which unites sodium with chlorine cannot. Therefore the use of Couper's bonds in expressing the constitution of many inorganic compounds is being discontinued. The modern view regarding the mode of union of the elements in these compounds will appear later.

Variability of Valency.

Early in the development of the theory of valency the question arose whether valency is a fixed and inherent property of an atom, like its mass, or whether it can vary under varying circumstances. Kekulé, who showed the quadrivalency of carbon, believed valency to be unalterable; and the study of carbon compounds alone appeared to justify Kekulé's opinion. The following compounds were cited by Kekulé to illustrate the constant quadrivalency of carbon:



Frankland, on the other hand, observed that nitrogen formed not only NH_3, in which the element is evidently tervalent, but also NH_4Cl, in which it was apparently quinquevalent. Thus was expressed the idea of a maximum potential valency, and an actual valency, exercised in specific compounds, which might be less than this. And it was observed that the actual valency frequently fell

[1] It must not, however, be supposed that the atoms are cubical in shape.

short of the potential valency by two units, as, for example, in the pairs of compounds

$$NH_3,\ NH_4Cl;\quad P_2O_3,\ P_2O_5;\quad SO_2,\ SO_3;\quad SnCl_2,\ SnCl_4;$$

so it was supposed that when valency decreased from the maximum it was always by two units, and that consequently the valency of an element remained either odd or even. Then it was thought that the two valencies which remained disengaged in the lower compounds satisfied each other, so that no valencies remained free.

There are, however, some notable exceptions to this supposed rule, and it cannot be regarded as a natural law. Examples of these exceptions are shown in the sets of compounds

$$NO,\ N_2O_3,\ NO_2,\ N_2O_5;\quad ClO_2,\ Cl_2O_7;\quad IO_2,\ I_2O_5;\quad FeCl_2,\ FeCl_3;$$
$$InCl,\ InCl_2,\ InCl_3;\quad WCl_5,\ WCl_6.$$

The lower compounds are unsaturated, and combine with oxygen, chlorine, &c., to form higher compounds.

When rise of temperature causes dissociation it thereby causes the acting valency of the nuclear atom or atoms of a compound to diminish. Thus when ammonium chloride, NH_4Cl, in which the nitrogen atom is regarded as quinquevalent, dissociates into ammonia and hydrogen chloride, the nitrogen atom becomes in consequence tervalent. Similarly tungsten hexachloride, WCl_6, dissociates at high temperature into the pentachloride WCl_5 and chlorine. Occasionally dissociation involves the halving of molecules, as the following examples show:

$$\begin{aligned} N_2O_4 &\longrightarrow NO_2 + NO_2 \\ Fe_2Cl_4 &\longrightarrow FeCl_2 + FeCl_2 \\ Al_2Cl_6 &\longrightarrow AlCl_3 + AlCl_3. \end{aligned}$$

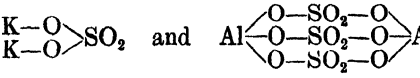
Presumably this dissociation involves a reduction in operative valency, since such valency is necessary to hold together the two parts of the double molecule, but becomes inoperative on dissociation.

It may be added that, unless there is reason to the contrary, association into double molecules, such as those represented above, is supposed to be effected by means of 1 unit of valency. Molecular association in liquids and solids must also be accounted for by the exercise of additional valencies. Thus liquid water contains double molecules, or molecules of even higher complexity; and the existence of these complex molecules is accounted for by assuming oxygen to be quadrivalent, thus:

$$\begin{matrix} H \\ H \end{matrix}\!\!>\!O = O\!<\!\!\begin{matrix} H \\ H \end{matrix};$$

since oxygen is known to be quadrivalent in some other compounds.

The existence of double salts and salts with water of crystallization cannot be explained by the narrower conceptions of valency. Consider, for example, potassium alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O$. The constitutional formulæ for potassium and aluminium sulphates have been constructed thus:



but it is difficult to see how these formulæ are to be united together, and 24 molecules of water to be incorporated in the scheme as well.

At one time it was customary to describe such compounds as "molecular" rather than "atomic", but such a distinction is no longer regarded as valid, and several theories have been proposed to account for the constitution of these compounds on the ground that auxiliary or latent valencies come into play in their formation. These theories cannot, however, be considered here.

The variation of valency with the kind of compound formed has been illustrated in the lists of hydrides, halides, and oxides already given. Thus it appears that whilst the valency of an element towards oxygen and the halogens[1] may rise as high as 8, valency towards hydrogen is never greater than 4; no single atom is known to combine with more than 4 hydrogen atoms. Now hydrogen and oxygen are reciprocally related, and it is a noteworthy fact that as the valency for hydrogen diminishes in a series of elements with increasing atomic weight, the valency for oxygen correspondingly increases, and the sum of the oxygen and hydrogen valencies remains equal to 8. This is shown in the following compounds, although fluorine and bromine fail to form oxides, and iodine is not known to form the oxide I_2O_7; moreover, tin has recently been shown to form an unstable hydride, though this has not been proved to be SnH_4.

CH_4	CO_2	SiH_4	SiO_2	GeH_4	GeO_2	SnH_4?	SnO_2
NH_3	N_2O_5	PH_3	P_2O_5	AsH_3	As_2O_5	SbH_3	Sb_2O_5
OH_2	—	SH_2	SO_3	SeH_2	SeO_3	TeH_2	TeO_3
FH	—	ClH	Cl_2O_7	BrH	—	IH	(I_2O_7)

These phenomena have a deep significance, which will appear later.

With regard to valency for the halogens, it must be noted that

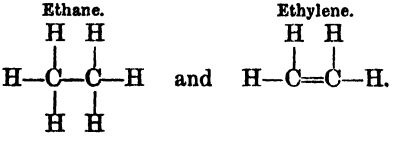
[1] The halogen elements are fluorine, chlorine, bromine, iodine.

as a rule halides are not so stable as the corresponding oxides. For example, NCl_3 is so unstable as to be highly explosive, whilst N_2O_3 does not split off oxygen; PCl_5 dissociates into PCl_3 and Cl_2, whilst P_2O_5 is stable; SO_2 may be united with oxygen to form SO_3, whilst SCl_4, formed below 0° C., easily loses chlorine.

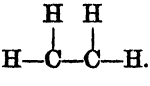
Fluorides, however, are much more stable than the other halides: PF_5 and SF_6 are stable gases, and the existence of OsF_8,[1] in addition to OsF_6 and OsF_4, shows a valency of 8 towards a halogen.

The Double Bond in Carbon Compounds.

Consider the two hydrocarbons ethane, C_2H_6, and ethylene, C_2H_4. The former is saturated, the latter is unsaturated; that is to say, it is capable of combining with 2 more hydrogen atoms or their equivalent. This state of unsaturation of ethylene is represented by a double bond, the graphic formulæ for the two compounds being



The question may be asked whether the double bond is simply employed to keep up the appearance of the quadrivalency of carbon, or whether it has any real meaning; whether, indeed, carbon is not really tervalent in ethylene, so that the formula might as well be



This question may be answered in the negative for several reasons.

First, no such compound as CH_3-CH_2 is known, in which one atom of carbon is quadrivalent, whilst the other is tervalent; so that both atoms must be either saturated or unsaturated. Here, at least, the idea that the two unsaturated atoms in ethylene satisfy one another appears justified; and the double bond expresses their mutual dependence.

Further, the double bond between carbon atoms, the ethylene linkage, as it is called, expresses something more than unsaturation; for the nature of this union differs from that represented by the single linkage. It is weaker than the single linkage, for when

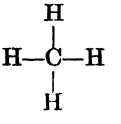
[1] Ruff and Tschirch, *Ber.*, 1913, *46*, 929.

a compound contains a chain of carbon atoms in which there is a double linkage, this is the point at which the chain breaks when the compound comes under disruptive influence. The fact that the double is weaker than the single linkage shows that no mechanical significance must be attached to bonds.

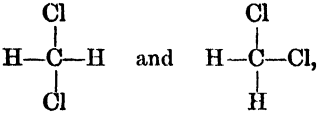
There is still a third characteristic of the double bond, which, however, can only be made clear by the study of the stereochemistry of carbon compounds.

"Chemistry in Space."

How far, it may be asked, is the graphic formula



supposed to represent the real configuration of the molecule of this simple hydrocarbon, methane? The answer may at once be given that it is probably an imperfect representation of the truth, because it is a flat formula, a formula in two dimensions, whereas matter exists in three dimensions; the formula has length and breadth, but the molecule of methane has thickness as well as length and breadth. Moreover, the adequacy of the formula may be tested in a very simple way. The formula suggests that there might be two methylene chlorides, CH_2Cl_2,



in which the two chlorine atoms are respectively opposite and adjacent to each other. Two such chlorides do not, however, exist; therefore a method of formulation must be found which does not suggest their existence. Only when the valencies of the carbon atom are equally distributed in tridimensional space is this requirement met; that is to say, when they are directed from the centre to the angular points of a regular tetrahedron, thus:

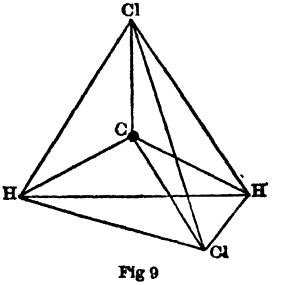


Fig 9

Since this figure is symmetrical, the positions of the 2 hydrogen and 2 chlorine atoms in methylene chloride shown upon it may be interchanged in any way without causing a difference in the relative positions of these 4 atoms. This conception of the disposition in space of the valencies of the carbon atom, which is due chiefly to van 't Hoff, has been very fruitful in organic chemistry. The aspect of the science thus suggested has been called "chemistry in space", or *stereochemistry*. Space-formulæ should, of course, be applied to all chemical compounds, and some progress has been made with elements other than carbon; but these formulæ are mainly of use in elucidating the structures of carbon compounds, where the question of constitution is of such vital importance.

It may be added that double and triple bonds are represented stereochemically by the joining of two tetrahedra along their edges and adjacent surfaces respectively. For example, ethylene, $CH_2{=}CH_2$, and acetylene, $CH{\equiv}CH$, are thus represented:

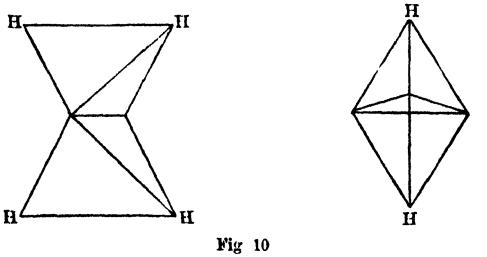


Fig 10

The Criterion of Valency.

The facts recorded in the foregoing pages suggest that valency might furnish a means of chemical classification of the elements, were it not that the exercise of this property varies somewhat irregularly. On the other hand, an independent classification of the elements might be expected to furnish information regarding valency. Such information is supplied by the Periodic Classification, which will shortly be studied. It will be sufficient to state here that in this classification the elements fall into nine groups—Groups O to VIII; and that the maximum valency of each element appears to be identical with the number of the group which contains it. Thus, the no-valency elements of the argon family are in Group O, the univalent metals of the alkalis in Group I, the bivalent metals of the alkaline earths in Group II, and so on.

Very seldom does the acting valency of an element exceed that indicated by the group to which it belongs; nevertheless in Group IB copper forms $CuCl_2$ and gold $AuCl_3$; more often, however, it falls below it. For example, the halogens belong to the seventh group, and should therefore have a maximum valency of seven. This is realized by chlorine in Cl_2O_7, and by iodine in H_5IO_6; but not by fluorine or bromine. Iron, nickel and cobalt, as well as osmium, ruthenium, &c., belong to the eighth group; but whilst the two latter metals realize octavalency in OsO_4 and RuO_4, the three former metals appear never to be octavalent.

Nevertheless the Periodic Law is the true criterion of the valency of an element. This will appear later when atomic structure is considered.

The Nature of Valency.

A study of the operation of valency, however detailed, or the graphic representation of the union of elements in chemical compounds by the use of bonds or solid geometrical figures, leaves the nature of valency itself quite unexplained. It may be said that the force which binds the atoms together is chemical affinity; but this explains nothing, and, moreover, the term "chemical affinity" has received a meaning in physical chemistry which is not closely associated with the idea of units of valency acting in specific directions through space.

More than a century ago H. Davy[1] expressed the opinion that "electrical effects are exhibited by the same bodies, when acting on masses, which produce chemical phenomena when acting by their particles". Berzelius extended this idea in his electro-chemical theory, whence is derived the method of classifying the elements as electro-positive and electro-negative. Faraday, later, showed that during electrolysis a definite quantity of matter is always associated with a definite quantity of electricity, a fact which suggests that electricity as well as matter is atomic. This suggestion starts a trail which might be followed into all the intricacies of modern knowledge and theory concerning the structure of the atom. The purpose of this chapter, however, has now been fulfilled; but when the earlier development of the periodic law has been considered in the next chapter the way will have been

[1] H. Davy, *Phil. Trans.*, 1807, 1.

fully prepared for an excursion into this new domain; and the promise may be made that in the course of this adventure the "nature of valency" will become illuminated in such a remarkable way that an entirely new and impressive conception will be gained concerning it.

SUMMARY

. VALENCY.—The valency of an element indicates the number of other atoms with which one of its atoms can directly combine.

CHAPTER IV

CLASSIFICATION OF THE ELEMENTS

The Periodic Law according to Mendeléeff

When the elements are regarded collectively, and in view of their ascertained atomic weights and properties, two considerations present themselves: (i) How may the elements be classified? (ii) What is their origin? These considerations are related, for the classification of material species is likely to lead to questions regarding the origin of such species.

Probably the first systematic classification of the elements was derived from the electro-chemical theory of Berzelius, to which reference has already been made. This theory grew out of the facts of electrolysis. Thus, if, for example, an electric current passes through an aqueous solution of sodium chloride, the sodium appears at the cathode or negative electrode, and the chlorine at the anode or positive electrode. Consequently sodium was regarded as electro-positive, being attracted to the electrode of opposite sign, while chlorine was, for a similar reason, electro-negative. Or, more generally, metals were considered to be electro-positive and non-metals electro-negative. Further, it was recognized that some metals are more electro-positive than others, power of metallic replacement being regarded as a criterion of electro-positiveness. For example, since zinc displaces copper from copper sulphate in solution, zinc is more electro-positive than copper; and, conversely, since chlorine displaces iodine from potassium iodide in solution, chlorine is more electro-negative than iodine.

So this method of classification served not only for the distinction of metals from non-metals, but also for the recognition of metallic and non-metallic intensity.

When the atomic weights of a sufficient number of the elements had been established with some degree of accuracy, it was perhaps inevitable that numerical relationships should be sought for between

them, and that attempts should be made to discover a connection between the properties of an element and its atomic weight.

The first attempt to establish numerical relations between the atomic weights was made in 1815–6 by an Edinburgh physician named Prout, who tried to prove that all the elements are condensations of hydrogen as the primordial substance, by affirming that all the atomic weights are whole numbers when that of hydrogen is unity. This affirmation was unjustified at the time, for Berzelius subsequently showed that a number of atomic weights, determined with accuracy by the use of material ordinarily available, were far removed from whole numbers. Nevertheless the fact remained that when the atomic weight of oxygen is made equal to 16·00 "the atomic weights tend to approximate to whole numbers far more closely than can reasonably be accounted for by any accidental coincidence";[1] and therefore it appeared, even a quarter of a century ago, that the complete rejection of Prout's hypothesis was unwarranted. Recent work, of which an account will be given in the sequel, has gone far to re-establish Prout's hypothesis; which, however, considering the time of its promulgation, must be regarded as a philosophic guess rather than a conclusion of inductive science.

Another attempt was made by Döbereiner, in 1817 and 1829, who showed that in various *triads* of related elements the central member of each group possesses properties and an atomic weight which are approximately the mean of the properties and atomic weights of the extreme members of the triad. These triads are: lithium, sodium, potassium; calcium, strontium, barium; phosphorus, arsenic, antimony; sulphur, selenium, tellurium; chlorine, bromine, iodine.

It will be sufficient to give numerical details for the first and last of these triads.

Element.	Atomic Weight.	Differences.	Mean of Extreme Atomic Weights.
Lithium	6·94		
		16·06	
Sodium	23·00		23·02
		16·10	
Potassium	39·10		
Chlorine	35·46		
		44·46	
Bromine	79·92		81·19
		47·01	
Iodine	126·93		

It will be observed that the atomic weight of sodium is almost

[1] R. J. Strutt, *Phil. Mag.* [vi], *1*, 311 (1901).

exactly the mean of the atomic weights of lithium and potassium, but that the atomic weight of bromine is considerably less than the mean of the atomic weights of chlorine and iodine. The relations suggested by these triads are therefore approximate only. It has been objected, moreover, that triads should not be made up to the exclusion of other related elements, that, for example, there are four halogens, and that it is arbitrary to exclude fluorine by forming a triad with the other three. But when it is recognized that fluorine differs from the other halogens, not only in atomic weight relationship, but also widely in the properties of its compounds, this objection loses force. So that without doubt the relationships shown by Döbereiner's triads are remarkable; nevertheless their value is historic only, for they are now merged in the generalization known as the periodic law.

Another kind of triad was, however, observed by Döbereiner, in which the three related elements have nearly identical atomic weights. These triads are:

Iron	55·84	Ruthenium	101·7	Osmium	190·8
Cobalt	58·94	Rhodium	102·9	Iridium	193·1
Nickel	58·69	Palladium	106·7	Platinum	195·2

They also find a place in the periodic classification. Döbereiner's observations were limited to the elements cited above. These observations could not give rise to a generalization, since they were concerned with only a minority of the elements; the majority did not form triads; and therefore it is difficult to see what significance could have been attached at the time to the existence of these triads.

Strecker, in 1859, initiated the idea of seeking relations between the elements placed in atomic weight sequence; whilst de Chancourtois, in 1862, placed the elements in sequence in a spiral round a cylinder divided into sixteen equal sectors to represent atomic weight magnitudes. Thus analogous elements of low atomic weights fell into places in vertical columns because properties recur in such elements after atomic weight differences of 16.

In 1863–6 J. A. R. Newlands arranged the elements in ascending order of their atomic weights, commencing with hydrogen, thus:

H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr	Ti	Mn	Fe, &c.

In this way he discovered that the eighth element is "a kind of repetition of the first", the ninth a repetition of the second, and so on; Na, for example, is a repetition of Li, Si of C, Cl of F. This discovery he called the

Law of Octaves.—"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 simple "law" did not apply to the elements of higher atomic weight; even in the above table manganese is wrongly classified with phosphorus; and it was suggested by a contemporary of Newlands that it would be as useful to arrange the elements in alphabetical order as in the order of their atomic weights! Nevertheless, the law of octaves is valid as an introduction to the periodic law. In the year 1869 Mendeléeff arranged all the elements in the order of their atomic weights, and discovered a periodicity in their properties. The fact of this periodicity he enunciated in the following statements:

1. The elements arranged according to the magnitudes of their atomic weights show a periodic change of properties.

2. Chemically analogous elements have atomic weights either in agreement (Pt, Ir, Os), or increasing by equal amounts (K, Rb, Cs). (Cf. Döbereiner's triads.)

3. The arrangement according to atomic weights corresponds with the valencies of the elements, and to a certain extent the difference in chemical behaviour, for example: Li, Be, B, C, N, O, F.

4. The elements most widely distributed in nature have small atomic weights, and all such elements are distinguished by their characteristic behaviour. They are thus typical elements, and the lightest element, hydrogen, is therefore rightly chosen as the typical unit of mass.

5. The magnitude of the atomic weight determines the properties of the element, whence in the study of compounds regard is to be paid not only to the number and properties of the elements and their mutual action, but to the atomic weights of the elements. Hence the compounds of S and Te, Cl and I, show, beside many analogies, yet striking differences.

6. It allows the discovery of many new elements to be foreseen; for example, analogues of Si and Al, with atomic weights between 65 and 75.

7. Some atomic weights will presumably experience a correction;

for example, Te cannot have the atomic weight 128, but 123 to 126.

8. From the table new analogies between elements become apparent. . . .

Some of these statements are open to criticism or require modification. Thus regarding statement 4, lithium and beryllium are not so widely distributed as the heavier metals sodium and potassium, and magnesium and calcium respectively, and conversely among the heavier metals tin and lead are more widely distributed than is the lighter germanium. Also the difficulty in statement 7 has been overcome recently, but not in the way suggested by Mendeléeff.

Nevertheless these generalizations marked a great advance on the position of earlier chemists, and Mendeléeff, whilst acknowledging the work of his predecessors, rightly claimed that he was the first "to foretell the properties of undiscovered elements, or to alter the accepted atomic weights".

The *Periodic Law*, according to Mendeléeff, may therefore be stated thus:

The physical and chemical properties of the elements and their compounds are periodic functions of the atomic weights; or

If the elements are arranged in the order of increasing atomic weight, their properties vary definitely from member to member of the series, but return to a more or less similar value at fixed points in the series.

The periodic system, according to Mendeléeff, may now be developed.

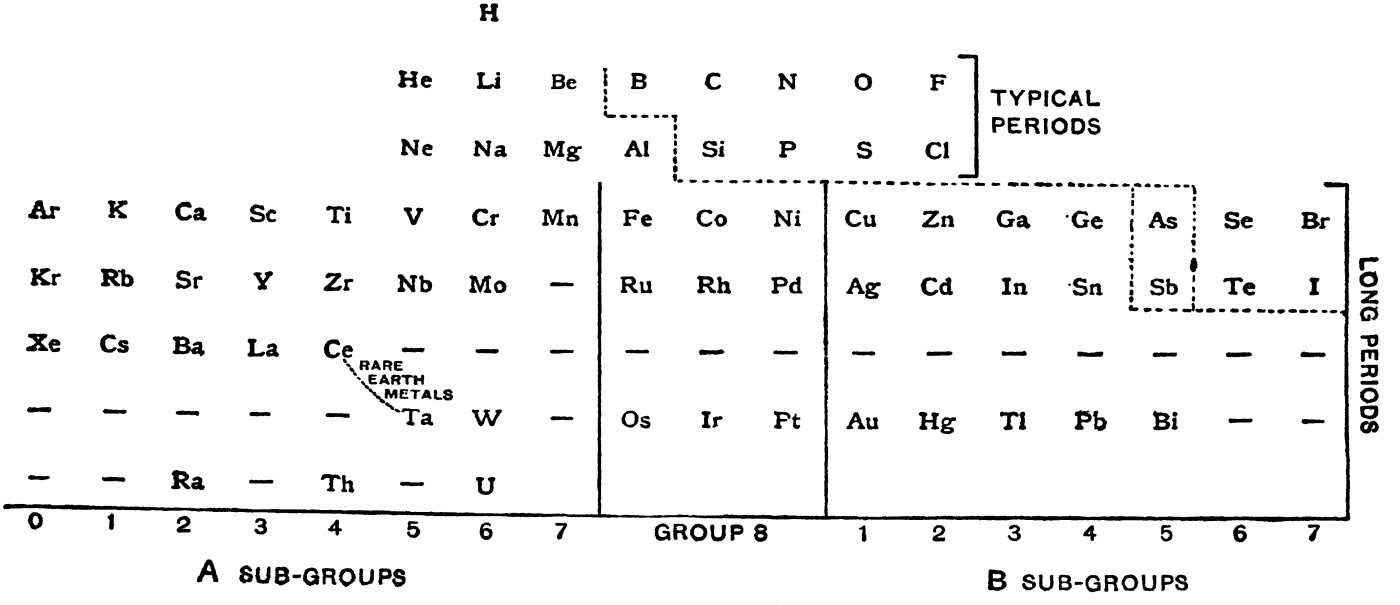
Hydrogen, the element of lowest atomic weight, became the sole member of Series 1 in Mendeléeff's system. Series (2) and (3) were the same as in the octaves of Newlands, thus:

(2)	Li	Be	B	C	N	O	F
(3)	Na	Mg	Al	Si	P	S	Cl.

The next two series were:

(4)	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni
(5)	Cu	Zn	Ga	Ge	As	Se	Br,			

being linked together by the triad Fe, Co, Ni; for to place these three elements in the consecutive positions occupied by Cu, Zn, Ga, thus displacing all that follow them, would have been not only to obliterate periodicity from the scheme, but also to ignore the


H
He Li Be B C N O F
Ne Na Mg Al Si P S Cl
TYPICAL PERIODS
Ar 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
Xe Cs Ba La Ce — — — — — — — — — — — — —
— — — — — Ta W — Os Ir Pt Au Hg Tl Pb Bi — —
— — Ra — Th — U
RARE EARTH METALS
LONG PERIODS
0 1 2 3 4 5 6 7 GROUP 8 1 2 3 4 5 6 7
A SUB-GROUPS
B SUB-GROUPS

peculiar relations these three elements bear to one other as members of a triad.

Series (6) and (7) connected by another triad were:

(6)	Rb	Sr	Y	Zr	Cb	Mo	—	Ru	Rh	Pd.
(7)	Ag	Cd	In	Sn	Sb	Te	I.			

Now it will be seen that Series (4) and (6) begin with the alkali metals K and Rb, whilst Series (5) and (7) begin with the metals Cu and Ag, which, whilst allied to each other, differ widely from the alkali metals. Similar differences exist between subsequent members of odd and even series. Elements in vertical columns constitute groups; of which, according to Mendeléeff, there were eight: seven groups corresponding with Newlands's octaves, and an eighth group in which Döbereiner's triads of nearly equal atomic weight were placed. When the inert gases were discovered, these were placed in a group by themselves: Group O, which preceded the other groups. Except with regard to the elements of Series (2) and (3), Groups I to VII were sub-divided into A and B Sub-groups, to show the above-mentioned differences between consecutive members of the same group. Thus the complete periodic system took the following form.

Groups	O	I	II	III	IV	V	VI	VII	VIII
Sub-groups		A B	A B	A B	A B	A B	A B	A B	
Series 1		H							
2	He	Li	Be	B	C	N	O	F	
3	Ne	Na	Mg	Al	Si	P	S	Cl	
4	Ar	K Cu	Ca Zn	Sc Ga	Ti Ge	V As	Cr Se	Mn Br	Fe Co Ni
5									
6	Kr	Rb Ag	Sr Cd	Y In	Zr Sn	Cb Sb	Mo Te	— I	Ru Rh Pd
7									
8	Xe	Cs	Ba	La	Ce		—	—	— — —
9		—	—	—	Rare Earth Metals	—	—	—	
10	—	—	—	—		Ta	W	—	Os Ir Pt
11		Au	Hg	Tl	Pb	Bi	—	—	
12	—	—	Ra	—	Th	—	U		
Oxides	—	X_2O	XO	X_2O_3	XO_2	X_2O_5	XO_3	X_2O_7	XO_4

The above arrangement was improved upon, and a clearer view obtained, by recognizing the existence of short and long periods. Thus Series (2) and (3) constituted short periods; Series

(4) and (5), with the linking elements of the eighth group, formed one long period. Other long periods followed, and the whole scheme shown in the chart on p. 74 resulted.

The great advantage of this mode of presenting the Periodic System was that the A and B Sub-groups were separated, so that elements which have little resemblance to one another were not classified together. For instance, it may well be objected that Cu, Ag, and Au, being very unlike the alkali metals, should not be placed with them in Group I. This objection is sufficiently answered when it is shown that these metals occupy positions near the centres of the long periods, whilst the alkali metals are quite differently situated at the beginning of these periods. Similar remarks apply to the relation between manganese and the halogens.

The arrangement of elements in any group now takes this form, illustrated by Group I:

(A)		(B)
	Li	
	Na	
K		Cu
Rb		Ag
Cs		
		Au

The table on p. 74 represents the final and most useful form of the Periodic System according to Mendeléeff, but before proceeding further it is desirable to point out some of its shortcomings, and thus to give a hint of the modification the system has necessarily undergone on account of recent knowledge.

Mendeléeff did not classify the metals of the rare earths. For one reason the number of these was unknown, and for another their properties did not progress from member to member as did the properties of elements in the recognized periods. Therefore the position of the rare-earth metals in the scheme could not be given in detail; but it was indicated that they intervened between Ce in Group IV and Ta in Group V.

Whilst the rare-earth metals could not be spaced, there remained, nevertheless, a large number of blank spaces following these elements; and in course of time it became increasingly improbable that these spaces ought to be reserved for elements hitherto undiscovered. It was scarcely credible that if 18 elements indicated by blank spaces existed not one of these should have been discovered. So it was

proposed to fill these blank spaces with Ta and the elements that follow it, moved up from the series below, so making one very long period including the rare-earth elements.

Thus A. Werner[1] suggested a long period of 33 elements from cæsium to the higher analogue of xenon, now know as radon; and except that his estimate of the number of existing rare-earth metals was one too many, time has proved that Werner was right.

It must be observed, however, that on account of the rare-earth metals, progression of properties from member to member is not shown throughout this long period; but that these metals may be regarded as functioning as a single element in the same sense as the individual members of the triads in the eighth group function together as a single element.

Atomic Weight Differences in the Periodic System.

Attention may now be drawn to atomic-weight differences between analogous elements in consecutive short and long periods. These differences are shown for a number of the elements in the following tables:

THE TWO SHORT PERIODS

	He	Li	Be	B	C	N	O	F
	Ne	Na	Mg	Al	Si	P	S	Cl
Differences	16·2	16·06	15·30	16·15	16·06	17·02	16·06	16·46

THE FIRST TWO LONG PERIODS

	Ar	K	Ca	Sc	Ti	V	Cr	Mn	Fe
	Kr	Rb	Sr	Y	Zr	Cb	Mo	—	Ru
Differences	42·99	46·34	47·56	43·8	42·9	42·14	43·99	—	45·86
	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Differences	43·97	48·01	44·31	47·03	45·08	46·1	46·81	48·3	47·02

It will be observed that the differences in the short periods are approximately 16, and in the long periods about 45; in the short periods 8 elements intervene before a recurrence of properties, and in the long periods 18 elements. The differences are by no means constant, for no mathematical relations exist between the atomic weights; but anomalies are seen in the differences between

[1] *Ber.*, 1905, *38*, 914.

krypton and argon, palladium and nickel, tellurium and selenium, in accordance with the anomalies in the atomic weights of argon, nickel and tellurium, to which attention will be drawn. It must be confessed, however, that there are other anomalies which are not pronounced enough to affect the order of the atomic weights of the elements.

Stress, however, must not be laid upon atomic-weight differences, because atomic-weight values themselves are now known to be of only secondary importance in matters of theory and classification of the elements. Indeed all the anomalies in atomic-weight relations, whether they affect the relative positions of the elements in series or not, are now removed, because the conception of atomic number (q.v.) has displaced that of atomic weight as of primary importance.

The elements of the short, or so-called typical periods, may be allied to those either of the A or the B Sub-groups. In the case of Group I, Li and Na are plainly related to the other alkali metals K, Rb, Cs, in the A Sub-group, rather than to Cu, Ag, and Au in the B Sub-group, but in Group VII, F and Cl are related to Br and I in the B Sub-group, rather than to Mn in the A Sub-group. This latter relationship obtains in all groups from II to VII.

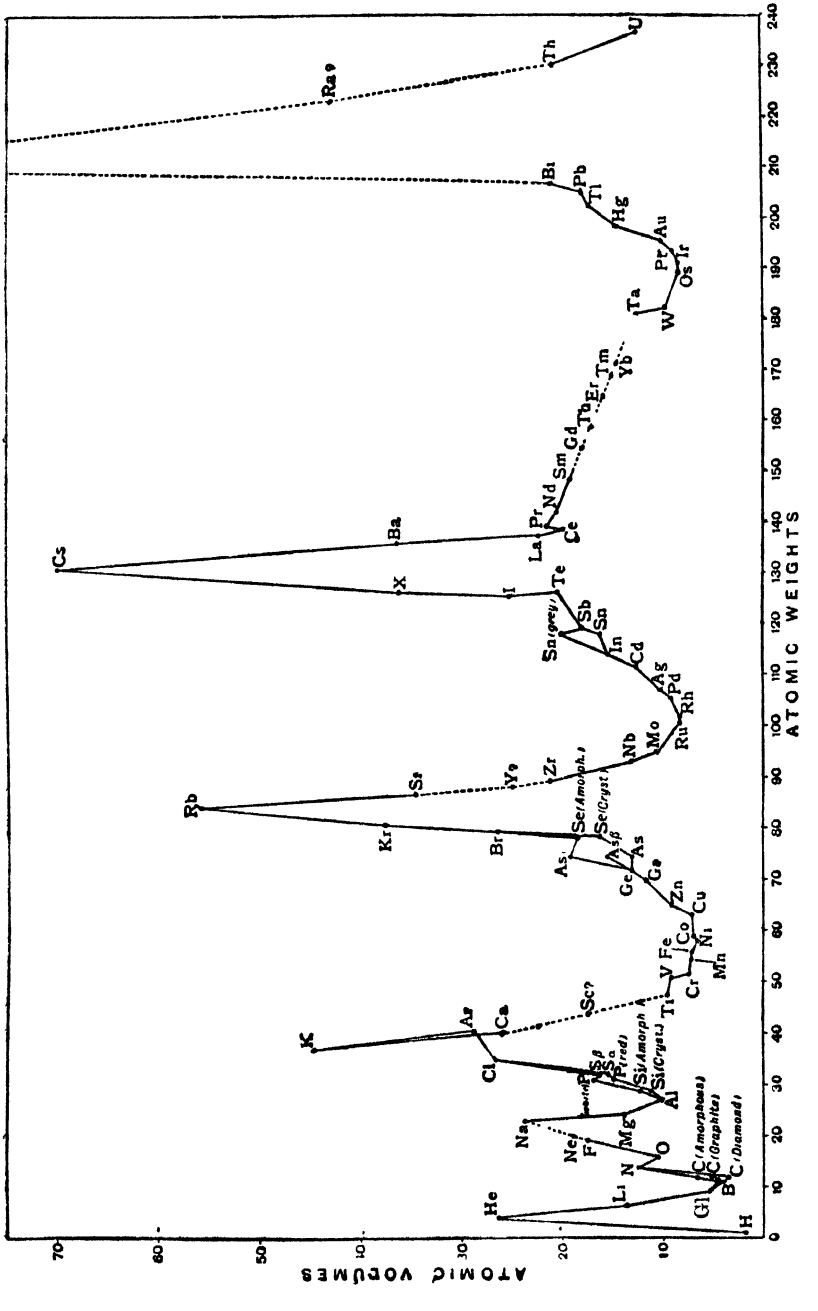
The periodic law, according to Mendeléeff, states that the physical and chemical properties of the elements and their compounds are periodic functions of their atomic weights. This statement must now be illustrated.

Periodicity of Physical Properties.

Perhaps the most obvious property of a solid element is its *density*. It was shown by Lothar Meyer, in 1870, that the densities of the elements vary periodically. Instead, however, of using the densities of the elements directly, L. Meyer calculated from them the *atomic volumes*, and plotted these values on a curve as ordinates, together with the atomic weights as abscissæ. The atomic volume of an element is related to its density in the following manner.

The reciprocal of the density is the *specific volume*,

$$\text{Specific volume} = \frac{1}{\text{density}} = \text{volume of unit mass};$$


ATOMIC VOLUMES
ATOMIC WEIGHTS
0
10
20
30
40
50
60
70
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
H
He
Li
Gl
B
C (Diamond)
C (Graphite)
C (Amorphous)
N
O
F
Ne
Na
Mg
Al
Si (Cryst.)
Si (Amorph.)
P (Fused)
P α
P β
S
Cl
K
Ar
Ca
Sc?
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
As α
As β
Se (Cryst.)
Se (Amorph.)
Br
Kr
Rb
Sr
Yt
Zr
Nb
Mo
Ru
Rh
Pd
Ag
Cd
In
Sn
Sn (grey)
Sb
Te
I
X
Cs
Ba
La
Ce
Pr
Nd
Sm
Gd
Tb
Er
Tm
Yb
Ta
W
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
U
Ra?

the *atomic volume* is this value multiplied by the atomic weight thus:

$$\text{Atomic volume} = \frac{\text{atomic weight}}{\text{density}}.$$

For example, the atomic weight of copper is 63·6, and its density 8·9; consequently

$$\text{Atomic volume Cu} = \frac{63{\cdot}6}{8{\cdot}9} = 7{\cdot}15.$$

This figure stands for the relative volume of a mass of copper proportional to the atomic weight of the element; it does not express the relative size of the copper atoms themselves; it could only do this if the atoms were packed without interspaces, or if the interspaces were constantly related in volume to the atomic material of the elements. What it does express is the relative volume of the atom plus its share of atomic interspace. The atomic volume curve shows a remarkable periodicity; for it is like a series of waves consisting of crests and hollows; moreover, the crests of successive waves increase in height with increasing atomic weight. The most important fact connected with the curve, however, is that related elements occupy analogous positions upon it. For example, the alkali metals, potassium, rubidium, and cæsium, are at the apices of successive curves, the halogens, chlorine, bromine and iodine, are on ascending, and the alkaline earth metals, calcium, strontium and barium, on descending parts of the curves.

The following other physical properties of the elements and their compounds are periodic.

Melting-point, malleability, coefficient of expansion, atomic refraction, conductivity for heat and electricity, colours of salts in solution. Consequently there are certain regions, which are similar on successive curves, where these properties are manifested, or reach their maxima. The student may test this statement with reference to the melting-points of the elements.

The periodic occurrence of colour in compounds is very striking. Thus all the metals whose salts give coloured solutions are included in the following series:

Ti	V	Cr	Mn	Fe	Co	Ni	Cu
		Mo	—	Ru	Rh	Pd	
		W	—	Os	Ir	Pt	Au
		U					

These series consist of metals in atomic weight sequence, and they occupy the lowest portions of successive parts of the atomic volume curve. There are other coloured compounds, however, which do not give coloured solutions; e.g. various sulphides and iodides. In the case of these compounds there is generally a deepening of colour with rise of atomic weight in a group, as in the sulphides of zinc, cadmium, and mercury. It is noteworthy that the colours of these compounds belong only to the solids; for when scarlet mercuric iodide is dissolved in alcohol, and yellow lead iodide in water, colourless solutions are obtained. This is to be expected, since colour is not associated with mercuric, lead, or iodide ions; thus the nitrates of mercury and lead are colourless, and so are the iodides of the alkali and alkaline earth metals.

Periodicity of Chemical Properties.

The fundamental chemical division of the elements is into metals and non-metals; and, according to the classification of Berzelius, metals are electro-positive, and non-metals electro-negative.

As the elements are traversed in the order of ascending atomic weights the variation of metallic and electro-chemical properties is periodic. Thus in the two short periods from lithium to fluorine, and from sodium to chlorine, there is continuous and regular transition from great metallic and electro-positive to extreme non-metallic and electro-negative characters. In the long periods which follow, for example the period from potassium to bromine, there are two phases; the first phase is from potassium through manganese to the eighth-group metals—iron, cobalt, and nickel; the second phase is from copper to bromine. The transition from potassium to bromine is similar in degree to that from sodium to chlorine, but the period contains more than twice as many elements; and the stages of this transition present an interesting phenomenon.

The elements of the first phase (K to Fe, Co, Ni) are all metals, but there is a continuous diminution of electro-positiveness throughout them; the elements of the second phase begin with the comparatively inert and electro-negative metal, copper, and there is actually a rise in metallic strength to zinc, followed by a regular fall to the non-metallic and electro-negative bromine.

Similar relations exist in the subsequent long periods; but the inertness of the central elements, i.e. those of the eighth group and of Group IB, becomes more pronounced with elements of higher atomic weight.

When the transition of properties within the separate groups, i.e. the elements in vertical columns, is considered, an increase of metallic nature or decrease of non-metallic nature is found to be the rule. Thus, for example, the alkali metals increase in electro-positiveness with rise of atomic weight; and the halogens similarly show a diminution of electro-negativeness with rise of atomic weight. Within the region of chemical inertness and metallic electro-negativeness, i.e. the eighth group, Group IB, and to a less extent Group IIB, an opposite state of things, however, exists; there is a diminution of electro-positiveness and chemical reactivity with rise of atomic weight. Thus the inert metals, platinum, gold, and mercury, occur consecutively as the last members of Groups VIII, IB, and IIB.

From all this it follows that the most powerful metals are to be found at the extreme left of the periodic diagram; cæsium, the most electro-positive metal, being in the lower left-hand corner; whilst the non-metals occupy the upper right-hand portion of the diagram; fluorine, the most powerful non-metal, being in the upper right-hand corner. The dotted line in the diagram on p. 74 delimits the region of non-metals.

Periodicity of Valency.

The following statement is generally true.

The maximum valency of an element corresponds with the number of the periodic group to which it belongs. The statement is illustrated by the formulæ of the typical oxides appended to the table on p. 75. In Chapter III valency was illustrated by lists of hydrides, halides, and oxides, and in most of the formulæ for the halides and oxides, but not the hydrides, the numerical value of the valency indicates the group to which the element belongs. A valency of seven is not always realized in the seventh group; less often is a valency of eight seen in the eighth group. On the other hand, copper and gold in Group IB show bi- and ter-valency respectively in $CuCl_2$ and $AuCl_3$, but the elements of this group are in any case somewhat anomalous in their relationships. A more striking exception is shown in the case of

boron, which forms the hydride B_2H_6 and other hydrides, in which the element can hardly be less than quadrivalent.

It was seen in the chapter on valency that the sum of the oxygen valencies and hydrogen valencies in volatile hydrides of an element is equal to eight; and this is true irrespective of the periodic group to which the element belongs. The elements of Groups I, II, and III, however, excepting boron, form no volatile hydrides, and exhibit only the lower valencies in the oxides. Thus in the first and second short periods the oxides and hydrides show valencies as follows:

I	II	III	IV	V	VI	VII	
Li_2O	BeO	B_2O_3	CO_2	N_2O_5	—	—	Oxides.
—	—	B_2H_6, &c.	CH_4	NH_3	OH_2	FH	Hydrides.
Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7	Oxides.
—	—	—	SiH_4	PH_3	SH_2	ClH	Hydrides.

Metals which form non-volatile hydrides exhibit the same valencies in these compounds as in the oxides; for example, K_2O, KH; CaO, CaH_2.

The periodic law constitutes a valuable criterion of valency, because the periodic group to which an element belongs indicates almost invariably the valency of the element in the highest oxide which it can form. The existence of super-oxides, such as Na_2O_2 and BaO_2, constitutes no real exception to this rule, because these compounds are constituted thus:

$$Na—O—O—Na, \quad Ba\begin{matrix}O\\|\\O\end{matrix}, \text{ or } \begin{matrix}Na\\Na\end{matrix}\!\!>\!O{:}O, \quad Ba{=}O{:}O;$$

and so the valencies of the metals are the same as in the corresponding basic oxides. The elements of Groups VI, VII, and VIII often fail to realize their maximum valency; and indeed some, e.g. iron, never exhibit the group valency. Since the chemical character of a compound depends largely upon the active valency of its nuclear element, the elements of these higher groups show great variety in the properties of their compounds, because they exhibit highly variable valency. The highest oxide is to be regarded as the typical oxide, provided it exhibits the valency of the group to which the element belongs; it is then found that lower oxides and their derivatives show relationships to oxides and their derivatives of similar type, but belonging to elements in other groups.

For example:

Derivatives of

Mn_2O_7	in	Group	VII	are	isomorphous	with	those of Cl_2O_7	in Group VII.
MnO_3	„	VII	„	„	„	SO_3	„	VI.
Mn_2O_3	„	VII	„	„	„	Fe_2O_3	„	VIII,
						and Al_2O_3	„	III.
MnO	„	VII	„	„	„	FeO	„	VIII,
						and ZnO	„	II.

Other examples might be given, all of which show that polyvalent elements, forming several classes of compounds, exhibit several relationships corresponding to these classes, and therefore that the type is the determining factor in chemical relationship. Consequently manganese, which can be septavalent, is not disqualified from appearing in Group VII by reason of relationships to metals in Groups VIII, VI, III, and II.

Uses of the Periodic Law.

Prediction of Unknown Elements.—In the periodic scheme, as first formulated by Mendeléeff, there were some significant omissions. The positions now occupied by scandium, gallium, and germanium were left blank, since no elements were known qualified to fill them. If every available space had been filled with the known elements, placed in the order of their atomic weights, there would have been no periodic system, or but a distorted one, because every element which now follows a space that should have been left unoccupied would thereby have been moved one space forward, and the arrangement of analogous elements in groups would have been interfered with. On the other hand, deliberately to leave certain spaces blank, so as to preserve the desired periodicity, was to suggest that elements remained to be discovered to fill these spaces, and so to provoke a severe test of the truth of the periodic law.

The latter alternative was chosen by Mendeléeff, and in particular the existence of three elements was foretold, which were named provisionally eka-boron,[1] eka-aluminium, and eka-silicon. The first of these lay between calcium and titanium in the periodic table; the other two were placed consecutively to fill two blank spaces between zinc and arsenic. Moreover, by reference to the properties of neighbouring elements in series and in group, it

[1] Eka is Sanskrit for one.

was possible to foretell with considerable accuracy the properties of these undiscovered elements.

This prophetic use of the periodic system by its discoverer has been rightly compared with the employment by Adams and Le Verrier of mathematical calculation to foretell the existence of the planet Neptune from observed irregularities in the movements of Uranus, and it has had an equally satisfactory vindication. For the elements scandium, gallium, and germanium, subsequently discovered, have been found to possess properties closely agreeing with those foretold by Mendeléeff. This is illustrated in the following comparison of eka-aluminium with gallium.

EKA-ALUMINIUM.	GALLIUM
Atomic weight, *cir* 68 Metal of density 5·9 and low melting-point; not volatile; unaffected by air; should decompose steam at a red heat and dissolve slowly in acids and alkalis. Oxide should have formula El_2O_3, density 5·5, and dissolve in acids to form salts of the type ElX_3. The hydroxide should dissolve in acids and alkalis. There should be a tendency towards the formation of basic salts. The sulphate should form alums. The sulphide should be precipitated by H_2S or $(NH_4)_2S$. The anhydrous chloride should be more volatile than zinc chloride. The element will probably be discovered by spectrum analysis.	Atomic weight, 69·9. Metal of density 5·94; melting at 30·15°; not volatile; unchanged in air; action on steam not known; dissolves slowly in acids and alkalis. Oxide, Ga_2O_3; density not known; dissolves in acids, forming salts GaX_3. The hydroxide dissolves in acids and alkalis. Salts readily hydrolyze and form basic salts. Alums are known. The sulphide can be precipitated by H_2S or $(NH_4)_2S$, but only under special circumstances. The anhydrous chloride is more volatile than zinc chloride. Was discovered by spectrum analysis.

There are other blank spaces in the periodic system which presumably correspond with hitherto undiscovered elements. Modern research, however, has shown that probably only three spaces remain unfilled, since most of the spaces shown in the table on p. 74 are obliterated when the table is rearranged according to recent knowledge.

The three elements required to fill these spaces are: another alkali metal to precede radium, one rare-earth metal, and a halogen element to precede radon. A fruitless search has been made for the analogue of cæsium, but the discovery of the two missing analogues of manganese has recently been announced.

Correction of Atomic Weight Values.

Since the periodic law requires sequence of atomic weight values and sequence of properties to be in accord, grossly erroneous atomic weight value placed in sequence must disturb the sequence of properties; or, conversely, if sequence of properties is maintained it will necessitate a departure from atomic-weight sequence. In either case the erroneous value is revealed when the element in question is considered in the light of the periodic law. Indeed the erroneous atomic-weight value must cause a position to be claimed for the element, which, according to its properties, should be occupied by another element, and must consequently leave vacant a place suited to the element and in accord with its true atomic weight. Therefore the periodic law is of value, not only for detecting false atomic-weight values, but also for suggesting true ones. For example, the atomic weight of cæsium was at first erroneously thought to be 123·4. This value would place cæsium after antimony, and, of course, cause the displacement of tellurium, iodine, and other elements one place to the right. Such a condition cannot be thought of; therefore the value 123·4 is condemned. On the other hand, since cæsium is an alkali metal it should follow rubidium in group, and consequently have an atomic weight of about 131·8, so that Cs − Rb = Rb − K = 45·35. The atomic weight of cæsium is now known to be 132·81, and so this metal occupies its proper place in the scheme. In the cases of beryllium, indium, and uranium the periodic law has furnished the means of deciding what multiple of the equivalent is the atomic weight. The equivalent weight of beryllium is 4·55, and the atomic weight of this element was at first thought to be 4·55 × 3 = 13·65. This value would place beryllium in an impossible position between carbon and nitrogen, whereas 4·55 × 2 = 9·1 would give it a place in harmony with the periodic law. Subsequent considerations have confirmed the value Be(Gl) = 9·1.

Indium with the equivalent weight 38·27 was thought to have an oxide InO, and atomic weight 76·54, which would place this element between arsenic and selenium, where it cannot stand. An atomic weight of 38·27 × 3 = 114·8, with the corresponding oxide In_2O_3, would satisfy the periodic law; and this value has subsequently been accepted on the grounds of specific heat.

The atomic weight of uranium was originally thought to be about 60, or else 120; but neither of these values enables the

element to be placed suitably in the periodic scheme. The value 240 was required by Mendeléeff, so that the element might become the last member of the sixth group, following tungsten. This high value, or more accurately 238·2, has been supported by the vapour-density method applied to the halides, and by the fact that uranium is radio-active, since radio-activity is characteristic of the heaviest atoms.

The criticism of the atomic weights of the elements by means of the periodic law may be carried further. The accepted atomic weight of argon is greater than that of potassium, that of cobalt is greater than that of nickel, and that of tellurium is greater than that of iodine; yet the individual members of these three pairs of elements are placed in the reverse order of their atomic weights in the periodic scheme, because their properties do not permit of any other arrangement. Repeated attempts were made in the case of tellurium to reduce the value of its atomic weight below that of iodine, but without avail, and it was supposed that the relationships of these three pairs of elements constituted exceptions to the periodic law. Such a conclusion was unsatisfactory; but the difficulty has been removed by the recognition of atomic number as the criterion which decides the position of an element in the periodic scheme; and the atomic numbers of the elements in question place them in a sequence which accords with their properties.

The Suggestiveness of the Periodic Law.

In spite of the apparent imperfections and anomalies it contains, the periodic law is true in principle. Indeed it cannot be doubted that the truth, beauty, and value of this law as an index to the material world have been enhanced by the discoveries of recent years. This fact is a challenge to the scientific imagination; it must provoke questionings and research. For example, in a group of allied elements, such as the *alkali metals*, Li, Na, K, Rb, Cs, there are series of compounds such as oxides, hydroxides, chlorides, sulphates, carbonates, and so forth, which may be expected to be related to one another somewhat as the metals themselves are related. The examination of the physical and chemical properties of these compounds may therefore be undertaken with a view to discovering the gradations which exist between them. Interesting relations will thus be established, and this fact will become apparent: that there is a break in the

gradation of properties between Na and K; in other words, that K, Rb, and Cs and their compounds are closely related, while Na and its compounds, as well as Li and its compounds, stand apart from them. The periodic classification affords an explanation of this phenomenon; it is that Na is situated in the second short period, whilst K occupies a different kind of position near the beginning of the first long period, and Rb and Cs follow K in quite analogous positions in subsequent long periods. Having observed this, the student may then remember that although caustic soda and caustic potash are thought of as very similar substances, sodium salts are after all not very similar to potassium salts, for they do not crystallize with the same amounts of water of crystallization as the latter, and frequently they are not isomorphous with them, while their solubilities in water are so different from those of potassium compounds that solutions of sodium salts are used to precipitate potassium, and vice versa.

At the other extremity of the periodic table the *halogens* present another interesting subject for study. The fact that the affinity for hydrogen diminishes from F to I in the hydrides HF, HCl, HBr, HI is well known, and is quite in accord with what occurs in other groups; e.g. in the hydrides OH_2, SH_2, SeH_2, TeH_2 in Group VI, or NH_3, PH_3 AsH_3, SbH_3, (BiH_3) in Group V; but fluorine is widely different from the other halogens. Why is this?

This is a sort of question that must be answered ultimately by reference to the constitution of the atom; but consideration elicits this remarkable fact: that all the elements of the first short period are unique, being widely separated in properties from those in the same groups which follow them. It suffices to draw attention to carbon, nitrogen, and oxygen, which cannot be properly classified with the elements succeeding them. Again, hydrogen fluoride differs remarkably in condensibility from the other halogen hydrides; is there any analogy to this phenomenon in neighbouring groups? Assuredly there is; if water were no more condensible than hydrogen sulphide, the world would be a very different place to live in!

In the region of the periodic chart where volatile hydrides occur the following compounds are found:

CH_4	NH_3	OH_2	FH
SiH_4	PH_3	SH_2	ClH
GeH_4	AsH_3	SeH_2	BrH
(SnH_4)	SbH_3	TeH_2	IH
	(BiH_3).		

The periodic law suggests a comparison between them in series and in group; and thus the following gradations of properties are discovered.

The hydrides diminish in stability with rise of atomic weight in every group. Thus, for example, in the fifth group ammonia is very stable, and is decomposed only slowly by the passage of electric sparks; phosphine, PH_3, is less stable than ammonia, and is rapidly decomposed by the same agency; AsH_3 is broken up into its elements when passed through a tube heated to 230°, SbH_3 is similarly decomposed at 150°, and BiH_3 is too unstable to be isolated.

In series, i.e. in the hydrides standing in horizontal lines, there is an increase of stability with rise of atomic weight, corresponding with the increase of non-metallic characters, and also the diminution of hydrogen valency, so that there is less hydrogen to be retained. Thus hydrogen fluoride is the most stable volatile hydride, and germanium and bismuth hydrides the least stable. It may be observed that Ge, As, Sb, and Bi are metalloids, that is, almost metals. No true metal forms a volatile hydride. The power to form alkyl compounds, i.e. compounds with radicles, such as methyl, $\cdot CH_3$, and ethyl, $\cdot C_2H_5$, is more extensive than that to form hydrides; so that some metals in the B sub-groups preceding in series the above non-metals form these so-called organo-metallic compounds. Perhaps the best known of these substances is zinc ethyl, $Zn(C_2H_5)_2$; but, in addition to zinc, cadmium, mercury, tin, lead, and bismuth form them, and thus come into line with the above non-metals, all of which form alkyl compounds as well as volatile hydrides.

Another interesting but rather difficult question is that of the relative acidic or base-producing power of these volatile hydrides. Consider the four hydrides:

$$CH_4, \quad NH_3, \quad OH_2, \quad FH.$$

Methane is inert; ammonia is base-producing, for its solution in water is alkaline owing to the reaction: $NH_3 + H^{\cdot} + OH' \rightleftharpoons NH_4^{\cdot} + OH'$; water is neutral, and hydrogen fluoride is acid. Why is not methane, CH_4, more base-producing than NH_3?—the gradation of properties seems to require it to be. The answer is that in CH_4 carbon is already saturated with hydrogen, so that this substance cannot form an additive compound with water or an acid as

ammonia does; for the peculiar base-producing power of ammonia is an additive property, viz.: $NH_3 + H^+ = NH_4^+$.[1]

Consider again the hydrides:

$$\begin{matrix} NH_3 & OH_2 \\ PH_3 & SH_2. \end{matrix}$$

There is a loss of base-producing power from NH_3 to PH_3, and an apparently analogous increase in acidity from OH_2 to SH_2; but it is difficult to generalize here, for ammonia is unique in base-producing power, just as nitrogen is unique as an element; and water, again, like oxygen, is unique in its properties. Moreover, it must not be concluded that increase in acidity of hydrides with rise of atomic weight in a group is general, for ClH, BrH, and IH are acids of about equal strength.

The comparison of properties of the oxides of elements in the various groups of the periodic system is a simpler and more satisfactory exercise. For there is in general a loss of acidic and a corresponding gain of basic properties with rise of atomic weight in a group. This is shown, for example, in the oxides

$$\begin{matrix} & N_2O_3 & P_2O_3 & As_2O_3 & Sb_2O_3 & Bi_2O_3, \\ \text{and} & N_2O_5 & P_2O_5 & As_2O_5 & Sb_2O_5 & Bi_2O_5. \end{matrix}$$

In the trioxides there is a gradual transition from wholly acidic, through amphoteric[2] to purely basic properties, and in the pentoxides from powerfully to very feebly acidic properties.

Again, the trioxides of Group VI A,

$$CrO_3, \quad MoO_3, \quad WO_3, \quad UO_3,$$

form an interesting series; for, in accordance with the above generalization, basic properties actually appear, together with acidic properties, in the oxide UO_3, which is basic with regard to one oxygen atom only, forming basic salts, such as $UO_2(NO_3)_2$, the uranyl salts.

Objections to the Periodic Law.

A consideration of the criticisms to which the periodic system has been submitted is valuable. If the criticisms are baseless, as some of them are, the process of their refutation will be illuminating; if they are valid, their consideration may exhibit the

[1] The meaning of this will appear when the subject of ionization is considered.

relations of the elements from a new point of view, and so increase our knowledge concerning them.

The most sweeping accusation which has been brought against the periodic system is that it places together dissimilar elements, whilst separating similar ones. It brings together the alkali metals and copper, silver, and gold in Group I, it is said—a most unnatural alliance. This objection has already been met by a denial of the statement that these dissimilar metals are brought together. It is further objected that the periodic classification separates copper from mercury and barium from lead. But it may be maintained that such separation is proper; for the similarities between the metals in these several pairs are superficial rather than fundamental, for copper and mercury are widely different in physical properties and in oxidizability; and, in spite of the fact that both metals form two series of salts, and that their lower chlorides are insoluble in water, there is little further resemblance between their corresponding salts. The differences between barium and lead are even more fundamental, so that to regard the elements as similar on account of the insolubilities of their sulphates, and the isomorphism of some other salts, is a grave error of judgment.

The discovery of argon, and the determination of its atomic weight, furnished material for adverse criticism of the periodic law. For not only was it supposed that no room could be found in the scheme for an element with such extraordinary properties as argon possessed, but the atomic weight of argon was found to be greater than that of potassium; and it was manifestly impossible to place this element between potassium and calcium. Then other inert elements were discovered — helium, neon, krypton, xenon, the companions of argon; and these have atomic weights less than those of the neighbouring alkali metals. Thus the atomic weight of argon is recognized as anomalous, like that of tellurium, and the inert gases therefore form a new group, which is like a *buffer* between the extremely different halogen elements and alkali metals; just as the metals of the eighth group intervene between manganese in Group VIIA and copper, silver, and gold in Group IB. So it is recognized that the elements of the argon family are properly placed as Group O, the periodic law is vindicated, and, in recogtion of their analogy with the noble metals, the elements concerned are sometimes called the noble gases.

The periodic law, however, needs no vindication. Modern

research, it is true, has modified it by causing the conception of atomic number to displace that of atomic weight; but this has served only to strengthen the law by removing its anomalies, so that it has now become the supreme generalization concerning the origin and constitution of matter as revealed by the inter-relations of the elements.

SUMMARY

PERIODIC LAW ACCORDING TO MENDELÉEFF.—The physical and chemical properties of the elements and their compounds are periodic functions of the atomic weights; *or*

If the elements are arranged in the order of increasing atomic weight, their properties vary definitely from member to member of the series, but return to a more or less similar value at fixed points in the series.

USES OF THE PERIODIC LAW.—Prediction of unknown elements. Correction of atomic weight values. Stimulation of thought and research regarding the elements.

CHAPTER V

THE MODERN VIEW OF THE ATOM

When the atom was introduced into science by Dalton it appeared in a theory brought forward to account for the laws of chemical combination; and since it was supposed to be an ultimate particle of matter the question of its structure did not arise, for structure involves parts. Newton had supposed that matter consisted of "solid, hard, impenetrable particles"; and although the atoms of different elements differed in weight, and presumably therefore in size, the reason for this was no more an active question than is the reason for the difference in size of the marbles in a bag to the boy who plays with them.

The question what the atoms were made of was, nevertheless, soon raised by Prout; and if it had been conceded that the atoms were made of hydrogen the great diversity of properties between the elements must have caused inquiry as to how one primordial material could give rise to such diversity. This inquiry might have become more urgent when periodicity of properties amongst the elements was discovered; but, owing to the suppression of Prout's idea, no inquiry regarding atomic constitution appears to have been made until recently. The generalization of Mendeléeff, however, that the properties of the elements are periodic functions of their atomic weights, appears inadequate apart from some idea regarding atomic constitution. For, consider the two short periods:

Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar.

Continuous increase of atomic weight is connected with progressive change of properties from Li to Ne; but why should this progressive change stop at Ne; why should the addition of about 3 units of atomic weight to Ne produce an element (Na) which with some modification reproduces the properties of Li? This fact was long ago represented by de Chancourtois by means of the "telluric

screw", a spiral curve on which the elements were marked; but the representation of a fact is a very different thing from its explanation. There is no explanation, unless the elucidation of atomic constitution can provide it. So the periodic system demands a theory of atomic constitution to give it meaning.

The facts of electrolysis investigated by Davy, the electrochemical theory of Berzelius, and the laws of electrolysis established by Faraday, have some bearing on the constitution of the atom, though this was not realized by these chemists. Metals were elements whose atoms could carry positive charges and travel to the negative electrode or cathode during electrolysis; non-metals were elements whose atoms carried negative charges and in electrolysis travelled to the positive electrode or anode. Thus elements were distinguished as electropositive or electronegative, and electricity and chemical affinity were seen to be closely allied; but these were forms or components of energy rather than of matter; and that electricity itself could form part of a material atom was an idea not entertained.

Nevertheless Faraday showed that an ion during electrolysis was always associated with a fixed quantity of electricity, a bivalent ion being associated with twice as much electricity as a univalent ion. This fact is now interpreted as signifying that electricity, like matter, is atomic, but such a conclusion was not reached by Faraday. The smallest quantity of electricity associated with an atom of matter in electrolysis was called by Johnstone Stoney, in 1874, an *electron*, and so at that date was recognized as an atom of electricity.

No real beginning, however, was made towards any knowledge regarding the constitution of the atoms of matter until these atoms themselves furnished evidence regarding their internal contents and structure. The first evidence of this kind was the outcome of the work of Crookes on high vacua. Crookes found that when an electric discharge took place through a high vacuum rays travelled from the cathode in straight lines, that these rays caused the glass of the containing vessel to fluoresce, but that they were intercepted by a material object which thus caused a shadow. These rays were considered by Crookes to consist of matter in an ultra-gaseous state, and they were subsequently called "cathode rays" or "cathode particles". Sir J. J. Thomson, in 1897, investigated these particles, found that they travelled with a velocity about

one-tenth that of light, and proved that their mass was 1/1850th part of the mass of a hydrogen atom. The most significant discovery concerning them, however, was that their nature was independent of the gas originally present in the vacuum tube, and of the metal used as cathode. Consequently they were judged to be not only disintegration products of material atoms, but invariable constituents of those atoms. This was the first piece of evidence regarding the constitution of the atoms of matter.

The next evidence was furnished by the facts of radioactivity, which began to be discovered after attention had been drawn by Röntgen to the fluorescence of the glass of the Crookes tube as the source of those peculiar rays called X-rays.

The radioactivity of uranium, radium, and thorium was found to be caused by the emission of two kinds of particles known respectively as α- and β-particles; and after a time these particles were recognized to be actually disintegration products of the atoms of those heavy metals, and were likewise identified. Thus an α-particle was found to be an atom of helium carrying a double charge of positive electricity, and a β-particle to be the same as a cathode particle which was now also identified with the *electron*, the atom of negative electricity.

Yet α-particles, i.e. positively charged atoms of helium, are not the smallest known particles of matter, for there are ions of hydrogen, or hydrogen nuclei, i.e. positively charged atoms of hydrogen which owe their charge to the loss of an electron. It has been inferred, without direct experimental evidence it is true, that the atom of helium has been formed by the condensation of four hydrogen atoms; i.e. four hydrogen nuclei plus four electrons have produced one helium atom; and further, that two of the electrons in the helium atom are detachable from that atom so as to leave a helium ion or doubly charged helium atom, which is the α-particle derived from radioactive matter. Incidentally it must be noted, however, that helium ions are unknown in chemistry, although they have been recognized in work upon positive rays; we have no power of removing two electrons by chemical means from the helium atom so as to produce a helium ion or α-particle. Moreover, α-particles, ejected from the atoms of radioactive elements, soon take to themselves electrons, and become helium atoms, as was shown by Ramsay and Soddy.

A helium atom or ion has never been known to yield hydrogen

atoms or ions by disruption, and hydrogen atoms or ions have never been observed as the products of spontaneous radioactive change. Nevertheless there is direct evidence that some of the lighter atoms of matter contain hydrogen nuclei as integral parts of their structure. This evidence has been furnished by the experiments of Sir Ernest Rutherford,[1] who has shown that hydrogen nuclei are discharged from the atoms of boron, nitrogen, fluorine, sodium, aluminium, and phosphorus under bombardment by α-particles; and it is significant that elements whose atomic weights are multiples of four, i.e. carbon and oxygen, do not yield hydrogen nuclei under such treatment. Therefore it is concluded that the massive parts of those atoms which contain hydrogen nuclei contain them as such in addition to the requisite number of helium nuclei. For example: $N = 14 = 3\,He + 2\,H$; and $F = 19 = 4\,He + 3\,H$.

Thus a clear idea has been reached concerning the different parts of which all atoms are composed. They are composed of hydrogen nuclei, helium nuclei (α-particles), and electrons (β-particles); and if each helium nucleus is regarded as reducible to four hydrogen nuclei, then the atoms of matter consist of hydrogen nuclei and electrons alone.

Now the electrons are atoms of negative electricity, and in an electrically neutral atom these must be balanced, whatever their number, by an equal number of atoms of positive electricity. These atoms of positive electricity must be the hydrogen nuclei, which are the only other constituents of a material atom; they are called *protons*; so that every neutral atom is composed of protons and electrons in equal numbers.

It is now desirable to discover something concerning the manner of distribution of the protons and electrons in an atom; and the first insight into this manner of distribution is gained by considering and placing in contrast two kinds of change which some atoms can undergo: chemical change, and radioactive change.

The main characteristic of chemical change in general is that it can be initiated by man and is reversible, whilst radioactive change is beyond man's control and, as far as we know, is irreversible. It is concluded from this—and the conclusion is now supported by strong evidence—that chemical change touches only the surface of the atom, whilst radioactive change affects its internal parts.

[1] *Trans. Chem. Soc.*, 1922, *121*, 400.

That chemical change affects even the surface of an atom is an idea which would not have been acceptable to Newton or Dalton, who regarded the atoms of matter as unchangeable. Indeed, a generation ago this idea would have been thought revolutionary. Chemical affinity, manifested through valency, was a force exerted by atoms, but exerted outside themselves; the atoms came unscathed through chemical change; they bore no superficial wounds to show that they had been in action. That chemical change actually affects and alters the surface of an atom is the idea which underlies the present-day electronic theory of valency; and in developing this theory it is well to begin with electrolysis.

It will be remembered that the electric charges upon the ions in an electrolytic solution are due to definite quantities of electricity which are the electrons. The question may be asked: whence do the electrons come which are associated with the atoms of matter in electrolysis? They are not brought into existence by the current; they must therefore be derived from the compounds in solution. Sodium chloride, for example, must contain electrons, which become available as electric charges when this compound is dissolved in water. Such a view is consistent with the theory of Arrhenius, which supposes that when a salt or other electrolyte dissolves in water it breaks up spontaneously into charged ions, which are ready to carry or be carried by the current when it comes.

The late Sir William Ramsay represented the electron in a sodium chloride molecule, and the behaviour of the molecule when it dissolved in water, in the following manner:

$$\mathrm{NaECl} \rightleftharpoons \mathrm{Na^{\cdot}} + \mathrm{ECl'}.$$

Thus an electron, as an atom of the chemical element electricity, was the binding material between the atoms of Na and Cl, but when the salt was dissolved in water this electron which was previously shared in common by both atoms became attached solely to the chlorine atom, with the consequence that the sodium atom by the loss of negative electricity became positively charged and functioned as a cation, whilst the chlorine atom, by the gain of negative electricity consequent on having the electron to itself, became negatively charged and was the chloride ion. This idea has now been developed so that the neutral sodium atom is believed to have on its surface one loosely attached electron which it easily parts with so as to become a univalent positive ion, whilst the

neutral chlorine atom is believed to receive easily and accommodate an electron, thus becoming a univalent negative ion, the chloride ion. So the chemical union between sodium and chlorine is believed to consist in the transfer of an electron from each sodium atom to each chlorine atom.

Such a view, however, necessarily modifies the electrolytic dissociation theory of Arrhenius. Ions are formed, according to the most recent view, when the compound is produced; for the transfer of electrons converts neutral atoms into ions. Sodium chloride is thus always ionized, it would not otherwise be sodium chloride; but in the solid state the positive and negative ions are held together by electrostatic attraction, just as two oppositely charged pith balls are attracted together. When, however, the salt is dissolved in water, the electrostatic attraction gradually gives way, and the ions become dissociated. We must not now speak of ionization as a consequence of solution, for that has occurred already in the formation of the salt; but electrolytic or ionic dissociation is a suitable term to describe the separation, through the medium of the solvent, of the already existing ions.

The idea of chemical change thus briefly outlined, by which a salt is produced by the transfer of electrons from metal to non-metal, clearly suggests that in the act of union the metallic atom loses part of its substance and the non-metallic atom receives an addition to its substance; that is to say, the atoms themselves suffer change in their substance. Thus in contrast with the old doctrine of the unchangeableness of the atoms of matter we have the new doctrine that in every chemical change the atoms suffer change. Nevertheless this change is superficial, and its reversibility depends upon its superficiality.

It is quite different with regard to radioactive change. This change is believed to affect the innermost recesses of the atom; that is to say, the nucleus where are situated the protons which, being hydrogen nuclei, constitute its effective mass. Such a change is profound; it has not been initiated by man; and when it occurs it is irrevocable, and so radically alters the properties of the atom that elemental transmutation is said to take place. Sometimes only electrons, or β-particles, are ejected from the atoms of an element by radioactive change; then the mass of an atom is unaffected though the properties of the element are altered. If, however, an α-particle, i.e. a helium nucleus, with an atomic weight

of 4, is cast forth, the atom changes not only its chemical properties but also its mass, for it becomes an atom having an atomic weight 4 units less.

It is possible, however, to show a little more clearly what is the effect of the loss of α- and β-particles by the atoms of an element through radioactive change.

When a β-particle is ejected from the nucleus of an element the predominating positive charge there is increased by one unit, and the atom as a whole will consequently carry one positive charge if it was previously neutral; it would therefore become a univalent positive ion if it did not at once take to itself an electron from outside. When such an electron is assimilated it does not enter the nucleus, or the radioactive change would be reversed; it remains on the exterior of the atom as a valency electron. The negative valency of the neutral atom, i.e. its power of appropriating electrons, will consequently be reduced by one. With regard to the periodic system, then, the loss of an electron from the nucleus of an atom transfers that atom one place to the right in the table. Examples of such change, with a corresponding effect on chemical properties, are known; e.g. radium-B in Group IVB, by losing a β-particle from the nucleus of its atom, becomes radium-C in Group VB. The fact, however, must be emphasized that there is no loss of mass in this radioactive change, for even the loss of an electron from the nucleus is compensated for by the gain of an electron at the exterior. Therefore it appears that two separate elements, as radium-B and radium-C, judging from the chemical properties, seem to be, may have the same atomic weights. Such elements are called *isobares*. Stress, however, must be laid upon the difference between the loss of an electron from the nucleus and from the exterior or sheath of an atom. The latter is the accompaniment of any change by which a neutral atom becomes a univalent positive ion; and it has no further significance.

When an α-particle is ejected from the nucleus of an atom two kinds of loss are sustained by the atom. The first kind of loss is that the atom loses two units of positive charge, since the α-particle is a helium atom carrying two units of positive charge, this particle being composed ultimately of four protons and two electrons, which are associated together inseparably, so far as experience goes. Such a change, when it has been compensated for by the eventual escape of two electrons from the atomic surface, transfers an element two

places to the left in the periodic system, because the positive valency of the neutral atom, i.e. its power of losing electrons, has thereby been reduced by two. Various examples of such radioactive change are known; e.g. the atom of radium in Group IIA, by losing an α-particle, becomes an atom of radium-emanation or radon in Group O. The second kind of loss sustained by an atom which ejects an α-particle is a loss of mass. Since an α-particle is a helium nucleus with atomic weight of 4, 4 units of mass disappear. So whilst the atomic weight of radium is 225·95, that of radon is 222.

Now the atoms of the heaviest elements are capable of successive radioactive changes in which both α- and β-particles are ejected. Suppose that an atom loses first an α-particle and then successively two β-particles. The loss of an α-particle moves the element two places to the left in the periodic table, and the loss of two β-particles brings it back again two places to the right, leaving it in the same group it occupied originally. This is the kind of change uranium, for example, undergoes. U_I in Group VIB loses an α-particle, with 4 units of mass, and becomes UX_1 in Group IVB; UX_1 loses a β-particle, becoming UX_2 in Group VB; and then UX_2 also loses a β-particle, becoming U_{II}, which again is in Group VIB. Thus U_I and U_{II} are both in Group VIB, having atoms which differ by 4 units of mass, but are chemically indistinguishable. Such elements have been called by Soddy *isotopes*.

The following conclusion regarding the manner of distribution of the protons and electrons in an atom has now been reached.

All the protons with some of the electrons are situated in the nucleus of the atom; the remainder of the electrons are external to the nucleus, and some of them are at the extreme superficial limit of the atom—in its sheath, that is to say. These external electrons are removable by chemical change, but the nucleus remains intact in all chemical changes, and is affected only in radioactive change or when submitted to intense bombardment by α-particles (Rutherford). In a neutral atom the number of protons must be equal to the number of electrons; therefore the number of electrons external to the nucleus must be equal to the excess of protons over electrons in the nucleus.

It thus appears that there is a number which is both the excess of protons over electrons in the nucleus of an atom and the number of electrons external to the nucleus when the atom is uncharged.

This number characterizes the atom as regards its chemical properties; it is called the *atomic number*. It does not depend upon the number of protons in the nucleus; for the loss from the nucleus of four protons and two electrons, constituting an α-particle, together with two more electrons, leaves the atomic number the same and the chemical properties the same, as, for example, was shown in the case of the uraniums cited above. Nevertheless diminution in the number of protons involves diminution in atomic weight. Since, therefore, atomic weight may alter while chemical properties remain identical, the generalization that the properties of the elements are periodic functions of their atomic weights no longer appears strictly true; for it is apparent the atomic number takes precedence over atomic weight so far as chemical properties are concerned.

Now it has already been seen, in the discussion of the periodic law according to Mendeléeff, that the question of atomic weight is not paramount in deciding the position which an element is to occupy in the system. The cases of argon and potassium, cobalt and nickel, and tellurium and iodine will be recalled. In each of these pairs of elements the first-named member has a greater atomic weight than the second. Yet it was agreed to place the elements in the order named because their properties demanded this in spite of their atomic weights.

If every element is to have an atomic number, these numbers cannot all be decided without reference to the total number of existing elements from hydrogen to uranium. The idea of numbering the elements is not new; it was entertained by Newlands, who, however, could not carry his law of octaves very far because he did not recognize gaps in the procession of the elements. Mendeléeff recognized the gaps but did not lay stress upon atomic number. No difficulty now arises in numbering the elements until the rare-earth metals are reached; for the only vacant place previous to these metals is that following molybdenum, where an undiscovered analogue of manganese should be. Decision as to the number of rare-earth metals existing, however, has always been a difficulty.

This difficulty has now been overcome by the discovery of an experimental method of determining the atomic number of an element. This method is the result of the work of Moseley on X-ray spectra.[1] It was discovered by Moseley that these spectra

[1] For an account of this work a special textbook should be consulted, e.g. *The Structure of Matter*, by Dr. J. A. Cranston.

are much simpler and more regular than the luminous radiation spectra of the elements, since the principal lines of the X-ray spectra of successive elements follow one another in regular gradation like a flight of steps, so that a missing element would be revealed by a gap in the series of spectra. Moreover, the vibration frequency V of the principal line in the X-ray spectrum of an element is connected with the atomic number N by the following formula, where A is a constant:

$$V = A(N - 1)^2.$$

Moseley's results may be summarized thus:

1. Every element is characterized by an integer N, which determines its X-ray spectrum.

2. This integer N, the atomic number of the element, is identified with the numerical value of the charge of positive electricity on the atomic nucleus.

3. The order of the atomic numbers is the same as that of the atomic weights, except where the latter disagrees with the order of the chemical properties.

It is interesting to report that the atomic number of uranium, the last of the elements, is 92; thus there are 92 elements in all, from hydrogen to uranium. Of these 87 have already been discovered, and five remain to be discovered; these are two analogues of manganese, numbers 43 and 75;[1] a rare-earth, number 61; a halogen to follow iodine in group, number 85; and an alkali metal to follow cæsium in group, number 87. With regard to element number 72, it is not yet quite decided whether this should be called celtium or hafnium.

Further, the placing of argon and potassium, cobalt and nickel, tellurium and iodine in their accepted order according to chemical properties rather than atomic weights has been justified; for the atomic numbers of these elements are: 18 and 19, 27 and 28, 52 and 53 respectively.

Since the atomic weight of an element must now be subordinated to its atomic number, it follows that the statement of the periodic law according to Mendeléeff must be modified.

Thus the statement that the properties of the elements are periodic functions of their atomic weights becomes:

[1] These appear recently to have been discovered, and it is proposed to name them masurium (Ma) and rhenium (Re) respectively.

The properties of the elements are periodic functions of their atomic numbers.

This is the *periodic law* in its modern form.

Further, since the order of sequence and total number of the elements are now definitely known, it is possible to develop the periodic system itself in a form likely to be permanent. These are the questions to be decided: (i) how many periods are there; (ii) how many elements are there in each period?

Already a partial answer has been given to these questions; for Mendeléeff showed short and long periods containing, if the inert gases are included, 8 and 18 elements respectively; and, as was stated on p. 77, Werner, in 1905, proposed a long period of 33 elements to include the rare earths. Rydberg, in 1897,[1] had attempted a classification of the elements according to numbers derived from their atomic weights, and Rydberg's system, corrected by means of Moseley's atomic numbers, now furnishes a very simple formula to express the numbers of the elements in successive periods.

The atomic numbers of the inert gases are these:

He	Ne	Ar	Kr	Xe	Rd
2	10	18	36	54	86;

therefore the successive periods, which are completed by these elements, contain the following numbers of elements:

$$\begin{aligned} & 2, \quad 8, \quad 8, \quad 18, \quad 18, \quad 32 \\ = 2[1^2, & \quad 2^2, \quad 2^2, \quad 3^2, \quad 3^2, \quad 4^2]. \end{aligned}$$

The successive periods or series represented by these numbers are called the Rydberg series; and although no ultimate explanation of these numerical relationships has yet been given, they are taken to express the manner of arrangement of the elements in series in the periodic system. There are thus six series or periods, with the beginning of a seventh, containing the elements from 87 to 92. So the modern periodic system, according to the Rydberg series, takes the form on p. 104.

If a clear idea of atomic number has now been gained, this will furnish a more complete conception of the nature of isotopes. It will be remembered that isotopes, according to the observations and definition of Soddy, were elements which, having made excursions into different groups of the periodic system, on account

[1] *Zeit. phys. Chem.*, 1897, *14*, 66.

PERIODIC TABLE OF THE ELEMENTS—ACCORDING TO ATOMIC NUMBERS

No. of Elements																																					
2 = 2 [1²]	1																H 1	He 2																			
8 = 2 [2²]	2													Li 3	Be 4	B 5	C 6	N 7	O 8	F 9	Ne 10																
8 = 2 [2²]	3													Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	Ar 18																
18 = 2 [3²]	4								K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36											
18 = 2 [3²]	5								Rb 37	Sr 38	Yt 39	Zr 40	Nb 41	Mo 42	—[1] 43	Ru 44	Rh 45	Pd 46	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54											
32 = 2 [4²]	6	Cs 55	Ba 56	La 57	Ce 58	Pr 59	Nd 60	— 61	Sa 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71	Hf 72	Ta 73	W 74	—[2] 75	Os 76	Ir 77	Pt 78	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	— 85	Rd 86				
Incomplete		— 87	Ra 88	Ac 89	Th 90	Bv 91	U 92																														

[1] ? Masurium (Ma). [2] ? Rhenium (Re).

of radioactive changes in their atoms, were accommodated in the same place in the system, either permanently, or else only temporarily because further radioactive changes removed them from that place. It will now be seen that since isotopy relates to elements having the same atomic number irrespective of their atomic weights, it is not necessarily limited to radioactive elements. Indeed there is no *a priori* reason why the phenomenon should not occur widely throughout the whole range of the elements. If, however, it did so occur, the phenomenon would result from different atoms of what is chemically the same element with the same atomic number having different atomic weights because of different numbers of protons in their nuclei.

The idea that different atoms of the same element may have slightly differing relative weights is not new. It was put forward by Crookes in 1888, with reference to yttrium, in the following words: "The atomic weight which we ascribe to yttrium therefore merely represents a mean value around which the actual weights of the individual atoms of the 'element' range within certain limits. But if my conjecture is tenable, could we separate atom from atom, we should find them varying within narrow limits on each side of the mean."

If this possibility is admitted for yttrium, we cannot refuse to consider it for other elements, as indeed Crookes realized. That the atomic weight of any of the elements represents not the weight of every atom of that element, but the mean weight of an unnumbered host of those atoms, is an idea which evidently has some connection with the subject of isotopes; but how can such an idea be put to the test, and how can it be regarded as any other than an unprofitable speculation? A banker in pre-war days would weigh a hundred sovereigns instead of counting them, because he knew the average weight of such a number to be constant. Yet the sovereigns might have been weighed one by one on a delicate balance, and differences in their weights detected. So the chemist weighs many atoms of an element together, and finds the average weight of the same number always the same. To detect differences in individual weights, however, he would need to weigh the atoms separately; but that he cannot do.

Yet an instrument called a mass-spectrograph has been devised by which the atoms of an element are separated in such a manner, when charged electrically, that they register themselves on a photo-

graphic plate in positions which depend only on their individual masses.

Sir J. J. Thomson began work upon this subject in 1912, carrying out what was called *positive-ray-analysis*, because the "rays", now called "mass rays", which produced the effects were positively charged particles or ions. Thus Thomson separated gaseous neon, with an atomic weight of 20·2, into atoms, most of which were shown to have a relative weight of 20, and a much smaller number a relative weight of 22. So it was demonstrated that the element neon is a mixture of isotopes, its accepted atomic weight being the mean of the atomic weights of the separate isotopes present in the requisite numerical proportions, viz. 90 per cent of Ne^{20} and 10 per cent of Ne^{22}.

After the war Dr. F. W. Aston developed the method of Thomson and elaborated the instrument, and thus has been able to show by means of "mass spectra" that a large proportion of the chemical elements are mixtures of isotopes. Up to the end of 1924, 56 elements had been examined by Aston and others, and of these 25 were found to consist of identical atoms, and 31 of mixtures of isotopes.

Now the elements, all of whose atoms are identical in weight, are also elements whose accepted atomic weights approximate very closely to whole numbers, whilst among the elements which are mixtures of isotopes are those whose atomic weights are far removed from whole numbers. Examples of the former are: C = 12·00, N = 14·01, O = 16, S = 32·06, P = 31·02, Cr = 52·00; and of the latter: Mg = 24·32, Cl = 35·46, Cu = 63·57, Zn = 65·38, Se = 79·20, Kr = 82·92, Hg = 200·60.

It is obvious, however, that the possession by an element of an atomic weight which is approximately a whole number is no proof that the element does not consist of isotopes; for the mean of a number of isotopes might happen to be nearly or exactly a whole number. Such is the case not only with Kr = 82·92 but also with Br = 79·92, which is a mixture of the isotopes Br^{79} and Br^{81}.

The question here arises how many isotopes of an element may there be, and what range of atomic weight, or mass number as it is now called, is possible. The answer seems to be that 8 is the maximum difference in mass number, and therefore 9 the maximum number of isotopes possessed by any element. Thus the following

data for tin and xenon, as well as for potassium and copper, are given by Aston (*Chem. Soc. Ann. Report*, 1924):

Element.	Atomic Number.	Atomic Weight.	Minimum Number of Isotopes.	Mass Numbers of Isotopes in order of Intensity.
Sn	50	118·70	7 (8)	120, 118, 116, 124, 119, 117, 122, (121)
Xe	54	130·20	7 (9)	129, 132, 131, 134, 136, 128, 130, (126), (124)
K	19	39·10	2	39, 41
Cu	29	63·57	2	63, 65

The greatest numbers of isotopes are possessed by elements of even atomic number; indeed elements of odd atomic number, e.g. potassium and copper, seem to consist of not more than two isotopes whose mass numbers differ by two units.

It appears that isobares are present amongst the above isotopes; e.g. Sn^{124} and Xe^{124}, provided the latter value is substantiated. Yet although some of their atoms have equal masses, tin and xenon are entirely distinct elements; for whilst the number of protons in the nuclei of their atoms may be the same, the numbers of electrons, and hence of electric charges therein, must differ. Other examples of isobares are furnished by Ar^{40}, Ca^{40} and Ge^{74}, Se^{74}. A striking fact in connection with the subject of isobares is that tellurium with mass numbers 120, 130, 126, and atomic weight 127·5, or more probably 127·8, shares all those numbers with xenon, with which it is thus trebly isobaric. Iodine, however, with atomic weight estimated to be 126·92, consists of I^{127} only.

The mass numbers of atomic isotopes are always given as whole numbers, whilst the estimated atomic weights of the elements are often fractional. Thus is raised a question which it is necessary to discuss. The mass of an atom is due to its protons, and a proton is a hydrogen atom minus an electron, which thus has a mass of 1·008 when O = 16·00.

The oxygen atom contains 16 protons, yet its mass is not quite 16 times the mass of a proton. This loss of mass is attributed to a "packing effect" in the nucleus, where the additive law of mass is not obeyed. On the basis of O = 16·00, however, the atomic masses of the isotopes are known to conform to the whole number rule except for a few small variations.

Thus since the masses of the individual atoms of all the elements

are, within a close approximation, whole numbers when O = 16·00, it is clear that the fractional atomic weights with which we have been long familiar, and which we are still compelled to employ in accurate analytical work, are averages due to mixtures of isotopic atoms; and so we understand why the atomic weight of an element which does not exhibit isotopy is very nearly, if not precisely, a whole number.

A further question connected with isotopy is this: If the same element is found in different parts of the world, will it always have the same estimated atomic weight? The idea that the same element, obtained from different sources, may have differing atomic weights is a disturbing one which strikes at the foundation of all accurate chemical work. For example, a redetermination of the atomic weight of antimony has resulted in a drastic change from 120·2 to 121·76. Can it be that different isotopic mixtures of antimony atoms have yielded those discordant results? This is believed not to be the case; but it is thought, rather, that the new figure is a correction of the old. Indeed there is abundant evidence that the atomic weights of naturally occurring elements which are not of radioactive origin are always constant whatever the sources of the elements. Thus cobalt and nickel of meteoric origin have the same atomic weights as the terrestrial elements, and the same is true of silicons from cosmic and terrestrial sources. Nevertheless it is highly desirable for those who undertake the redetermination of atomic weights to state the source of their material.

So far as present knowledge goes, the experimental atomic weights of normal inactive elements are still to be regarded as constants of nature, since nature has effectively mixed her isotopes, and never sorts them out again. Nevertheless the proved existence of isotopes is a challenge to man to separate them. Chemical methods of separation are unavailing, since isotopes do not differ in chemical properties; but physical methods, such as fractional diffusion and distillation, have been attempted with some success in the case of chlorine, mercury, and perhaps zinc (*Chem. Soc. Ann. Report*, 1922).

The case is very different with an element which is the residue of radioactive change. The uranium atom, for example, with atomic weight 238·17, passes through a succession of radioactive changes, in which it loses eight α-particles as well as β-particles, the final product being lead. This lead, therefore, should have an atomic

weight of 238·17 − 32 = 206·17. Now uranium minerals are found to contain a small proportion of lead, and the lead extracted from such minerals has been estimated to have an atomic weight of 206·46, whilst that of ordinary lead, not associated with radioactive material, is invariably found to be 207·20.

Again, the thorium atom, with atomic weight 232·15, loses six α-particles in the series of radioactive changes which end in lead; therefore the lead derived from thorium would be expected to have an atomic weight of 232·15 − 24 = 208·15. Lead obtained from thorite has been found experimentally to have an atomic weight of 207·77; which, although a little lower than that it would be if the lead were derived from thorium alone, is considerably higher than the atomic weight of ordinary lead.

Uranium-lead and thorium-lead are indistinguishable from ordinary lead in chemical properties and in all physical properties except density. Thus three leads have been named which, chemically speaking, are one lead. These, with their experimental atomic weights and densities, are:

	Uranium-lead.	Thorium-lead.	Ordinary Lead.
Atomic weight ...	206·08	207·77	207·20
Density	11·213	11·376	11·352
Atomic volume ...	18·28	18·26	18·25

It is seen, moreover, that the densities of these leads vary as their atomic weights, so that their atomic volumes are constant.

There is more to tell about the internal structure of an atom. Since an atom consists of a nucleus and surrounding electrons, it is desirable to gain some idea of the size of the nucleus as compared with that of the atom as a whole. The experiments of Rutherford on the scattering of α-particles yield the desired information. These experiments have already been referred to because they furnish information regarding the description of the atoms of some of the lighter elements; but if attention is concentrated on the tracks of the α-particles themselves rather than on the havoc they work by their bombardment, some quite different information is obtained.

When the α-particles from a radioactive source traverse a gas, their tracks can be made visible by the condensation of supersaturated aqueous vapour which occurs along them. Thus it is discovered that whilst some of the α-particles undergo sharp

deflections, these deflections are many times fewer than they would be if collision with an atom as a whole caused deflection. So it is concluded that a large proportion of the α-particles pass through the atoms as through empty space, and that only when an α-particle collides with or comes very near to a nucleus is it deflected. Thus it has been calculated, owing to the rarity of these collisions, that the diameter of the nucleus of an atom is about one ten-thousandth part of the diameter of the entire atom.

On account of this relation of the nucleus to the surrounding electrons, an atom of matter has been compared with the solar system, the nucleus being analogous to the sun, and the electrons to the planets.

The different planets of the solar system have different orbits, and they revolve round the sun. Have the planetary electrons of an atom different orbits, and do they revolve round the nucleus in their several orbits? This is a question to which some answer must now be given, though the details of the answer are not yet beyond the region of controversy.

The number of electrons external to the nucleus of an atom of an element is the same as the atomic number of the element; and thus with elements of high atomic number these electrons are numerous. In the atom of uranium there are 92 electrons external to the nucleus, and it is not to be supposed that these are all situated or revolve on the surface of a single shell or envelope. Rather must it be supposed that the electrons are distributed in a number of shells which succeed one another like the layers of an onion. How many electrons are present in each layer is a question on which in some cases there is difference of opinion. It must be remembered, however, that since the electrons on the outer layer of the atom, which is called the sheath, are the valency electrons, their number will be related to the valency of the element; and further, that since the atom of an inert gas has no valency, the sheath of such an atom will presumably consist of a completed layer of electrons, to or from which no electron can be added or removed.

To form a mental picture of the structure of the atoms of matter it will be best to begin at the beginning, with hydrogen. The neutral hydrogen atom consists of 1 proton + 1 electron, and the helium atom of 4 protons + 4 electrons, 2 of these electrons being bound up in the nucleus with the 4 protons, and the other

two being in a sheath which is complete since the helium atom manifests no valency, although it can exist momentarily without these two electrons as an α-particle ejected from a heavy atom during radioactive change. A consideration of the hydrogen atom under different circumstances will illuminate the subject of valency. When a hydrogen atom becomes a cation, i.e. the hydrion, as in the formation, say, of an acid in aqueous solution, this atom parts with its solitary electron and becomes reduced to a naked proton. It is possible, however, for the hydrogen atom to assimilate a second electron and so become an anion. This is shown by the fact that lithium hydride, LiH, yields on electrolysis hydrogen at the anode. Thus the hydrogen atom shows a tendency either to lose its single valency electron, or more rarely to gain another, by which means it would assume an external configuration characteristic of the uncharged helium atom.

Now consider the short period Li to Ne.

	Li	Be	B	C	N	O	F	Ne
Atomic number ...	3	4	5	6	7	8	9	10
Number of electrons in sheath of neutral atom	1	2	3	4	5	6	7	8
Valency (Abegg) normal ...	+1	+2	+3	±4	−3	−2	−1	0
Valency (Abegg) contra ...	−7	−6	−5		+5	+ 6	+7	

The atomic number of each atom in this period exceeds the number of electrons in the sheath of the neutral atom by two, because there are two electrons in the under layer which correspond with the two electrons in the complete sheath of the helium atom. Now when the significance of the numbers in the above table is understood, the nature of valency will stand revealed.

It is the great merit of Abegg[1] to have drawn attention to the fact that the sum of the hydrogen and oxygen valencies of a number of elements is equal to 8, e.g.

SiH_4	PH_3	SH_2	ClH
SiO_2	P_2O_5	SO_3	Cl_2O_7,

and to have derived therefrom the theory of normal and contravalencies, an example of which is given in the table above. According to Abegg, the normal valencies of an element are the more usual and characteristic; the contravalencies are more seldom

[1] *Z. anorg. Chem.* (1904), *39*, 330.

exercised, at any rate with the more extreme members of a period. Now if, in addition to this, valencies are regarded as positive or negative according to whether they are exercised towards electronegative or electropositive elements respectively, and it is supposed that the actual exercise of valency implies the loss or gain of electrons by the sheath of an atom, and further, that every atom undergoing chemical combination tends to assume the condition of an inert gas as regards its sheath, then the following ideas regarding the valencies of the elements of the first short period follow.

Lithium, with 1 electron in its sheath, can assume the external condition of an inert gas either by losing 1 electron, so as to simulate the helium atom which precedes it, or by gaining 7 electrons, so as to have a sheath identical with that of a neon atom. It is, however, much easier for an atom to lose 1 electron than gain 7; hence lithium invariably manifests a valency of +1 by becoming a cation carrying one positive charge, rather than a valency of −7, that is, an anion carrying seven negative charges.

Similarly beryllium loses 2 electrons on ionization, becoming a bivalent cation, rather than gaining 6 electrons to become a sexavalent anion.

With carbon, however, the chances of losing or gaining electrons are about equal; and with nitrogen the alternative of the loss or gain of electrons also exists. Oxygen and fluorine, however, are too electronegative ever to become cations by losing electrons, the contravalencies, at any rate in the case of fluorine, being entirely latent.

The same considerations apply to the next short period from sodium to argon, the only difference being that the atoms of both the inert gases, neon and argon, to the external configuration of which the intervening elements tend to conform when they enter into chemical union, are both alike in having 8 electrons in their sheaths.

So far it appears that valency depends on the number of electrons in the sheath of an atom; and whether that atom exercises positive or negative valency depends upon whether it more easily loses or gains electrons, so as to present a completed sheath on its outer surface.

Langmuir, who, following G. N. Lewis, has developed this idea,[1] carried it further, and applied it to the whole of the periodic

[1] *J. Amer. Chem. Soc.*, 1919, *41*, 868.

system, so that whilst neon and argon at the end of the two short periods have each 8 electrons in their sheaths, krypton and xenon have each 18, and radon has 32. Thus Langmuir postulates[1] that "the electrons in atoms tend to surround the nucleus in successive layers containing 2, 8, 8, 18, 18, and 32 electrons respectively".

In the long periods, however, it is not possible to connect valency with the electronic content of the atomic sheath in the same simple fashion as in the short periods. Consider the period of 18 elements from K to Kr. This period begins and ends like the preceding short period; i.e. K, Ca, Sc resemble Na, Mg, Al in valency, and As, Se, Br similarly resemble P, S, Cl; but with the intermediate elements, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, more complicated relations appear. In one sense the elements K to Mn resemble a short period; e.g. with regard to the oxides

$$K_2O,\ CaO,\ Sc_2O_3,\ TiO_2,\ V_2O_5,\ CrO_3,\ Mn_2O_7.$$

Thus Mn_2O_7 resembles Cl_2O_7, permanganates being isomorphous with perchlorates, so that a similar arrangement of electrons on the atomic sheaths of Cl and Mn may be inferred. The oxides

$$Cu_2O,\ ZnO,\ Ga_2O_3,\ GeO_2,\ As_2O_5,\ SeO_3,\ —,$$

again, less perfectly reproduce the relations of the oxides of the first short period. Moreover, a new phenomenon occurs in the centre of this long period; this is reducibility of the higher compounds with the loss of single units of valency, and the simultaneous appearance of coloured ions.

Thus salts corresponding with the following oxides have coloured ions:

	(V_2O)						(Cu_2O)
TiO	VO	CrO	MnO	FeO	CoO	NiO	CuO
Ti_2O_3	V_2O_3	Cr_2O_3	Mn_2O_3	Fe_2O_3	Co_2O_3		
(TiO_2)	V_2O_4	—	MnO_2	—			
	V_2O_5	—	—	—			
		CrO_3	MnO_3	FeO_3			
			Mn_2O_7				

In view of these considerations, Mendeléeff's division of the long periods into the elements of the A and B sub-groups may be brought forward again, thus:

Elements of A Sub-groups	K	Ca	Sc	Ti	V	Cr	Mn	Fe Co Ni
Elements of B Sub-groups	Cu	Zn	Ga	Ge	As	Se	Br	

[1] *Science*, July, 1921.

and so it may be pointed out that the triad (Fe Co Ni) appears to function like a single element, i.e. like an inert gas at the end of a period; and although Ni cannot be compared with an inert gas, Pt may, because it is so inert. Thus if the non-valent, inert gases are regarded as "standards of atomic stability", Ni, Pd, Pt, or more accurately, imaginary inert forms of these elements, are sometimes regarded as "sub-standards of atomic stability".

Now if Langmuir's postulate is examined in the light of all these considerations, it will appear difficult to account for valency by reference to the electrons supposed to be contained in the atomic sheaths of the neutral atoms. Nickel, for example, would have 10 electrons, and require 8 to complete the sheath; copper would have 11 electrons, and require 7 to complete the sheath, and so on. And whilst the existence of $Ni(CO)_4$ would seem to justify a valency of 8 for nickel, there are no properties of copper or the succeeding elements to show such high valencies as would thus be attributed to them.

Consequently attention may be drawn to other views regarding the distribution of the electrons in an atom.

In 1921 Bury[1] modified Langmuir's theory by assuming that the number of electrons in a completed sheath of an atom never exceeds 8; and in the same year Bohr, from a consideration of the spectra of the elements (see later), adopted a similar view.

The following table sets forth the atomic structures of the non-valent gases according to Bohr. The numbers in brackets are the atomic numbers of the elements, and therefore the numbers of electrons external to the nucleus.

Orbits, numbered outwards from Nucleus.	1	2	3	4	5	6
Helium (2)	2					
Neon (10)	2	8				
Argon (18)	2	8	8			
Krypton (36)	2	8	18	8		
Xenon (54)	2	8	18	18	8	
Radon (86)	2	8	18	32	18	8

An advantage of this view is that it provides for the addition of electrons either in the sheath of an atom or in an orbit or shell below it. When the latter occurs there need be no change of

[1] *J. Amer. Chem. Soc.*, 1921, *43*, 1602.

valency in passing from one element to the next, as is shown, for example, in the chlorides

$$VCl_2,\ CrCl_2,\ MnCl_2,\ FeCl_2,\ CoCl_2,\ NiCl_2,\ CuCl_2,\ ZnCl_2.$$

The idea is specially helpful, however, in accounting for the 14 elements of the rare earths, all of which have the same valency. Successive additions of electrons are here supposed to be made to the electrons in the fourth orbit, so increasing these from 18 to 32.

A final question, so far as the present study of atomic structure is concerned, is that of the activities of the electrons within the atom. Regarding these activities the views of the physicist and the chemist appear to be at variance. The physicist believes the electrons to be revolving round the nucleus in their several orbits as the planets revolve round the sun. To him an electron at rest is as unthinkable as a planet in such a condition. The chemist, however, is well content to think of a stationary electron; indeed he seems to demand it by his ideas of valency and the constitution of compounds. How can chemical compounds be formed without points of attachment between the atoms, and how can points of attachment be provided by swiftly revolving electrons? It is true that an electrolyte like sodium chloride might exist; for the chemist has learned to regard its atoms as held together not by bonds, but by electrostatic attraction between oppositely charged ions. But what is to be said about such compounds as methane and the host of organic substances, concerning whose structure and stereochemistry the chemist has such elaborate and satisfying ideas, based upon the doctrine of bonds?

The physicist, however, needs to account for those beautiful phenomena, the luminous spectra of the elements. It used to be asked: how can the atom of iron vibrate in hundreds of ways at once so as to give rise to the hundreds of lines in its luminous spectrum? It is sufficient now to ask how the hydrogen atom, consisting of one proton and one electron, can vibrate in various ways so as to produce the various lines in its spectrum. We are indebted to Bohr[1] for an explanation of this phenomenon, based on Planck's Quantum Theory of Energy, which now finds general acceptance.

Imagine an atom with revolving electrons which are radiating energy into space. If this radiation were continuous, the electrons

[1] *Vide The Theory of Spectra and Atomic Constitution*, by Niels Bohr: Cambridge University Press, 1924.

would be continually losing energy, and in consequence continually approaching the nucleus in a spiral path. Moreover, such continuous radiation could not produce a discontinuous line spectrum. To avoid the nemesis of the atom by the collision of planetary electrons and nucleus, it is assumed that a revolving electron loses no energy so long as it remains in a single orbit; that it is only change of orbit which is accompanied by change of energy; a loss of a definite amount of energy, the so-called *quantum*, will thus accompany the fall of an electron from one orbit to that beneath it, i.e. nearer to the nucleus; and a corresponding gain of energy will accompany the restoration of the fallen electron to its former state. It is now easy to understand, if there are numerous possible orbits, that each kind of fall gives rise to a particular radiation which produces its own line in the spectrum; and that the several lines occurring simultaneously in the hydrogen spectrum are produced by corresponding simultaneous falls from several different orbits in the peripheries of hydrogen atoms with their electrons in several different states, although each atom contains only one electron.

The apparently irreconcilable views of the physicist and chemist may be expressed thus: to the physicist an atom is a hive of activity, a home of swarming electrons; to the chemist it is an abode, if not of rest, then of nothing more than vibratory motion of electrons about their mean positions. Can these views be reconciled? It is possible that they may be if a revolving electron can be considered to be more in one place than any other, if there is any point through which it passes very frequently whilst otherwise tracing out divergent paths. This is impossible if an electron describes circles in the same plane round the nucleus as centre, or if its path is a simple ellipse, like the path of a planet, with the nucleus at one of the foci of the ellipse.

If, however, the motion of an electron is compounded of a circular or elliptical motion, and a circular motion at right angles to it, the path travelled will be precessional upon the surface of an ellipsoid,[1] i.e. it will be represented by a series of curved lines whose directions are constantly altering so as to cover the whole surface of the ellipsoid very much as the coloured and twisted lines on an ornamental glass marble cover its surface. The consequence of such a motion will be that the rotating electron will pass, during

[1] An ellipsoid is the solid figure formed by rotating an ellipse about its major axis, just as a sphere is the solid figure formed by rotating a circle about its diameter.

one cycle, many times through two points, which are at the extremities of the major axis of the ellipsoid, but only once through every other point.

Such a conception, which is due to J. D. Main Smith, provides for the localization of an electron, as well as satisfying some requirements of the physicist. Whether, however, it will suffice to account for both the physical and the chemical properties of the atom cannot yet be said. Meanwhile the idea of stationary electrons within or upon the surface of an atom is so very valuable a contribution to the theory of chemical structure that it will be adopted and developed in the next chapter, which deals with the modern view of the molecule.

CHAPTER VI

THE MODERN VIEW OF THE MOLECULE

The student of chemical history is aware that two views have been held regarding the structure of chemical compounds. The first view was expressed in the electrochemical theory of Berzelius, which postulated electricity as the binding force between atoms, so that a molecule consisted of atoms held in electrical equilibrium by mutual attractions.

There were two kinds of electricity, and each atom in a compound possessed some of both kinds, but in unequal quantities, so that a positive or negative charge preponderated, according to whether the atom was metallic and electropositive, with a larger positive than negative charge, or non-metallic and electronegative, with a larger negative than positive charge. Thus it followed that every molecule consisted of two parts, a positive and a negative part; and these parts in turn might consist each of two smaller positive and negative parts, and so on, down to the individual atoms. For example, the double salt potassium-alum, apart from its water of crystallization, would be accounted for somewhat in this way:

$$\overset{+}{K}\overset{-}{O}\overset{+}{S}\overset{-}{O_3} \qquad \overset{+}{Al_2}\overset{-}{O_3}\,3\left[\overset{+}{S}\overset{-}{O_3}\right].$$

This was the *dualistic system*; and it was successful in accounting for the structure of electrolytes, which are polar compounds, but failed when applied to organic compounds, which are non-electrolytes or non-polar compounds. Thus if every compound is composed of positive and negative parts, in equilibrium, what, it may be asked, are these parts in such a compound as CH_4; and again, if + and − parts are balanced in CH_3COOH, how is it

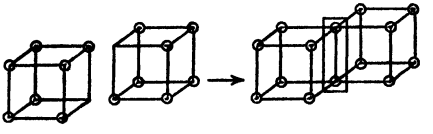
possible for electropositive hydrogen to be replaced by electronegative chlorine, so as to produce CCl_3COOH?

In view of questions like these, Dumas propounded a second view in his *unitary system* of chemical compounds, in which every compound formed a complete whole, and did not therefore consist of two opposite and balanced parts. He thus referred the properties of a compound to its type rather than to the properties of its constituent atoms. The consequence was that unitary views prevailed and dualism was discredited. When, therefore, the doctrine of valency was developed, graphic formulæ with "bonds" were employed indiscriminately to represent the structure both of electrolytes and non-electrolytes.

The electrolytic dissociation theory of Arrhenius, however, marked a return in part to dualism; and that theory, together with the properties of solutions to which it was related, emphasized the real difference which exists between electrolytes such as sodium chloride, and non-electrolytes such as chloroform. Since, however, "bonds" were supposed equally to join the atoms of sodium and chlorine in sodium chloride, and carbon, hydrogen, and chlorine in chloroform, simple solution in water involved the breaking of bonds in one case, but not in the other; and it was difficult to find a valid reason for such an extraordinary difference of behaviour of different compounds as they dissolved in water.

Now it has been seen that the electronic theory of valency, so far as it was developed in the last chapter, appears to deal with valency in electrolytes alone. This is true of Ramsay's idea of valency, and also of the theory of transference of electrons during the combination, say, of sodium and chlorine to form sodium chloride; so that a conception of the molecule is reached resembling that of Berzelius, because it represents atoms, or, more strictly, charged ions, as held together by electrostatic attraction. There is difficulty, however, in applying this simple theory to all molecules; and to realize the difficulty it is only necessary to consider the molecule Cl_2. Sodium and chlorine combine because of an electrochemical difference between these elements; the sodium atom loses an electron which the chlorine atom, because of its different chemical nature, readily takes up. No such reason can account for the union of two chemically identical chlorine atoms to form a molecule, so that there cannot be transfer of electrons in such a case.

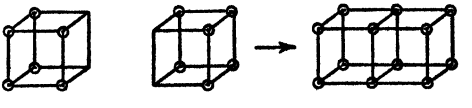
This difficulty is met by a conception due to G. N. Lewis and developed by Langmuir: the conception of covalency, as distinct from electrovalency, which is the kind of valency hitherto considered. Now an atom of chlorine has 7 electrons in its sheath, and requires 1 to complete the *octet* characteristic of the sheath of an inert gas. Such an atom, however, cannot gain its required electron from a similar neighbouring atom, and even if it did it would become a chloride ion such as does not exist in chlorine gas. It is possible, however, for two chlorine atoms, with identical requirements to satisfy these requirements, mutually, by the sharing of a pair of electrons, each chlorine atom providing one electron of the pair. The accompanying figure makes this plain.



Thus two octets containing only 14 electrons between them, are possible because two of these electrons are common to both octets. The shared electrons held in common by both chlorine atoms, which are shown in the figure within the rectangle, constitute a *duplet.* This duplet is a unit of covalency, and is equivalent to a single valency bond. According to Langmuir, it is the only sort of bond, and it represents the kind of union which exists between the atoms of compounds which are not electrolytes.

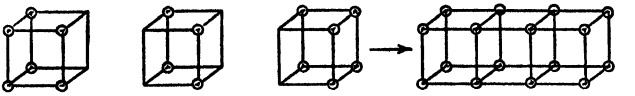
Thus, by this view, there are two kinds of valency: *electrovalency* and *covalency.* The theory of electrovalency is the modern equivalent of the dualistic theory of Berzelius; that of covalency corresponds with the unitary theory of Dumas.

Covalency may now be further illustrated. The molecule O_2 consists of a pair of atoms, each of which separately has six electrons in its sheath, and therefore requires two electrons to complete the octet. Two oxygen atoms can combine together to produce a pair of octets if each atom shares two electrons with its neighbour, producing a pair of duplets representing a double bond, O = O, thus:



Similarly, carbon dioxide, O = C = O, can be represented by

showing the carbon atom sharing two duplets with each oxygen atom thus:



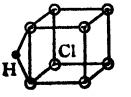
O + C + O = CO_2

The combination of hydrogen with oxygen, and with chlorine, to form water and hydrogen chloride respectively, may now be considered. Since water is a non-electrolyte, the two hydrogen atoms in each molecule are supposed to unite with the oxygen atom by covalency, in a manner which may be represented thus:

H + O + H = HOH

Thus each hydrogen atom completes its sheath of two electrons, and the oxygen atom its sheath of eight.

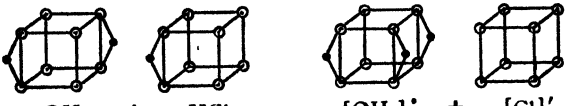
As regards hydrogen chloride, since in the anhydrous state this compound is a non-electrolyte, its molecule may be represented thus, the atoms of hydrogen and chlorine being united by covalency:



In presence of water, however, the covalency bond is broken, and the hydrogen chloride is ionized, becoming hydrochloric acid. It is now believed, however, that the hydrogen ion of hydrochloric acid is hydrated, that, indeed, it is an unstable oxonium ion $(OH_3)^{\cdot}$ analogous to the ammonium ion $(NH_4)^{\cdot}$, and formed thus:[1]

$$OH_2 + HCl = (OH_3)^{\cdot} + Cl'.$$

This change would be represented structurally thus:



OH_2 + HCl = $[OH_3]^{\cdot}$ + $[Cl]'$

The explanation of this change of hydrogen chloride from a neutral, non-electrolytic substance to a powerful acid through the assimilation of water is to be found in the principle of symmetry.

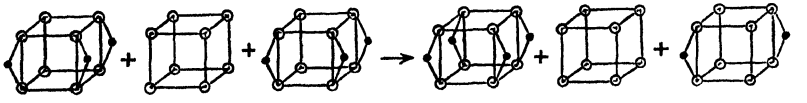
[1] *Vide* Lowry, *Chemistry and Industry*, 1923, 46.

The molecular condition of non-ionized hydrogen chloride is an unsymmetrical and therefore relatively unstable one, whilst the water molecule requires two hydrogen nuclei to be attached to the four remaining electrons to create perfect symmetry. Having attached one hydrogen nucleus, however, the water molecule, which has now become a positive $[OH_3]^{\cdot}$ ion, is unable to take up another because, being positively charged, it repels similarly charged hydrogen nuclei. Hence the condition of things shown in the figure is arrived at.

Now when hydrogen chloride solution is mixed with ammonia, neutralization takes place thus:

$$[OH_3]^{\cdot} + [Cl]' + NH_3 \longrightarrow [NH_4]^{\cdot} + [Cl]' + H_2O,$$

or

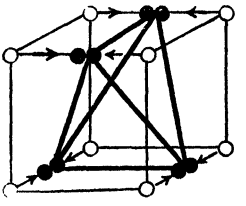


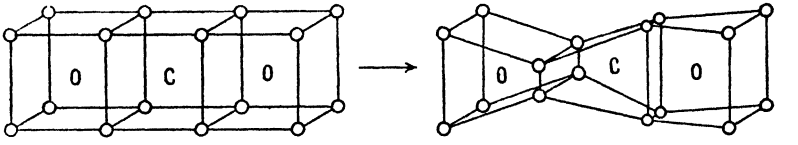
the neutralization being due to the fact that the ammonia molecule appropriates another hydrogen nucleus to form the highly symmetrical ammonium ion with greater force than the water molecule retains it. Nevertheless, just as $[OH_3]^{\cdot}$ is unstable, easily losing a hydrogen nucleus in presence of the hydroxidion of an alkali to leave a stable OH_2 molecule, so $[NH_4]^{\cdot}$ is also unstable, and in presence of much hydroxidion similarly loses a hydrogen nucleus to provide hydrion and form water. That is why ammonium salts evolve ammonia in presence of alkalis.

The student of organic chemistry is conversant with the theory that the four valencies of the carbon atom are directed towards the angular points of a regular tetrahedron; and he knows that this theory has been most fruitful in elucidating the structure and stereochemistry of carbon compounds. It is therefore necessary to inquire how the stereochemical theory is related to the electronic theory of valency, so far as this applies to the carbon atom.

In the preceding figures the atoms of all the elements except hydrogen have been represented as having a cubical structure, or rather, the eight electrons in the completed sheath of an atom have been placed at the angular points of a cube. Now a regular tetrahedron is the hemihedral form of the cube; if, therefore, the eight electrons draw together into four pairs, two pairs being produced by movements at right angles to the movements of the other two, a tetrahedral figure will be produced (see fig., p. 123). Thus it is

believed that whilst the cubical form of the atom as regards the distribution of its electrons is preserved when chemical union is by electrovalency as in sodium chloride, union by covalency involves the distortion of the cubical form into the tetrahedral. So the structure of carbon dioxide is represented by the following figure. Thus the tetrahedral model of the carbon atom is preserved, and union by single, double, and triple bonds becomes union at an angle, a side, and a face of the tetrahedron respectively, by one, two, or three pairs of electrons.





It is troublesome though picturesque to represent atoms by cubes, and molecules by numbers of united cubes. A simpler plan is to use the ordinary atomic symbol surrounded by dots to represent electrons. Thus the molecule of chlorine, instead of being represented as in fig. on p. 120, becomes

$$:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:,$$

and other formulæ are:

H_2	NaCl	O_2	CO_2	C_2H_2
H:H	$\mathrm{Na}:\ddot{\underset{\cdot\cdot}{\mathrm{Cl}}}:$	$:\ddot{\mathrm{O}}::\ddot{\mathrm{O}}:$	$:\ddot{\mathrm{O}}::\mathrm{C}::\ddot{\mathrm{O}}:$	H:C:::C:H,

which are equivalent to

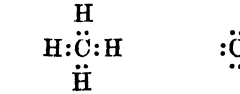
H—H	Na· Cl′	O=O	O=C=O	H—C≡C—H.

So it appears that a pair of electrons, acting as a unit of covalency, is equivalent to a single chemical bond. It is to be noted, moreover, that with the exception of H, which has two electrons, and Na, which is an ion with eight electrons in a lower layer, every atom is represented as having or sharing eight electrons, since all the electrons which bind two atoms together are shared by both atoms concerned.

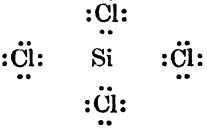
The question may be asked whether there is an absolute distinction between electrovalency and covalency, or otherwise

between polar and non-polar compounds; or whether one kind of valency merges into the other in a series of compounds, which thus show transition from polarity to non-polarity. Thus, while electrovalency is the mode of union in sodium chloride, it may be asked whether all chlorides, metallic and non-metallic, are constituted similarly. Now electrovalency must be the mode of union in the case of the chloride of a univalent atom, for such an atom, e.g. Na, cannot share the two electrons which are necessary to a covalent bond; and covalency must be the mode of union when two similar atoms unite, as in the case of Cl_2, for there is no reason for electronic transfer.

It may be questioned, however, whether electrovalency is the mode of union of the atoms in CCl_4. Rather may it be supposed that this compound, which resembles methane in inertness, is similarly constituted, in which case the two molecules may be represented thus:



With $SiCl_4$, however, the case is different, for this compound is distinguished from CCl_4 by its reactivity towards water. Possibly, therefore, the state of union between the silicon and chlorine atoms may be represented as something intermediate between covalency and electrovalency, thus:



the eight electrons which in covalency the silicon atom would share with the chlorine atoms being drawn towards these atoms, so that the silicon atom becomes charged positively and the chlorine atoms negatively, though these charges are not sufficiently free to constitute the compound an electrolyte. This can be understood if it is remembered that the electrons in the sheath of a silicon atom are farther from the positively charged nucleus than those in the sheath of a carbon atom, and so would be held less tenaciously by the nucleus; or in other words, that the silicon atom is more electropositive than the carbon atom, and more ready to shed the electrons of its sheath.

The stability of CCl_4, as well as of CH_4, as compared with $SiCl_4$ and SiH_4, is probably to be referred eventually, however, to the inner structures of the atoms of the two elements. Between the sheath of the carbon atom and its nucleus there is only the shell of two electrons which constitute the sheath of the helium atom, whilst in the case of the silicon atom the completed octet which constitutes the sheath of the neon atom intervenes. Consequently the eight electrons of the completed sheath of the carbon atom in a compound such as CCl_4 can assume the tetrahedral position without strain, whereas the neon octet in the case of the silicon atom makes tetrahedral symmetry and resulting stability more difficult of attainment.

The idea of gradations between polar and non-polar molecules is due to G. N. Lewis. Thus Lewis accounts for the properties of hydrogen chloride by supposing that the two electrons which are shared between the hydrogen and chlorine atoms in the anhydrous molecule may be displaced in the direction of the chlorine atom so as to cause this to become negatively charged, whilst the hydrogen atom becomes positively charged to the same degree, but that when displacement is complete hydrion and chloridion result thus:

$$H:\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow H\ :\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow [H]^+ + \left[:\ddot{\underset{\cdot\cdot}{Cl}}:\right]^-.$$

Langmuir, on the other hand, believes that the electrolytic properties of hydrogen chloride solution are due to the hydrogen nucleus uniting with the water molecule to form a hydrated hydrogen ion, or oxonium ion, according to the theory already given.

The octet theory—that is, the theory that the completed sheath of an atom contains eight electrons—accounts for the frequency with which four atoms are joined to a central atom, to form a molecule if the product is electrically neutral, or an ion if it is not.

Examples are the molecules CH_4 and OsO_4, the cation $NH_4^{\cdot}$, and the anions SiO_4'''', PO_4''', SO_4'', MnO_4'', MnO_4', ClO_4', which are formulated thus:

$$\left[\begin{matrix}&:\ddot{O}:&\\:\ddot{O}:&\ddot{Si}&:\ddot{O}:\\&:\ddot{O}:&\end{matrix}\right]\equiv\left[\begin{matrix}&:\ddot{O}:&\\:\ddot{O}:&\ddot{P}&:\ddot{O}:\\&:\ddot{O}:&\end{matrix}\right]\equiv\left[\begin{matrix}&:\ddot{O}:&\\:\ddot{O}:&\ddot{S}&:\ddot{O}:\\&:\ddot{O}:&\end{matrix}\right]\left[\begin{matrix}&:\ddot{O}:&\\:\ddot{O}:&\ddot{Mn}&:\ddot{O}:\\&:\ddot{O}:&\end{matrix}\right]\left[\begin{matrix}&:\ddot{O}:&\\:\ddot{O}:&\ddot{Mn}&:\ddot{O}:\\&:\ddot{O}:&\end{matrix}\right]\left[\begin{matrix}&:\ddot{O}:&\\:\ddot{O}:&\ddot{Cl}&:\ddot{O}:\\&:\ddot{O}:&\end{matrix}\right]$$

the valencies of the separate atoms, and of the ions, their algebraic sum, being:

$Si = +4$	$P = +5$	$S = +6$	$Mn = +6$	$Mn = +7$	$Cl = +7$
$4O = -8$	$4O = -8$	$4O = -8$	$4O = -8$	$4O = -8$	$4O = -8$
$SiO_4 = -4$	$PO_4 = -3$	$SO_4 = -2$	$MnO_4 = -2$	$MnO_4 = -1$	$ClO_4 = -1$

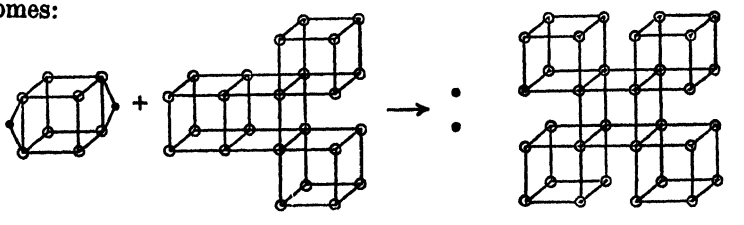
It is noteworthy that the covalent bond, i.e. the duplet, is the same whether the uniting element is univalent like H or bivalent like O. Consequently the practice of representing O as united with other elements by means of double bonds, unless these are double covalent bonds, disappears.

The way in which the ions represented above are built up may, however, be elucidated a little further. Consider the SO_4 ion. The sulphur atom, when neutral, had a valency of +6 with six electrons in its sheath, and needed two more to complete its octet; the four oxygen atoms, when neutral, similarly possessed six electrons in their sheaths, so that each also required two more electrons to complete its octet, eight in all being required, of which the sulphur atom was ready to provide six for covalent union. Two more electrons were therefore necessary, and these were provided by two neutral hydrogen atoms, which so became ions. Thus H_2SO_4 consists of two hydrogen ions each with one + charge, because of the loss of an electron, and the SO_4 ion having two negative charges owing to the gain of two electrons.

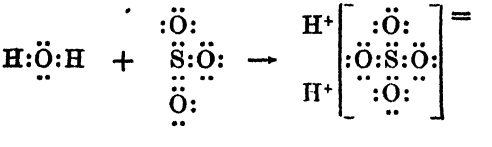
Actually, of course, H_2SO_4 is produced by the union of H_2O and SO_3, both of which are neutral molecules because their component atoms mutually satisfy each other in covalent union. In order that the sulphur octet in SO_3 may be completed, however, one oxygen atom is represented as united with the sulphur atom by a double covalent bond, thus: $O{=}S{<}^{O}_{O}$, so that the reaction

$$H_2O + SO_3 \rightarrow H_2SO_4$$

becomes:

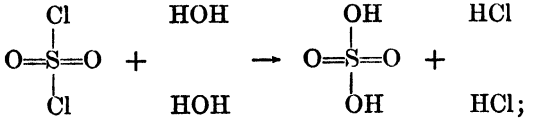


or

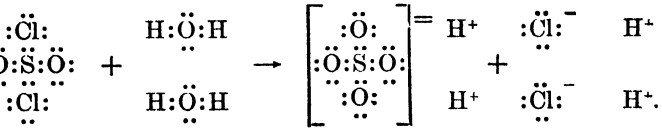


It is thus plainly seen that the two extra electrons provided by the hydrogen are necessary because, owing to the opening out of the double bond, an oxygen atom fully furnished with an octet of electrons must be available to convert the molecule SO_3 into the ion SO_4.

It has been usual to show the constitution of sulphuric acid by its derivation from sulphuryl chloride thus:

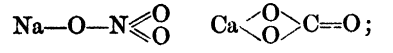


this reaction now becomes:



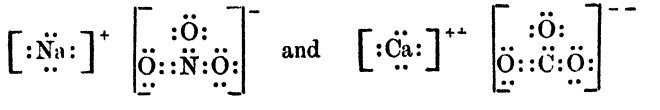
Thus the connection between the old and the new way in chemistry is perceived. In this new way, or something like it, chemical compounds will be formulated in the textbooks of the future.

The methods of representing the constitutions of inorganic salts according to the older ideas of valency sometimes led to difficulty on account of the isomorphism of compounds not related chemically. Thus sodium nitrate, $NaNO_3$, and calcspar, $CaCO_3$, are isomorphous; yet they are chemically unrelated, and were given constitutional formulæ to accord with their chemical properties, thus:



in which nitrogen was shown to be quinquevalent and carbon quadrivalent.

Now in the modern method of formulation the valencies of the individual atoms in a compound radicle disappear when the octets of the constituent atoms are completed. Thus the nitrate and carbonate ions are similar in constitution though they differ in the electric charges they carry, the two salts being formulated thus:



It is thus an argument in favour of the electronic theory of valency

that these formulæ accord with the fact of isomorphism, which is obscured by the older formulæ.

Moreover, it now becomes clear that Mitscherlich, who enunciated the law of isomorphism, was right when he stated that isomorphism depended primarily on the number and mode of arrangement of the atoms in the molecule of a compound rather than upon the chemical nature of those atoms.

This chapter on the modern view of the molecule would be incomplete without reference to the question of the existence of the molecule in the solid state, although this subject has already been dealt with briefly under the subject of molecular association (p. 46).

Molecular formulæ have long been used in expressing the reactions of solids without consideration whether they stand for realities. There is no harm in their use, provided it is understood that they represent, on an atomic basis, only the quantitative relations of reacting substances. Formulæ such as NaCl and $CaCO_3$, &c., suggest no more in their common use than the atomic relations within the compounds they represent; and it is immaterial for general purposes whether the true molecular formulæ of these compounds should be simple, or, say, $(NaCl)_m$ and $(CaCO_3)_n$. Nevertheless it is desirable to form a mental picture of a solid, and if possible obtain a true conception of its molecular state. When a chemical compound is truly solid it is crystalline, for the amorphous state is really the state of super-cooled liquid. The arrangement of the atoms in a crystal is revealed by X-ray spectrography, according to the researches of Sir W. H. and W. L. Bragg[1]; and the method can be applied not only to obvious crystals, but also to powders,[2] such as precipitated calcium carbonate, which are thus shown to be essentially crystalline.

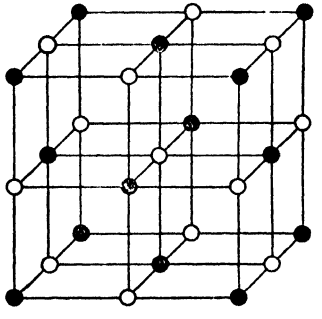
In connection with the arrangement of the atoms within the crystal, the idea of a space-lattice has been introduced. Consider a piece of wooden trellis-work, which can be opened to show a pattern of diamond-shaped spaces. Such a pattern, indefinite in extent, but with units which are similar parallelograms, is a lattice, i.e. a plane lattice, a lattice in two dimensions; and all that is essential to form it is two sets of parallel lines, the lines in each set being equidistant. Now extend the idea to three dimensions, and let there

[1] *X-rays and Crystal Structure* (G. Bell & Sons).
[2] Hull, *J. Amer. Chem. Soc.* (1919), *41*, 1168.

be three sets of parallel planes which intersect. Thus a series of identical units or cells is produced, each cell being a parallelopiped. This is a space-lattice. Moreover, the pattern is preserved, whether in two or three dimensions, if the lines or planes are obliterated, provided the points of intersection of these lines or planes are preserved. Such a pattern in three dimensions is a picture of the disposition of the atoms in a crystal; for the lines, of course, are only imaginary, and the atoms may be regarded as points in space.

Further, a lattice unit, whether in two or three dimensions, is a single parallelogram or parallelopiped; similarly there is a crystal unit or crystal cell, which is the smallest unit in which the essential properties of the crystal, as regards the space disposition of the atoms of the substance, are expressed without repetition.

The figure below depicts a crystal unit of sodium chloride as revealed by X-ray spectrography, white spheres representing sodium atoms, and black spheres chlorine atoms. The space-lattice, of which this is the smallest essential part, is called the face-centred cube lattice, because an atom—in this case a chlorine atom—is at the centre of each face of the cube. It is immaterial whether a sodium or a chlorine atom forms the face centre, for by bisecting the cube parallel to a face and adding to one of the halves another half cube a sodium face-centred cube would be formed.



It is to be observed, however, that each sodium atom in such a structure is surrounded by six equidistant chlorine atoms, as is seen to be the case with the central atom in the figure; and similarly, that each chlorine atom is surrounded by six equidistant sodium atoms. The question may therefore be asked: what has become of the molecule of sodium chloride? and the answer is that no such molecule exists in the solid salt. Such an answer, moreover, is quite in accordance with the electronic theory of valency as applied to sodium chloride. It is ions, however, and not neutral atoms of sodium and chlorine, which are packed together in solid salt; and when the salt disintegrates in water these ions wander freely in the solvent without existing as NaCl molecules.

It is therefore quite impossible to write a molecular formula for

solid sodium chloride, and therefore the simple formula NaCl for the salt serves every useful purpose.

The electrostatic attraction which binds the ions of sodium and chlorine together in sodium chloride is the cause why this compound is a solid at ordinary temperature and not a gas.

There are no molecular boundaries, and all the ions in a mass of the salt are fastened together in one bundle by a pervasive force or field of electric attraction, which hitherto has been called cohesion. When, however, such a mass is fused, and so strongly heated as to be converted into vapour, ions of sodium and chlorine pair off and exist as NaCl molecules. It could hardly be otherwise. Oppositely charged ions of sodium and chlorine could remain separate in the state of vapour only if they possessed such high velocities on account of elevated temperature that the attractive force between them was rendered ineffective. That would be thermal dissociation, such as occurs even when pairs of identical atoms have been united by covalency, as with I_2.

In view of the conception of the crystal unit as the smallest portion of the solid necessary to represent completely the properties of the crystal, it may be asked whether this unit is identical with the chemical molecule. It has been seen that in the case of crystallized sodium chloride no chemical molecule can be said to exist; yet molecules of organic compounds, that is, compounds whose atoms are united by covalent bonds, are believed to be present even when these compounds are solid. Nevertheless, according to Sir William Bragg,[1] there is no reason why the crystal unit should be identical with the chemical molecule; and X-ray analysis has shown that this unit generally consists of two, three, or four molecules; e.g. the crystal unit of naphthalene consists of $(C_{10}H_8)_2$, and that of α-naphthol, where the symmetry is reduced by the introduction of an OH group, of $(C_{10}H_7OH)_4$. Similarly two molecules of benzene, C_6H_6, constitute a crystal unit, but four of benzoic acid, C_6H_5COOH.

Consider the two solid and related elements carbon and silicon. When carbon burns it forms an oxide which is a gas, but when silicon burns the oxide formed is a solid. What is the reason for this difference? The answer is that carbon dioxide consists of molecules of three atoms compactly joined together by covalency, each forming a self-satisfied system with very little outside in-

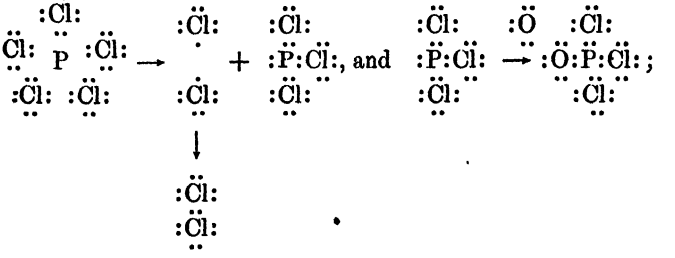
[1] "The Significance of Crystal Structure", *Trans. Chem. Soc.*, 1922, *121*, 2766.

fluence, so that only at low temperature and high pressure do the separate molecules unite to produce liquid and then solid carbon dioxide; but that it is otherwise with silica. Silica has long been recognized to consist of polymerized molecules, and it is now known that as quartz its crystal unit is $(SiO_2)_3$. It may well be doubted, however, whether Si_3O_6 molecules, existing side by side with little attractive force between them, would be competent to produce an inert and non-volatile solid like quartz. Rather it would seem that a cohesive force of great strength exists between the Si_3O_6 molecules, to overcome which very high temperature is necessary; or otherwise that the mode of union pertaining between silicon and oxygen in silica is analogous to that between the elements in TiO_2, SnO_2, and other related oxides. Indeed, as compared with other dioxides it is carbon dioxide which has exceptional properties, not silica; and, as was said earlier in this chapter, it is the inner structure of the carbon atom that fits it for covalent union, which then confers volatility on the compounds carbon forms with other elements.

Nevertheless, it is remarkable that silicon tetrachloride (B.P. 57°) is so volatile compared with silica. This may be because the silicon atom in the tetrachloride is unable to exercise much attractive influence on its similar neighbours owing to the cordon of four chlorine atoms with which it is surrounded; whereas the oxygen atoms of silica are not numerous enough to exercise this influence. It may be noted, moreover, that SO_3, Cl_2O_7, and even OsO_4 are volatile.

Compounds such as PCl_5 and SF_6 call for comment. If it is believed that the halogen atoms are attached to the other atom in these molecules by covalency, then ten and twelve electrons respectively are concerned in the process; but it seems unlikely that the octet of electrons is exceeded in the sheaths of atoms of such low atomic number as phosphorus and sulphur. The alternative is to regard the halogen atoms as united by electrovalency, in which case the five and six electrons originally present in the sheaths of phosphorus and sulphur atoms respectively will have left these atoms to become attached severally to the halogen atoms. In this case the stability and volatility of SF_6, as of other polyfluorides, is to be attributed to the simplicity of internal structure of the fluorine atoms which allows them to come very close to a sulphur atom; whilst the dissociation of PCl_5 vapour into PCl_3 and

Cl_2, with subsequent oxidation of PCl_3, may be represented as taking place in the following way:



which shows two chlorine atoms returning an electron each to the phosphorus atom, and then forming a chlorine molecule by covalent union; whilst the other three chlorine atoms also enter into union with the phosphorus atom, so that PCl_3 becomes a covalent compound, which may be subsequently oxidized to phosphoryl chloride in the manner shown.

These illustrations suffice to show the trend of the modern theory of the molecule; and they leave no doubt that the kinds of formulæ which have embellished our textbooks for a generation must soon give place to formulæ of another kind. The present position of the theory, however, must be regarded as a phase, for many of the ideas are speculative; but so long as chemical science remains alive and active, so long must its theories continue to undergo modification.

PART II

STATES OF MATTER

PART II—STATES OF MATTER

CHAPTER VII

THE PROPERTIES OF GASES

The states of matter which are commonly recognized are three—solid, liquid, and vapour or gas. Matter in these three physical states is composed of molecules, the inter-relations of which determine the state of the matter. A *solid* is characterized by a volume which is but slightly affected by changes in temperature and pressure, and by a shape of its own, which may be naturally assumed or artificially induced. By reason of the heat energy they possess, the molecules —or it may be ions—of a solid are in motion; but, inasmuch as the volume of the solid does not tend to change spontaneously, this motion does not affect the distance apart of the molecules; and, since the shape of the solid is permanent, the molecules do not change their positions relatively to each other. The motions of the molecules of a solid, therefore, are restricted to vibrations about mean fixed positions, and the molecules themselves are retained in these positions by the exercise of the force of *cohesion*, which in solids is at its maximum. Even in some solids, however, cohesion does not prevent vaporization or diffusion, as in the case of some solid metals. A *liquid*, like a solid, has a definite volume, little affected by changes of temperature and pressure; it has no definite shape of its own, however, but when placed in a containing vessel assumes for the time being the shape of the vessel. It is thus the property of a liquid to flow, to spread itself out, and adapt itself to external conditions, while maintaining its volume unchanged; consequently the molecules in their motions must keep the same mean distances apart while the liquid changes its shape. Thus the force of cohesion in a liquid, although weakened so that the molecules are not maintained in a fixed mean position as in a solid, is yet sufficient to confine these molecules within a definite volume so long as they remain part of the liquid.

The characteristic of a *gas* is its power of indefinite expansion, so that it will distribute itself uniformly over whatever space is at its disposal. Thus a gas has neither definite shape nor definite volume, and it must be confined within an impervious envelope or it will be lost in space. The latter, of course, is true to a limited degree of most liquids and some solids; that is to say, they slowly disappear when left exposed in the air on account of evaporation.

The reason that a gas tends thus to expand, and so exerts a pressure upon the envelope designed to keep it in bounds, is that its molecules are not held together by cohesion, but are independent of each other, and free to move in accordance with their inherent kinetic energy. Consequently they move in straight lines, according to Newton's first law of motion, until they encounter other molecules or the sides of the containing vessel, when the direction of their path is changed.

Ideal gases are entirely devoid of cohesion between their molecules, whilst these molecules are wide enough apart to behave towards one another like points in space. In so far as gases conform to these conditions, they behave similarly, and independently of their chemical composition, under changes of temperature and pressure. In this respect they differ from liquids and solids, which show individuality of behaviour under such changes. Consequently the two fundamental gas laws connecting the volume of a gas with its temperature and pressure are of universal application; and, although in no case rigidly true, are only seriously departed from at high pressures and low temperatures, when the molecules of a gas are being brought into closer relations with one another.

1. The Gas Laws

The Law of Boyle (or Marriotte).

The volume of a gas at constant temperature is inversely proportional to its pressure.

$$p \propto \frac{1}{v} \text{ or } pv = \text{constant},$$

or, since density and volume are reciprocal, *the density of a gas varies directly as its pressure.*

The Law of Charles (or Gay-Lussac).

The volume of a gas, at constant pressure, increases by $\frac{1}{273}$

(= 0·00367) part of its value at 0° C. for every degree rise of temperature.

Thus 273 vol. of gas at 0° become 274 vol. at 1°.
" " 283 " 10°.
" " 263 " −10°, &c.,

and if the law held for all ranges of temperature, the volume of a gas would vanish at − 273°. Although no such event takes place, because conditions are modified at extremely low temperatures, − 273° is called the absolute zero of temperature, and ($t°$ + 273) is absolute temperature, or T°. Consequently the law of Charles may be stated in another way—*the volume of a gas varies directly as its absolute temperature*; and to correct the volume of a gas for change of temperature it is only necessary to add 273° to each temperature concerned, and multiply or divide by one or other absolute temperature, according to whether expansion or contraction is taking place. Thus, for example, a volume V at 10° becomes $\frac{283}{283}$V at 15°.

It may be added that, **if the volume of a gas is kept constant, while its temperature changes, the pressure of the gas varies directly as its absolute temperature.** This follows from Boyle's law.

The Gas Equation.

Since pv is constant at constant temperature, and p or v varies directly as the absolute temperature, while the other remains constant, it follows that pv varies directly as the absolute temperature, or

$$pv = \mathrm{RT} \text{ where R is a constant.}$$

Thus, if, with a given quantity of gas, p, v, and T undergo change, their values must be so related that R remains constant, or

$$\frac{pv}{\mathrm{T}} = \mathrm{R} = \frac{p_1v_1}{\mathrm{T}_1}, \text{ and so } \frac{pv}{\mathrm{T}} = \frac{p_1v_1}{\mathrm{T}_1}.$$

This is a useful form of the gas equation which may be employed in correcting the volume of gas for simultaneous changes of temperature and pressure; for

$$v_1 = \frac{vp\mathrm{T}_1}{p_1\mathrm{T}}.$$

Example.—100 cu. cm. of air at 15° at 750 mm. pressure are

heated to 30°, while the pressure becomes 770 mm. What is the new volume?

$$v_1 = \frac{100 \times 750 \times 303}{770 \times 288}$$

The problem may, however, be solved quite easily without any formula by considering whether the changes in temperature and pressure, respectively, will cause increase or decrease of volume, and then arranging the data accordingly.

2. Diffusion of Gases

Owing to their powers of indefinite expansion, gases mix when free to do so. Thus, if a jar of ammonia, hydrogen sulphide, or other strongly-smelling gas is opened in a room, the odour of the gas will soon be perceived at some distance from the jar. This process of mixing is called *gaseous diffusion.* It may be demonstrated by placing a jar of hydrogen closed with a glass plate above a similar jar of the brown gas nitrogen peroxide, and carefully withdrawing the glass plates which separate the gases. The brown gas, although much heavier than hydrogen, will be seen to be rising in the upper jar, and after a time the contents of both jars will be uniformly brown. Or a jar of carbon dioxide may be opened beneath one of hydrogen, and very soon the presence of carbon dioxide in the upper jar may be proved by lime-water.

These effects, taking place in spite of gravitation, which tends to keep the heavier gas in the lower cylinder, must be due to the intensely active motion of the molecules of the diffusing gases. Nevertheless the process takes a little time; it is not instantaneous, as the process of free expansion of a gas into a vacuum appears to be. A mental picture of the process would show the molecules of one gas rapidly threading their way through the obstructing molecules of the other gas, with consequent and frequent deflections and hindrances in their course, which are the cause of the time consumed before the mixing process is completed.

The fact that mixed gases do not separate again on account of their different densities was known to Priestley; but it was Dalton, in 1803, who proved that a lighter gas cannot rest permanently upon a heavier, as oil upon water. Döbereiner, in 1823, observed that hydrogen escaped through a crack in a glass flask containing it, so that the gaseous pressure inside the flask

diminished; and Graham, in 1832, examined systematically the phenomena of gaseous diffusion, and established the law regarding them. Graham employed a glass tube closed at one end with a plug of plaster of Paris. This material, as well as unglazed porcelain, or a thin plate of artificial graphite, is porous, i.e. it will allow a gas to pass through it by diffusion whilst preventing its escape in bulk. Consequently an alteration of gaseous pressure may take place inside such a tube on account of diffusion; and this when measured will indicate the extent to which diffusion is taking place. Graham confined various gases in this tube over water, and observed sometimes a rise, sometimes a depression of the water, corresponding to a diffusion of the gas from the tube into the air at a faster or slower rate than that at which the air diffused into the tube. Then, by an analysis of the gas remaining in the tube, data were obtained by means of which the following *law of gaseous diffusion* was established.

The rates of diffusion of different gases are inversely proportional to the square roots of their densities.

For example, oxygen is 16 times as heavy as hydrogen; so hydrogen diffuses $\sqrt{16} = 4$ times as quickly as oxygen.

The law is true whether diffusion takes place into another gas or into a vacuum.[1]

The following results of Graham's experiments substantiate the law.

Gas.	Density: Air = 1.	$\frac{1}{\sqrt{\text{density}}}$.	Velocity of Diffusion: Air = 1.
Hydrogen	0·06949	3·7935	3·83
Methane	0·559	1·3375	1·344
Carbon monoxide ...	0·9678	1·0165	1·1149
Nitrogen	0·9713	1·0147	1·0143
Ethylene	0·978	1·0112	1·0191
Oxygen	1·1056	0·9510	0·9487
Hydrogen sulphide ...	1·1912	0·9162	0·95
Nitrous oxide ...	1·527	0·8092	0·82
Carbon dioxide ...	1·52901	0·8087	0·812
Sulphur dioxide ...	2·247	0·6671	0·68

The statement of the law may be modified by saying that the **times of molecular passage of gases through a porous septum are directly proportional to the square roots of the densities of the gases;**

[1] Probably the same law always applies to the rates at which different gases expand into a vacuum under comparable conditions; but the speed is ordinarily too great for measurement.

and this aspect of the law is illustrated by the following results of Graham.

Gas.	Time of Molecular Passage into Air at 100 mm. Pressure.	$\sqrt{}$ Density: Oxygen = 1.	Time of Molecular Passage into a Vacuum.
Hydrogen	0·2472	0·2509	0·2505
Air	—	—	0·9501
Oxygen	1·0000	1·0000	1·0000
Carbon dioxide ...	1·1886	1·1760	1·1860

The phenomena of diffusion may be illustrated in an interesting manner by employing a large glass U-tube partly filled with coloured water, and having a cylindrical porous pot attached to one end of it by means of a tightly-fitting rubber bung.

When an inverted beaker of hydrogen is brought over the porous pot (fig. 11), the water in the adjacent limb of the U-tube is depressed, because hydrogen enters the pot quicker than air escapes from it, and consequently an excess of pressure is set up within the pot. When, however, the beaker is taken away, the hydrogen now within the pot diffuses out quicker than air can enter, so that not only does the water rise again in the adjacent limb, but it goes beyond its original level, showing a temporary pressure within the pot less than that of the atmosphere. Finally, the water slowly falls till it attains the same level in both limbs.

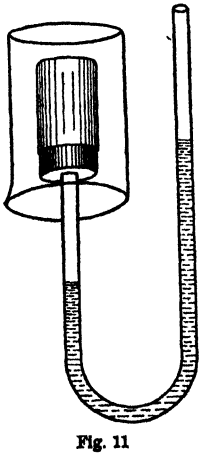


Fig. 11

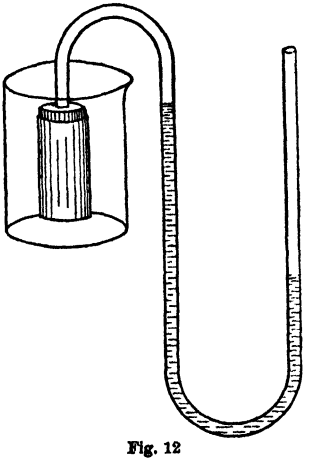


Fig. 12

If the apparatus is now modified so that the pot is attached to the U-tube the other way up (fig. 12), a beaker of carbon dioxide may be brought round it so that the pot is immersed in this heavy gas. In this case the water will rise in the adjacent limb, because carbon dioxide diffuses into the pot more slowly than air diffuses

out of it; and when the beaker is removed the pressure will gradually be restored again, as the carbon dioxide escapes from the pot and air takes its place.

The first part of the experiment may be modified so as to cause a fountain to play (fig. 13), or the displaced liquid may be caused to complete an electric circuit and so to ring a bell. The presence in mines of methane, which is lighter than air, may be indicated by an alarm given in this manner.

When gases pass through a minute aperture ($\frac{1}{300}$ in. diameter) in a thin metallic plate, they obey the law of diffusion. This phenomenon was called by Graham the *effusion of gases.*

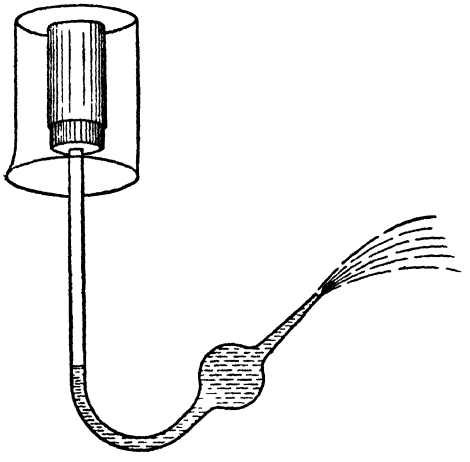


Fig 13

Diffusion or effusion may be employed (*a*) to determine the relative densities of gases, or (*b*) partially to separate the constituents of a mixture of gases. The latter process is called *atmolysis.*

(*a*) The density of ozone relative to that of chlorine was determined by Soret, who showed that 227 volumes of chlorine diffused in the same time as 271 volumes of ozone; or that the rates of diffusion of the two gases were as 0·8376 : 1. If the density of chlorine is 35·46, then that of ozone is consequently 24·9; for

$$1 : 0{\cdot}8376 :: \sqrt{35{\cdot}46} : \sqrt{24{\cdot}9}.$$

Similarly, Ladenburg found that a mixture of oxygen and ozone containing 86·16 per cent of ozone required 430 seconds to effuse, while pure oxygen required 367·4 seconds. Putting the density of oxygen = 1, then

$$367{\cdot}4 : 430 :: \sqrt{1} : \sqrt{1{\cdot}3698};$$

and if the density of this mixture of 86·16 per cent ozone with 13·84 per cent oxygen is 1·3698, that of pure ozone may be calculated to be 1·429 (O = 1).

(*b*) *Atmolysis* takes place when electrolytic gas, i.e. a mixture of 2 volumes of hydrogen with 1 of oxygen, passes through an unglazed earthenware tube, such as the stem of a "church-warden" tobacco-pipe; the gas which is collected does not explode, but, owing to the escape of hydrogen by diffusion, contains a sufficient proportion of oxygen to ignite a glowing wood splint.

Also, when ammonium chloride is vaporized in a glass tube through the centre of which an unglazed pipe-stem passes, the products of dissociation are partially separated by atmolysis; the lighter ammonia, passing through the stem, may be blown out against red litmus paper, which it turns blue, while the denser hydrogen chloride, remaining in the glass tube, shows its presence by reddening blue litmus paper.

Atmolysis has been employed partially to separate heavier argon from lighter nitrogen derived from air, but the process is imperfect and of little practical use.

From the standpoint of dynamics, diffusion may be attributed to the velocity of the molecules of a gas, and the different rates of diffusion to differences in molecular velocities.

Now the kinetic energy of a particle of mass m, moving with a velocity v, is $\frac{1}{2}mv^2$. Consider, therefore, two gases whose molecular weights are m_1 and m_2; when these two gases are in thermal equilibrium, that is at the same temperature, the following relation will hold:

$$\begin{aligned} & \tfrac{1}{2}m_1v_1^2 = \tfrac{1}{2}m_2v_2^2; \\ \text{or} \quad & d_1v_1^2 = d_2v_2^2; \\ \text{or} \quad & v_1 : v_2 :: \sqrt{d_2} : \sqrt{d_1}. \end{aligned}$$

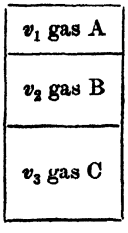
This relation, however, expresses the law of diffusion if v_1 and v_2 stand for rates of diffusion. It may therefore be concluded from the kinetic theory of gases, to which the above argument belongs, that the rate of diffusion of a gas depends directly upon the velocity of its molecules.

3. Pressure of Gaseous Mixtures

Dalton's Law of Partial Pressures states that **the total pressure of a mixture of gases is equal to the sum of the partial pressures of the individual gases.**

Otherwise regarded, the law states that the different kinds of molecules present in a gaseous mixture do not interfere with

each other, so that each gas exercises a pressure proportional to the concentration of its molecules, as if that gas alone occupied the whole space. A priori, there is no reason why this should not be true; and, indeed, it must be true if Boyle's law is true for all the gases in the mixture, and these gases have no chemical influence on each other. For, to use a well-worn analogy, gases occupy a space as the soldiers of an army might occupy a country, not in massed battalions but in widely separated units, so that the soldiers of another army might equally occupy the country if they were evenly distributed between the men of the first army.



The law may be examined in this way. Suppose a rectangular box divided by removable partitions into several spaces, I, II, III, &c.; let the volume of these spaces be respectively v_1, v_2, v_3, &c., and let

$$v_1 + v_2 + v_3 + \&c. = v.$$

Let different gases, A, B, C, &c., which have no chemical action on one another, be contained in these spaces, and let them all be at the same pressure, p. Now let the partitions be withdrawn, so that the gases mix by diffusion and their molecules become evenly distributed over the whole space. The partial pressure of gas A will then be, according to Boyle's law, $\frac{v_1}{v}p$, that of B $\frac{v_2}{v}p$, and so on; the law then states that the sum of these partial pressures will equal the original pressure p:

$$\text{i.e. } \frac{v_1}{v}p + \frac{v_2}{v}p + \frac{v_3}{v}p + \&c. = p.$$

Again, it may be seen that the validity of this law depends on the validity of Boyle's law, for the above statement is reducible to this: $v_1 + v_2 + v_3 + \&c. = V$; and so it may be said that **the volume occupied by a mixture of gases is equal to the sum of the volumes occupied by its constituents under the same conditions of temperature and pressure.**

The truth of this statement may be tested in the following way. From the densities of air, oxygen, and atmospheric nitrogen the percentage composition of air by weight may be calculated; it may also be determined from the volumetric composition, if the density of air is left out of account, by multiplying the

relative volumes of the gases by their respective densities, and converting the resulting values into percentages. By calculation air has thus been found to contain 23·21 per cent of oxygen and by estimation 23·18 to 23·23 per cent.

Dalton's law underlies the correction which is made for the pressure of water vapour when a gas is measured over water, and is therefore saturated with water vapour. The pressure of water vapour at the temperature of the gas, which is subtracted from the pressure under which the gas is measured, was estimated, originally, *in vacuo*; and yet the correction is applied to a gas at atmospheric pressure, under the justifiable assumption that the presence of the air makes no difference to the pressure the water vapour exerts. For example, if a quantity of gas is measured over water, and the barometric pressure is 765 mm., whilst the room temperature is 14° C., the pressure of the dry gas will be 765 − 12 = 753 mm., since the pressure of water vapour at 14° C. is 12 mm.

4. Deviations of Gases from Boyle's Law

Boyle's law is true only for perfect gases, that is for gases whose molecules are independent units, behaving like points moving in space without attracting one another, and rebounding after impact with unabated energy. The law is most nearly true for gases at comparatively low pressures, and far from their liquefaction temperatures. It is therefore truer at ordinary temperatures for difficultly than for easily condensable gases. The following table shows the values of $\frac{pv}{PV}$ at atmospheric temperatures, where $p = 0{\cdot}5$ atmospheres and $P = 1$ atmosphere for a series of gases arranged in the order of their condensability.[1] For a perfect gas $\frac{pv}{PV} = 1$.

Gas.	B.-P. Atmospheric Pressure.	Temperature.	$\frac{pv}{PV}$
Hydrogen	(−253° C.)	10·7°	0·99974
Nitrogen	(−196° C.)	14·9°	1·00015
Air	(about −190° C.)	11·4°	1·00023
Carbon monoxide	(−190° C.)	13·8°	1·00026
Oxygen	(−183° C.)	11·2°	1·00038
Nitrous oxide	(−89·8° C.)	11·0°	1·00327
Ammonia	(−33·5° C.)	9·7°	1·00632

[1] Lord Rayleigh, *Proc. Roy. Soc.*, 1905, *74*, 446.

It will be observed that hydrogen at atmospheric pressure is actually less compressible than accords with Boyle's law; it is therefore sometimes spoken of as a more than perfect gas. The deviations of the other gases from Boyle's law are very slight because they are far removed from their liquefaction temperatures. With a more condensable gas, like carbon dioxide, the deviation is much greater.

The accompanying diagram (fig. 14) expresses the deviations of gases from Boyle's law graphically. Along the horizontal axis pressures in atmospheres are plotted, and along the vertical axis values of pv. The state of an ideal gas at constant temperature is therefore represented by a horizontal straight line.

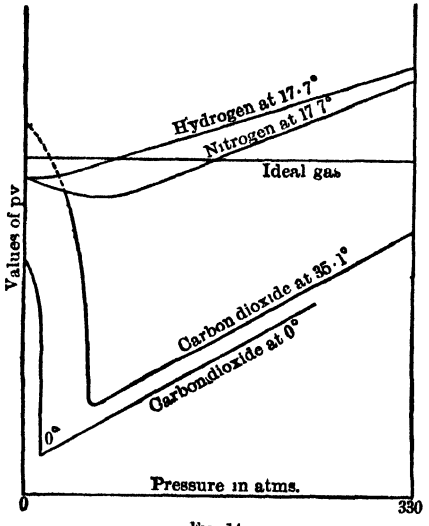


Fig. 14

It will be seen that, except at very low pressures and up to 330 atmospheres, hydrogen at atmospheric temperature is always less compressible than an ideal gas, and nitrogen at atmospheric temperature is more compressible than an ideal gas at moderate pressures, but less compressible at high pressures; and the same is true in a much exaggerated degree of carbon dioxide, which as an easily liquefiable gas departs widely from Boyle's law. An interpretation of the shape of the carbon dioxide curve for 35·1° may now be sought. The downward trend of the curve at first shows that the value of pv rapidly diminishes when that of p is increased. If the curve descended vertically, liquefaction would be taking place, i.e. continuous diminution of volume at constant temperature and pressure. Therefore the early part of the curve shows an approach to the process of liquefaction. The latter part of the curve, on the other hand, shows a difficulty of compressibility approaching that of a liquid. This foreshadowing of the condition and properties of a liquid by a substance still a gas suggests that these two states of matter are not always sharply divided; and, as will be seen directly, there is a condition

in which the two states merge into one and become indistinguishable. Meanwhile it may be noted that another curve, representing conditions of carbon dioxide at 0°, contains a vertical portion ending in an angle whence it diverges sharply upwards. It need hardly be pointed out that true liquefaction is represented as taking place in the part of the curve descending vertically, and that when this is completed the upward turn of the curve represents the compression of liquid carbon dioxide.

The physical properties of carbon dioxide may be expressed, perhaps more simply, by a diagram in which pressures are plotted directly against corresponding volumes. The *isothermals*, i.e. lines of equal temperature, then take the form shown in the following figure:

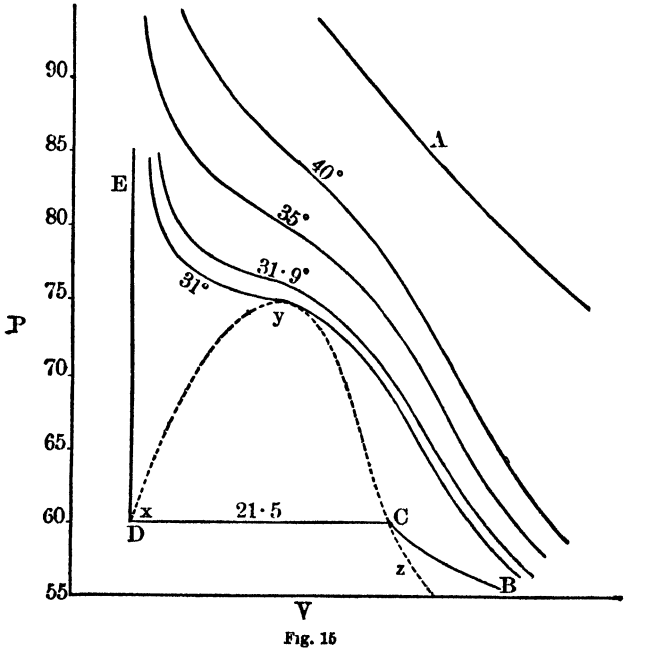


Fig. 15

A is the isothermal of a perfect gas, which accords with Boyle's law that pv = constant. Whatever point is chosen on A the product of the numerical values of p and v corresponding to this point is always the same.

With the isothermals of carbon dioxide for temperatures down to 31° there is a diminution in the value of pv at moderate pressures

and an increase in its value at high pressures. This is shown in the bulging of the isothermals, the curves being flattened in the middle, where the value of pv diminishes owing to the increased compressibility of the gas, and steepened towards their upper ends, where on account of greatly diminished compressibility the value of pv rapidly increases. If the curve in any part became horizontal, that would represent liquefaction. Such is the case with the isothermal for 21·5°, which consists of three distinct parts: firstly, an upward sloping part, BC, representing compression of carbon dioxide gas; secondly, a horizontal part, CD, representing diminution of volume at constant pressure which is the condition of liquefaction; thirdly, a steeply sloping, almost vertical, part, DE, representing the slight compressibility of liquid carbon dioxide. Liquefaction of carbon dioxide is possible only at temperatures whose isothermals consist in part of horizontal straight lines. The dotted line xyz marks the upward boundary of liquefaction. At temperatures whose isothermals pass at all within the region thus outlined, liquefaction will take place if sufficient pressure is applied; at other temperatures liquefaction is impossible at any pressure.

Attention may now be drawn to the isothermal which touches the top of the curve xyz. Its temperature is 31° or 304° absolute. This is the highest temperature at which liquefaction can take place, or the lowest at which it can be avoided. It is evidently a critical temperature, and the carbon dioxide is in a critical state. The temperature is called *the critical temperature* for carbon dioxide, and the state *the critical state*. But what is to be seen there? The experiment of Dr. Andrews answers this question.

Carbon dioxide gas at 21·5° was compressed in a strong glass tube until it was seen to liquefy at a pressure of 60 atmospheres. Thus two layers were observed in the tube, the dense gas above and the light liquid beneath. When the temperature was raised, the liquid expanded and at the same time partially evaporated, so that, since the total volume was kept constant, the gas became denser because of what it received from the liquid, while the liquid became specifically lighter because of expansion. Thus the densities of the two phases, liquid and gas, approached each other. At 31°, under a pressure of 73 atmospheres, these densities became identical, the line of demarcation between liquid and gas disappeared, and the tube became filled with a homogeneous fluid hardly describable as liquid or gas.

When the temperature was slightly lowered, a flickering was seen like the air currents faintly visible above a heated object; and then the liquid appeared again, only to disappear in the same way if the temperature was slightly raised. These changes were brought about, it is to be observed, by slight variations of temperature under constant pressure; they could not be induced by slight variations of pressure at constant temperature; i.e. if the temperature was maintained slightly above 31°, so that no liquid appeared in the tube, it was impossible by increasing the pressure at this temperature to liquefy the carbon dioxide.

The fluid state, above described, which is common ground, so to speak, between liquid and gas, and is reached from either side by an approximation of density, is the *critical state* of carbon dioxide; the temperature 31° C. is the *critical temperature* of this substance; 73 atmospheres is its *critical pressure*; the density of the fluid at the critical temperature and pressure, which is 0·464, is its *critical density*, and the specific volume $\left(\frac{1}{\text{density}}\right)$ its *critical volume.*

These terms may now be defined as follows:

The *critical temperature* of a gas is the highest temperature at which the gas can be liquefied by compression.

The *critical pressure* of a gas is the pressure under which it is liquefied at its critical temperature.

The *critical state* of a substance is the state in which its gaseous and liquid phases merge into one homogeneous fluid.

The *critical density* is the density of the fluid in its critical state; and

The *critical volume* is the specific volume of the fluid in its critical state.

One possible misunderstanding must be avoided. It is not necessary to realize the critical pressure in order to liquefy a gas; the critical pressure is not the lowest pressure under which a gas can be liquefied. A gas may be liquefied under a pressure of one atmosphere or less if the temperature is low enough.

5. The Liquefaction of Gases

The student has already learned that the two conditions necessary for the liquefaction of a gas are the lowering of its temperature and the increase of its pressure. He is also acquainted with

the fact, unknown to the earlier experimenters in this region, that no amount of pressure can compensate for insufficient lowering of temperature; that unless a gas is cooled below its critical temperature it cannot be liquefied.

The history of the liquefaction of gases is the history of the gradual elucidation of fundamental physical principles, and of their ingenious experimental application; and the subject well repays careful study.

It will be well first to set forth a list of the commoner gases with their critical temperatures and pressures, and boiling-points under atmospheric pressure.

Gas.	Critical Temperature.	Critical Pressure. Atmospheres.	B.-P. under 760 mm. Pressure.
Sulphur dioxide	157·2°	77·7	−10·1°
Chlorine	141°	83·9	−33·7°
Ammonia	132·9°	112·3	−33·46°
Hydrogen sulphide	100·4°	89·1	−61·8°
Hydrogen chloride	51·4°	81·6	−83·0°
Nitrous oxide	36·5°	71·7	−89·8°
Acetylene	35·5°	61·5	sublimes at −83·6°
Carbon dioxide	31°	72·9	−80°
Ethylene	10°	—	−103·5°
Methane	−82·8°	45·6	−164°
Nitric oxide	−93·5°	71·2	−149·9°
Oxygen	−118·8°	50·8	−182·9°
Carbon monoxide	−139·5°	35·5	−190°
Nitrogen	−145°	33·6	−195·5°
Hydrogen	−241°	19·4	−252·5°
Helium	−267·75°	2·75	−268·7°

It will be seen that the gases in the above table, as far as ethylene, might be liquefied by the application of sufficient pressure with little or no cooling; but that the remaining gases could not be liquefied by the earlier experimenters, because they had not the means of securing sufficiently low temperatures, even if they had recognized the necessity for them. Consequently, these gases were called "permanent gases".

The following are the methods which have been employed for the liquefaction of gases:

i. The Method of Simple Compression, with or without Cooling.

Monge and Clouet liquefied sulphur dioxide before the year 1800 "by extreme artificial cold and a strong pressure exerted at

the same time"; and in 1805–6 Northmore liquefied sulphur dioxide, chlorine, and hydrogen chloride. The most important and interesting of the earlier experiments, however, were those carried out by Faraday under the direction of Sir Humphry Davy.

Faraday sealed up solid chlorine hydrate, $Cl_2 \cdot 8H_2O$, in a glass tube, and immersed the tube in boiling water. The hydrate melted, and produced two liquids, one of which was chlorine water, and the other liquid chlorine. Faraday generally employed, however, a sealed glass tube bent at right angles. At one end of the tube were placed the ingredients from which the gas could be generated by heat; whilst the other end, which was empty, was immersed in a freezing-mixture. The pressure produced by the confined gas then sufficed to liquefy it in the cooled end. In this way Faraday liquefied all the common gases, except methane and those that follow it in the above list; these latter he thus considered to be "permanent".

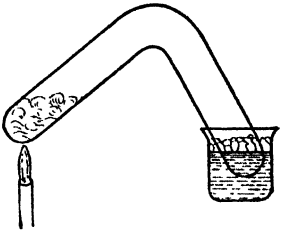


Fig. 16

Faraday's results were communicated to the Royal Society in a series of papers during the years 1823–45; and in 1834 Thilorier liquefied carbon dioxide on a large scale by decomposing sodium carbonate with sulphuric acid in a strong copper vessel connected with another copper vessel in which the gas was condensed. He also obtained carbon dioxide snow by the rapid evaporation of the liquid.

The results of Andrews's experiments on carbon dioxide were first published in 1863, and formed the subject of his Bakerian lecture on "The Continuity of the Gaseous and Liquid States" in 1869. Thenceforth the necessity of cooling a gas below its critical temperature in order to liquefy it was recognized; and this principle was kept in view by all subsequent experimenters.

ii. The Cascade Method of Cooling.

Sulphur dioxide can be liquefied at atmospheric temperature by moderate compression; and it may then be evaporated again at a lower temperature under reduced pressure. The liquid sulphur dioxide, thus cooled, may serve to cool the carbon dioxide, so that the latter gas can be liquefied in turn by suitable compression.

By rarefaction the liquid carbon dioxide may be made to evaporate quickly, so that its temperature falls while it solidifies;

and so a "permanent gas", cooled below its critical temperature by means of this solid carbon dioxide, may be liquefied by compression. This is the principle of the cascade method, by which Pictet liquefied oxygen in 1877.

Liquid sulphur dioxide was made to boil under reduced pressure at − 65° in a cylinder surrounding an inner tube containing carbon

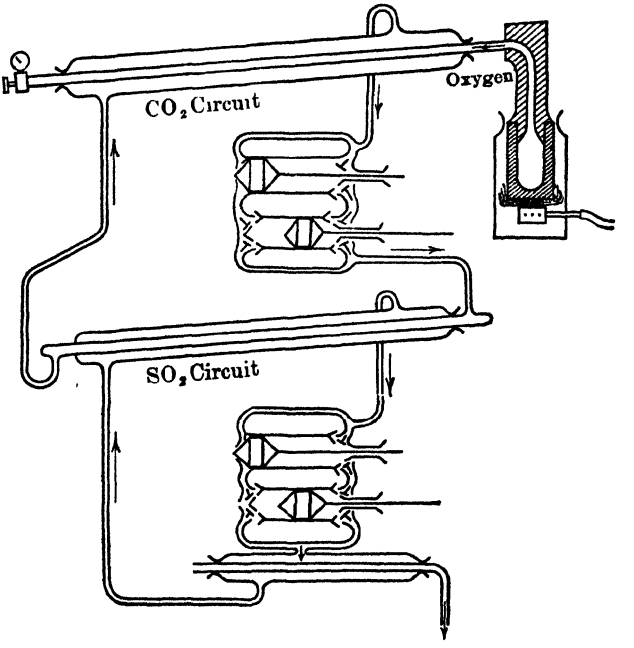


Fig. 17

dioxide, which was liquefied at this temperature under a pressure of 4 to 6 atmospheres (fig. 17). The liquid carbon dioxide then flowed into another cylinder, which surrounded oxygen highly compressed in a steel tube connected with a steel retort in which it was being generated. By evaporation under low pressure the carbon dioxide was here cooled to a temperature of −140°, which is well below the critical temperature of oxygen.

The pressure under which the oxygen was contained in the steel tube was 320 atmospheres; which was much in excess of what was necessary. Since, therefore, oxygen gas had been cooled below its critical temperature, under adequate pressure, it was liquefied.

iii. The Method of Adiabatic[1] Expansion.

If a force f moves through a space s, work is performed which is numerically equal to the product fs; and if a gas expands by a volume v against a pressure p, it performs work equivalent to pv. If the expansion is adiabatic, the only source of energy is the heat of the gas; consequently a gas is cooled by adiabatic expansion on account of the performance of *external work*.

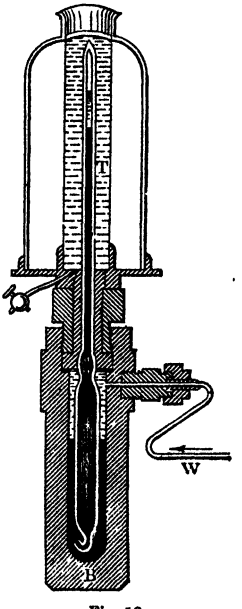


Fig. 18

Cailletet applied this principle to the cooling of gases in 1877, and succeeded in liquefying methane, nitric oxide, oxygen, carbon monoxide, air, and nitrogen. The apparatus employed (fig. 18) consisted of a strong capillary glass tube (T) to contain the gas over mercury. This tube was immersed in a closed wrought-iron mercury bath, into the upper part of which water (W) could be forced by hydraulic pressure applied by a screw. Thus the gas in the capillary tube could be highly compressed, and then by the sudden releasing of the pressure made rapidly to expand against the pressure of the mercury. The work performed in this expansion deprived the gas of sufficient energy to cool it below its critical temperature, whilst sufficient pressure remained to liquefy it. A mist seen inside the tube was evidence of liquefaction.

The principles underlying the methods of Pictet and Cailletet have been subsequently employed by Wroblewski, Olszewski, and Dewar, but a different principle forms the basis of more recent work upon the liquefaction of gases.

iv. The Method of Self-intensive Refrigeration.

When a perfect gas expands into a vacuum it does no kind of work, and therefore does not change its temperature. But most gases are less than perfect; they are more compressible at moderate pressures than corresponds with Boyle's law, because their molecules are not quite independent of one another. Intermolecular

[1] "Adiabatic" means allowing nothing to pass through. The term signifies the condition of imperviousness to heat.

attractions thus constitute a force to overcome which energy must be supplied. Consequently, when a compressed gas expands into a vacuum it is cooled slightly by reason of the *internal work* it performs in overcoming the attractive force between its own molecules. Thus a lowering of temperature is observed when a gas expands through a small orifice; this effect, which is called the *Joule-Thomson effect*, is, however, quite small, amounting, for air at 0° C., to only 0·29° C. for a fall in pressure of 1 atmosphere. The effect has, however, been made cumulative, and of use for gaseous liquefaction by an ingenious device, which may be simply explained in the following way.

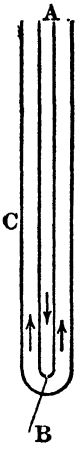


Fig 19

Suppose a compressed gas within the tube A (fig. 19) escapes through the small orifice B, and passes back at reduced pressure up the outer tube C, in which the inner tube is enclosed. Whilst the gas is expanding, the orifice is cooled a little, and in consequence serves to cool the gas within the tube A, as it passes through. Thus the temperature of the gas delivered through the central tube continuously falls until at length the critical temperature is passed, and liquid drops from the orifice through which the compressed gas has hitherto been driven. The temperature at which this takes place depends upon the internal pressure upon the gas, whilst the rate of the liquefaction process depends chiefly upon the efficiency of the cooling. The meaning of the term "self-intensive refrigeration" should now be plain.

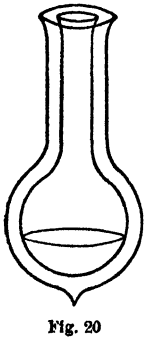


Fig. 20

This principle was successfully applied to the liquefaction of air by Linde and Hampson in 1895. The apparatus consists essentially of a long copper spiral tube, surrounded concentrically by a larger tube, and packed in insulating material. The gas, either compressed specially to 150 atmospheres or more, or delivered from a gas cylinder directly into the apparatus, passes down the inner tube, through the valve at its base, and back at a low uniform pressure through the annular space between the two tubes. The liquid is collected in a "Dewar vessel" (fig. 20), which is a double-walled glass flask with the space between the walls completely evacuated. In consequence, convection of heat from the air to the contents of the vessel does

not take place, and the heat which penetrates by radiation is only about one-sixth what would otherwise be conveyed. If the glass is silvered, the heat entering is reduced to about one-thirtieth part of what would enter through a single-walled glass vessel. The well-known thermos-flask is constructed on the same principle as the Dewar vessel.

Liquid air, which is now commonly used for low-temperature research, was prepared in large quantities by Dewar, who employed liquid ethylene, boiling *in vacuo* at − 152°, as a cooling agent.

Air is now generally liquefied, however, by the self-intensive process of Linde or Hampson, which depends on the performance of internal work, and takes advantage of the Joule-Thomson effect, or by the Claude process, in which cooling is secured by the performance of both internal and external work.

In the *Linde* or *Hampson* process air carefully freed from carbon dioxide and water vapour expands from a pressure of 150–200 atmospheres within the coil of the apparatus to a little more than atmospheric pressure outside the nozzle. About 5 per cent of the air that passes through the apparatus is liquefied, and about 1½ litres of liquid air are obtained per hour. Since oxygen is more condensable than nitrogen, liquid air contains a larger proportion of the former element than gaseous air.

The cooling effect of expansion of a compressed gas with performance of external work is much greater than that of free expansion; and the *Claude* process combines these two effects, in which air is compressed to 40–50 atmospheres, and then divided into two parts. One of these parts is allowed to expand in a cylinder, so as to perform external work, and the air so cooled then surrounds the other compressed part of the air, which is thus sufficiently cooled to liquefy at once by free expansion. Considerable economy of power is effected by this device.

The Liquefaction of Hydrogen and Helium.

Pictet imagined that he had liquefied hydrogen, and described this substance as a steel-blue liquid. This, however, was a mistake. Wroblewski, in 1884, first converted hydrogen into a "liquide dynamique" having the appearance of an instantaneous froth, by cooling the gas to the boiling-point of the oxygen, and then suddenly expanding it, according to Cailletet's method, from 100 atmospheres to 1 atmosphere pressure; and, Olszewski, in 1891,

performed similar experiments, but failed to obtain hydrogen as a "static liquid" showing a meniscus, because no liquid was available having a boiling-point lower than that of oxygen, by means of which the hydrogen gas might be cooled. Dewar in 1898 overcame this difficulty by employing the self-intensive process to cool the gas. It will be remembered, however, that hydrogen is a "more than perfect" gas at atmospheric temperatures; it is less compressible than accords with Boyle's law, and is actually warmed by free expansion. Below $-80{\cdot}5°$ C., however, which is called its "inversion temperature", hydrogen becomes, like other gases, less compressible than Boyle's law requires, and like them is cooled by free expansion. Consequently, when cooled by liquid air below its inversion temperature, hydrogen was liquefied in quantity by self-intensive refrigeration.

Helium is even more difficult to liquefy than hydrogen, but, in 1908 Kamerlingh Onnes liquefied this gas by the self-intensive process, after first cooling it to the temperature of liquid hydrogen.

Practical Applications of Liquefied Gases.

In addition to their use for low-temperature research, liquefied gases find practical application in several ways. *Liquid ammonia* is employed in the manufacture of ice. In the oldest freezing-machine, that of Carré, concentrated solution of ammonia is employed in the following way.

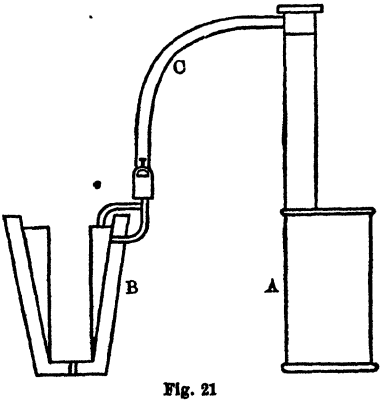


Fig. 21

The iron vessel A contains water saturated with ammonia at 0° C. When this vessel is heated, ammonia gas distils by the pipe C and condenses between the walls of the cup-shaped vessel B. Condensation takes place at atmospheric temperature when the pressure of the gas reaches about 7 atmospheres. After most of the ammonia has thus been liquefied in B, A is immersed in cold water, and gaseous ammonia at once begins to redissolve in the water contained in A so as to re-form the original solution. Consequently liquid ammonia evaporates from B, and the heat necessary for this evaporation is drawn

from the surroundings; so water, placed within the cup, may be frozen.

In more modern ice-machines use is made of anhydrous ammonia, which is liquefied by pressure, and then evaporated again, the latent heat of evaporation as before being drawn from water, which is thereby frozen.

When a kilogram of liquid ammonia evaporates at $-10°$ C., 322·3 calories[1] are absorbed. It must be remembered, however, that this same amount of heat is evolved when an equal quantity of ammonia gas is liquefied by compression; and provision must be made for the removal of this heat. In practice water is frozen, not by the direct contact of vessels containing it with evaporating ammonia, but by their immersion in brine cooled to $-10°$ by the ammonia which is evaporating in coils that pass through it.

The parts of the machine are represented diagrammatically as follows:

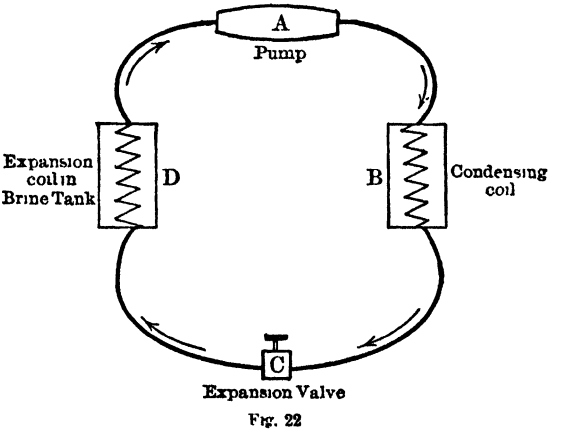


Fig. 22

Gaseous ammonia is compressed by the pump A, and liquefied in the condensing-coil B, the heat generated during condensation being removed by water. The flow of the liquid ammonia is regulated by the expansion-valve C, and this liquid evaporates in the expansion-coil immersed in the brine-tank D, which also contains rectangular cans in which is the water to be frozen. The evaporated ammonia returns to the pump, again to go through the same cycle of condensation and evaporation.

Chlorine, *carbon dioxide*, and *sulphur dioxide* gases are liquefied

[1] A calorie is the amount of heat necessary to raise 1 grm. of water through 1° C.

for convenience of storage and portability. Liquid chlorine is employed in large quantities for chlorination in the manufacture of organic chemicals; and its use in recent warfare is notorious. Carbon dioxide is stored in cylinders in the liquid state; for, unlike oxygen and hydrogen, this gas is liquefied at atmospheric temperature by moderate pressure; consequently cylinders containing as much as 28 lb. of the liquid can be supplied. When such a cylinder is tilted, and the valve opened so that liquid carbon dioxide can escape into the air, some of it is solidified and appears in the form of carbon dioxide snow, on account of the heat removed by the portion which evaporates. Liquid carbon dioxide is also used in the manufacture of aerated waters, as a refrigerant in place of ammonia, and for other purposes. Liquid sulphur dioxide is supplied in steel cylinders or in thick glass siphons, convenient for laboratory use. It is employed in bleaching, for antiseptic purposes, and as a refrigerant.

The *liquefaction of air*, and the fractional distillation or rectification of the liquid, are now employed as a means of preparing oxygen and nitrogen gases from the air.

If liquid air is caused to evaporate as fast as it is produced, the more volatile gas which escapes from it is nitrogen containing about 7 per cent of oxygen; while the liquid that remains, and can be drawn off and evaporated, is practically pure oxygen.

By a process of rectification, also, that is by allowing a sufficiently cooled air-current to pass upwards through a down-flowing stream of liquid air, nitrogen and oxygen may be separated. This is because the more condensable oxygen in the up-flowing air-current is liquefied, while the heat thus liberated serves to gasify some of the nitrogen of the down-flowing liquid air. By liquefying the escaping nitrogen, and repeating the process, gaseous nitrogen may be obtained practically free from oxygen.

The uses of oxygen are well-known. Nitrogen, obtained from the air through liquefaction, is employed in large quantities for the manufacture of calcium cyanamide and synthetic ammonia.

Hydrogen is now obtained from water-gas—which consists of this gas and carbon monoxide in approximately equal proportions—by fractional condensation of the carbon monoxide, which leaves the hydrogen nearly pure.

SUMMARY

THE GAS LAWS: *Law of Boyle.*—The volume of a gas at constant temperature is inversely proportional to its pressure.

$$p \propto \frac{1}{v}, \text{ or } pv = \text{constant.}$$

Law of Charles.—The volume of a gas at constant pressure increases by $\frac{1}{273}$ (= 0·00367) part of its value at 0° C. for every degree rise of temperature; *or*

The volume of a gas varies directly as its absolute temperature.

The Gas Equation: PV = RT. (T = absolute temperature, V = the gramme-molecular volume.)

Law of Gaseous Diffusion.—The rates of diffusion of different gases are inversely proportional to the square roots of their densities.

Dalton's Law of Partial Pressures.—The total pressure of a mixture of gases is equal to the sum of the partial pressures of the individual gases.

DEFINITIONS OF THE CRITICAL STATE.—The *critical temperature* of a gas is the highest temperature at which a gas can be liquefied by compression.

The *critical pressure* of a gas is the pressure under which it is liquefied at its critical temperature.

The *critical state* of a substance is the state in which its gaseous and liquid phases merge into one homogeneous fluid.

The *critical density* is the density of the fluid in its critical state.

The *critical volume* is the specific volume of the fluid in its critical state.

METHODS OF LIQUEFACTION OF GASES:

i. The method of simple compression, with or without cooling
ii. The cascade method of cooling.
iii. The method of adiabatic expansion.
iv. The method of self-intensive refrigeration.

CHAPTER VIII

THE PROPERTIES OF LIQUIDS

It has already been seen how liquids differ from gases in the relations of their molecules. An outcome of this difference is that liquids possess more highly individualized properties than gases. Perfect gases behave alike towards changes in pressure and temperature; liquids are unequally though very slightly compressible, and have separate co-efficients of thermal expansion.

This is because whilst the molecules of perfect gases are so far removed from one another that they behave as points in space, and their chemical composition has no influence on their physical properties, the molecules of liquids approximate to each other, with the result that their chemical composition influences their physical behaviour.

The relation between the liquid and gaseous states has been studied in the former chapter, and it has been seen that liquids and gases appear to be sharply distinguished except in the critical state. There is no such sharp distinction between liquids and solids, and there is no question of critical state. Liquids are distinguished as *mobile* and *viscous*, or, in simpler words, as thin and thick, and a liquid may be so viscous as to be scarcely distinguishable from a solid. Thus, while water is a mobile liquid, and ether is still more mobile, glycerine is comparatively viscous, and pitch and beeswax are so extremely viscous as scarcely to flow at all, and therefore frequently to be regarded as solids. Experience shows that a viscous liquid increases in viscosity as it is cooled, and becomes more mobile when heated. Pitch, for example, which at low temperatures is brittle and may be broken with a hammer, softens gradually and becomes definitely liquid when sufficiently heated; but it does not possess a melting-point, that is to say, there is no fixed temperature at which change from solid to liquid takes place.

The *viscosity* of a liquid is an important physical property,

which is measured by observing the rate of flow of the liquid through a capillary tube under standard conditions.

Of the various other physical properties of liquids those which will be considered here are: *density*, and its reciprocal value *specific volume*; and *vapour pressure*, together with *boiling-point*.

Density.

Different liquids differ much in density. Water, being the commonest liquid, provides the standard of density; but since changes of temperature affect the densities of liquids on account of thermal expansion, a definite temperature must be chosen at which the density of water is reckoned to be unity; and similarly a definite temperature at which the liquid under consideration is to be examined.

Water assumes its maximum density at 4° C., from which temperature it expands and becomes specifically lighter whether warmed or cooled. Consequently the density of water at 4° C. is usually regarded as the standard, and said to be unity. Thus the densities of other liquids may be compared with that of water at 4° C. For example, the density of chloroform at 11·8° C. has been found to be $d\frac{11\cdot8^\circ}{4^\circ} = 1\cdot5039$, whilst at 15°, compared with water at 15°, $d\frac{15^\circ}{15^\circ} = 1\cdot5009$.

The reciprocal of density or specific gravity,[1] $\frac{1}{\text{density}}$, is *specific volume*. Thus the specific volume of chloroform is $\frac{1}{1\cdot5039} = 0\cdot665$; and the product of specific volume and molecular weight is *molecular volume*, so that the molecular volume of chloroform is $0\cdot665 \times 119\cdot4 = 79\cdot4$.

The relationships between molecular volumes of related compounds have been found to be a subject worthy of study and to yield results of interest. Thus the molecular volumes of successive members of series of analogous carbon compounds, i.e. of homologous series of such compounds, are found to stand in arithmetical progression. For example, the fatty acids:

		Molecular Volumes.	Differences.
Formic acid	$H\cdot COOH$	41·4	
			22·3
Acetic acid	$CH_3\cdot COOH$	63·7	
			21·7
Propionic acid	$C_2H_5\cdot COOH$	85·4	
			21·7
Butyric acid	$C_3H_7\cdot COOH$	107·1	

[1] The terms density and specific gravity are generally used as synonymous by chemists.

Thus, for an atomic difference of CH_2, there is a difference of molecular volume of approximately 22 units; or, for every addition of CH_2 to the molecule there is an addition of 22 to the molecular volume. On this account molecular volume is said to be an *additive property.* It is even possible to go further and attribute a volume-effect to each atom within the molecule. Thus, from the work of Kopp, the following values in the case of acetic acid, $CH_3 \cdot COOH$, are obtained:

2C = 11 × 2	= 22	
4H = 5·5 × 4	= 22	
0″ (in CO)	12·2	
0′ (in OH)	7·8	
	64·0	calculated.
	63·7	observed.

In the following table are given the densities of a number of liquids:

Liquid.		Density.
Liquid hydrogen	.....	0·0763 (−259·9°)
Liquid helium	.....	0·154 (cir. −269°)
Liquid methane, CH_4	.....	0·415 (−164°, B. P.)
Pentane, C_5H_{12}	.....	0·627 (14°)
Ethyl ether, $(C_2H_5)_2O$	.....	0·72 (17·4°)
Ethyl alcohol, C_2H_5OH	.....	0·806 (0°)
Paraffin oil	.....	0·8 to 0·85
Benzene, C_6H_6	.....	0·874
Carbon disulphide, CS_2	.....	1·292 (0°)
Carbon tetrachloride, CCl_4	.....	1·595 (0°)
Ethyl iodide, C_2H_5I	.....	1·944
Methyl iodide, CH_3I	.....	2·293
Bromoform, $CHBr_3$	.....	2·9 (15°)
Bromine	.....	3·188 (0°)
Methylene iodide, CH_2I_2	.....	3·293
Mercury	.....	13·595 (0°)

From these figures it is seen that the range of density is very great; thus, mercury is about 178 times as heavy as liquid hydrogen. Heavy liquids, such as bromoform and methylene iodide, are used in mineralogy to separate mineral fragments of different densities, the lighter of which will float and the heavier sink in a liquid of intermediate density.

Mercury, the only liquid metal, has a density far exceeding that of any other liquid. Were it not for this, the manufacture of accurate barometers of reasonable dimensions would not be possible.

Vapour Pressure and Boiling-point.

Liquids differ much in volatility or rate of evaporation at atmospheric temperature and pressure. Thus a little ether, poured upon a flat surface, will soon evaporate and disappear, whilst a similar quantity of water will be little diminished. On the other hand, sulphuric acid and glycerine when left exposed to the air actually increase in bulk, because they do not evaporate but are hygroscopic, and absorb water vapour from the air.

The idea of vapour pressure will be made plain by the following consideration. Suppose a liquid is contained in a closed evacuated vessel, which it does not fill. At a given temperature a certain quantity of the liquid will evaporate into the space above it until the pressure of the accumulating vapour reaches a certain value, when a state of dynamic equilibrium will be established in which evaporation and condensation take place at equal rates. The pressure thus established is called the vapour pressure of the liquid at the given temperature.

The vapour pressures of water at different temperatures are shown in the following table:

Temperature C.	Pressure mm. Hg.	Temperature C.	Pressure mm. Hg.
0°	4·6	80°	354·3
5°	6·5	90°	525·5
10°	9·2	100°	760·0
15°	12·7	111·7°	1140·0
20°	17·4	120·6°	1520·0
30°	31·5	127·8°	1900·0
40°	54·9	133·9°	2280·0
50°	92·0	144·0°	3040·0
60°	148·8	180·3°	7600·0
70°	233·1	213·0°	15200·0

The relationships between these temperatures and the corresponding pressures are shown graphically in the diagram (fig. 23) on the following page, in which pressures are recorded on the vertical and temperatures on the horizontal axis.

The vapour pressure curves for other liquids take a similar form.

It will be observed that the vapour pressure at 100° C. is 760 mm. Now, 100° C. is said to be the boiling-point of water, and 760 mm. is normal atmospheric pressure. A liquid boils when its vapour pressure has become equal to atmospheric

pressure; so that the various temperatures in the table on p. 161 represent the boiling-points of water under the corresponding pressures. Thus on a mountain, where the barometer registers 525·5 mm., which is at a height of about 8500 ft., water will boil at 90° C.; and on a higher mountain, where the pressure is

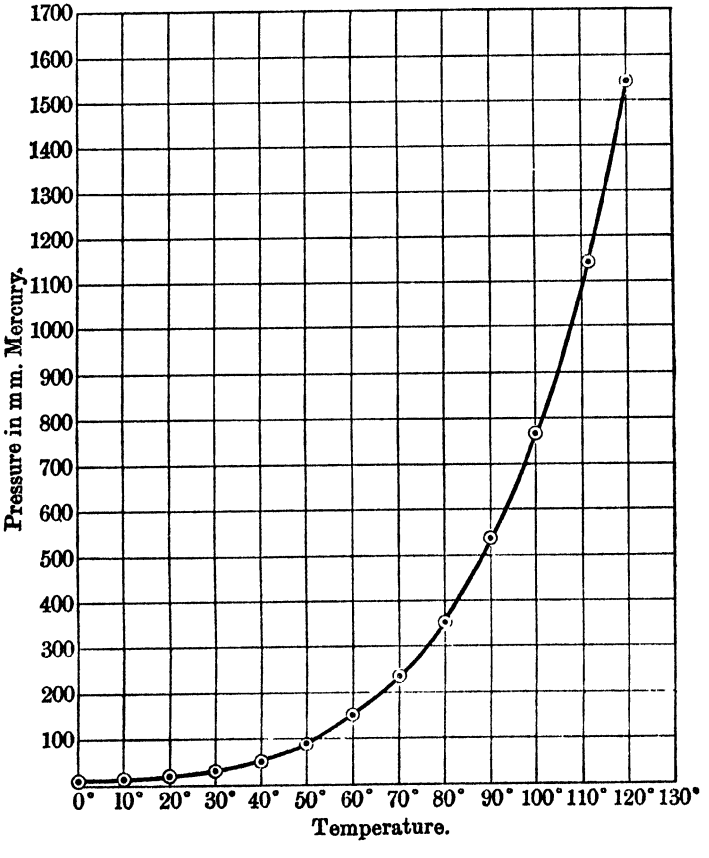


Fig. 23

only 354·3 mm., at an altitude of 14,600 ft., it will boil at 80° C. When a gas is measured over water, as is frequently done in the estimation of gases, it is saturated with water vapour, and its pressure is that of the dry gas plus the pressure of water vapour at the observed temperature. The pressure of the dry gas is therefore found by subtracting the pressure of water vapour at the temperature of the experiment from the barometric pressure,

provided the level of the water is the same inside and outside the measuring-tube.

Not all liquids can be distilled at atmospheric pressure, for some are decomposed by heat before they can reach a boiling-point under these conditions. Pure hydrogen peroxide, for example, decomposes when heated above 70° C., but does not boil at this temperature under atmospheric pressure. It has already been seen, however, that the boiling-point of a liquid is lowered by lowering the superincumbent pressure; and the application of this principle permits of the distillation and purification of various liquids which could not otherwise be purified.

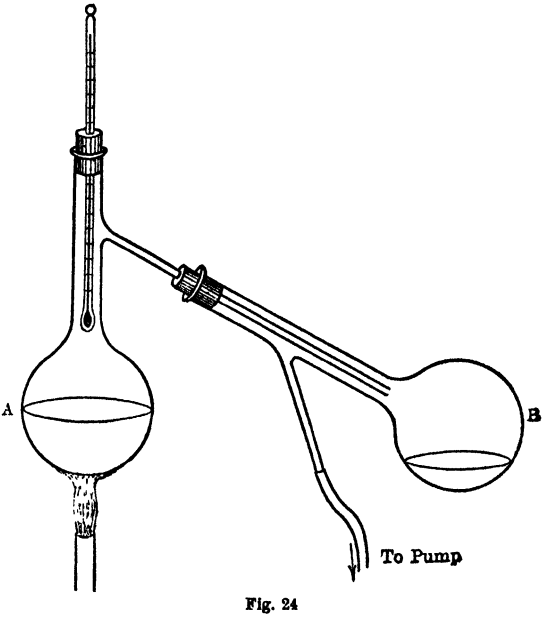


Fig. 24

Distillation under reduced pressure can be carried out on a small scale by means of two distilling-flasks fitted together as shown in the figure. The liquid to be distilled is contained in the flask A, which is closed by a tightly-fitting cork, through which a thermometer passes. The delivery-tube of this flask passes through a cork which fits tightly into the neck of a second flask B; and to the delivery-tube of this flask is attached a rubber tube which leads to an air-pump capable of reducing the pressure inside the flasks to about 15 mm. of mercury. The liquid in the distilling-flask is liable to bump when boiled; this is due to overheating whilst boiling is delayed, followed by a sudden ebullition, which is liable to carry the liquid bodily over into the collecting-flask. To prevent this, and steady the boiling process, a few fragments of pipeclay or unglazed earthenware are placed in the liquid. Air escapes from the pores of the earthenware before the liquid boils, and vapour

of the liquid is generated at the surface of the earthenware, which thus helps to steady the boiling by preventing overheating. In this, or a similar apparatus, pure hydrogen peroxide can be distilled at 69·2° C. under a pressure of 26 mm.

Relation between Boiling-points of Liquids in Homologous Series.

The boiling-point of a substance depends upon its molecular weight and chemical constitution. This is well seen in the various homologous series of carbon compounds.

Saturated normal Hydrocarbons, C_nH_{2n+2}

Formula.		B.-P. C.	Diff.
C_5H_{12}	.....	37°	
			32
C_6H_{14}	.....	69°	
			29
C_7H_{16}	.....	98°	
			27
C_8H_{18}	.....	125°	
			25
C_9H_{20}	.....	150°	
			23
$C_{10}H_{22}$	.....	173°	

Normal Monohydric Alcohols

Formula.		B.-P. C.	Diff.
$CH_3 \cdot OH$	.....	66°	
			22
$C_2H_5 \cdot OH$	.....	78°	
			19
$C_3H_7 \cdot OH$	.....	97°	
			20
$C_4H_9 \cdot OH$	.....	117°	
			21
$C_5H_{11} \cdot OH$	.....	138°	
			19
$C_6H_{13} \cdot OH$	.....	157°	

It is seen that in the case of the hydrocarbons the differences between the boiling-points of successive members of the series diminish as the series is ascended, whilst with the normal monohydric alcohols these differences remain approximately constant.

Further, it is interesting to notice that constitution as well as molecular weight affects boiling-point, for the more compact the molecules of a liquid are the lower is the liquid's boiling-point. Thus there are three pentanes which have the following constitutions and boiling-points:

Normal pentane

$CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$

B.-P. 37° C.

Isopentane

$CH_3 \cdot CH_2 \cdot CH(CH_3)_2$

B.-P. 30° C.

Tetramethylmethane.

$C(CH_3)_4$

B.-P. 9·5° C.

So it seems that molecules consisting of simple elongated chains are more difficult to disengage from the state of liquid than molecules of equal weight which are branched, and consequently not so elongated.

SUMMARY

The *specific volume* of a liquid is the reciprocal of its *density*.

Molecular volume is the product of specific volume and molecular weight.

The molecular volume of a liquid is an additive property; it is the sum of the atomic volumes of the constituent atoms of its molecule.

A *vapour pressure curve* represents the relation between the vapour pressures of a liquid at different temperatures, or otherwise the temperatures at which the liquid will boil under different pressures.

The boiling-points of successive members of a *homologous series* of chemical compounds rise regularly with successive increments of molecular weight.

CHAPTER IX

THE PROPERTIES OF SOLIDS

It has already been seen that solids differ from liquids in possessing a shape of their own, and from gases by possessing, in addition, a definite volume at a given temperature, which is little affected by changes of pressure; and, further, that these properties depend upon the fact that the molecules of solids possess only vibratory, and not to any extent translatory, motion.

The following topics will be considered in this chapter: The manner of formation of solids from a state of (*a*) vapour, (*b*) fusion, (*c*) solution; and then the following properties: physical form, including the crystalline and amorphous states; isomorphism, polymorphism, and allotropy.

The Formation of Solids.

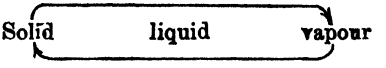
(*a*) Solidification of Vapours

Most vapours, when sufficiently cooled under atmospheric pressure, liquefy, but there are some which solidify without passing through the liquid state. Examples of these are ammonium chloride and arsenious oxide. There are other substances, such as iodine, sulphur, and water, which may either liquefy or solidify from the state of vapour, according to circumstances. Atmospheric water vapour, for example, becomes rain or snow, according to temperature; and sulphur, when distilled, will yield flowers of sulphur or liquid sulphur according to the rate of cooling.

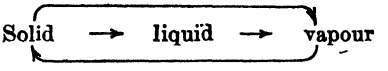
When solid iodine is kept in a bottle at atmospheric temperature it slowly vaporizes and produces crystals on the sides of the bottle. If, however, it is gently heated in a test-tube, it is observed to melt and to produce a violet vapour simultaneously; but when this vapour becomes cooled in the upper parts of the

tube it yields crystals of iodine without passing through the liquid state.

In the former case the iodine behaves thus:



in the latter case thus:



The former is a true case of *sublimation*, in which no liquid appears at all. In the latter case, although a sublimate of iodine appears, the melting of the iodine during heating precludes the description of the whole process as one of sublimation only.

A solid evaporates, or volatilizes, because it possesses a vapour pressure, and this vapour pressure increases with rise of temperature till the melting-point of the solid is reached. After the substance has melted, the vapour pressure, which continues to increase with rising temperature, is, of course, that of the liquid, and not of the solid.

The vapour pressures of many solids are very small, even near their melting-points, but those of iodine are considerable. In the following table are given the vapour pressures of iodine at different temperatures.

From these figures it appears that much iodine could be sublimed without melting at, say, 100° C., since the vapour pressure at that temperature amounts to more than 40 mm. of mercury.

VAPOUR PRESSURES OF IODINE

Temp. C.	Press. mg. Hg.
58·1°	4·9
75·2°	11·5
91·9°	29·6
102·7°	50·7
114·3° (m.-p.)	90·0
120·4°	113·4
125·5°	135·8
166·6°	475·0
177·6°	630·3
184·35° (b.-p.)	760·0

It will be observed that 114·3° is the melting-point of iodine, so that the vapour pressures above this temperature are those of the liquid element.

Now, suppose that the pressure of the vapour above heated iodine is kept below 90 mm., the consequence will be that the temperature of the iodine will never reach 114·3°, its melting-point. It will therefore be impossible to melt iodine under these conditions, and heat energy supplied to it will cause it to sublime without melting. And, conversely, if the heated vapour of iodine is quickly

cooled, so that its pressure falls below 90 mm., liquid iodine will not appear, but crystals of the solid instead. Thus it is easy to see that the true sublimation of iodine will necessarily occur when it is so heated that its vapour pressure does not reach 90 mm.

These considerations will explain why, for example, arsenious oxide, when heated, sublimes without melting. If this substance is heated under ordinary conditions in the air, its vapour pressure does not rise to a value corresponding with its melting-point. When, however, this compound is enclosed in a space which is continuously and uniformly heated, so that instead of condensing the vapour accumulates, fusion eventually takes place under the increased pressure.

(*b*) Solidification of Liquids—Melting-points of Solids

Water freezes and ice melts at 0° C. under a pressure of 1 atmosphere. Alteration of pressure affects the melting-point of ice to a very small but perceptible extent. The change amounts to about 0·0076° C. per atmosphere, so that under a pressure of 2 atmospheres, for example, ice melts at − 0·0076° C. Thus increase of pressure causes ice to melt without the supply of heat energy; consequently when the pressure is removed the water formed by the melting of the ice freezes again. This phenomenon is called *regelation*.

Now water expands on freezing, or ice contracts on melting; 1 volume of water at 0° C. becomes 1·09082 volumes of ice at the same temperature; or the density of ice at 0° C. is 0·91674, if that of water at 0° C. is unity.

The lowering of freezing-point of water by compression and the contraction of ice on melting are related phenomena. Ice melts when compressed, because in so doing it accommodates itself to the pressure by changing into water, which occupies a smaller volume.

Most solids, however, e.g. mercury and phosphorus, expand when liquefied; consequently compression promotes the formation of solid rather than liquid; in other words, increase of pressure raises the melting-point.

The influence of pressure upon melting-point is shown for ice and phosphorus in the following table:

Ice		Phosphorus	
Pressure in Atmospheres.	Melting-point.	Pressure in Atmospheres.	Melting-point.
1	0° C.	..... 1	44·10° C.
336	− 2·5°	..... 50	45·50°
615	− 5°	..... 100	47·00°
1155	−10°	..... 150	48·45°
1625	−15°	..... 200	49·85°
2042	−20°	..... 300	52·80°

When a pure liquid is cooled, its temperature may fall below the freezing-point of the liquid, or melting-point of the solid, without the separation of solid. If this takes place, the liquid is said to be super-cooled,[1] and is in a *metastable* state,[2] a state which is disturbed by the addition of a crystal of the solid substance. Thus, when water is being frozen in the Beckmann apparatus for molecular weight determination by Raoult's method (q.v.), the thermometer is often observed to fall continuously, and then to rise again quickly to a fixed point directly any ice is formed. The point to which the thermometer rises, and at which it remains stationary, is the freezing-point of the water. The lower temperatures show a state of super-cooling.

Melting-points.

It has been seen that some solids, when heated, sublime instead of melting. Many other solids, which are compounds, decompose before a melting-point is reached. Chalk, for example, cannot be melted, for when heated it decomposes into lime and carbon-dioxide gas. Some salts, which contain much water of crystallization, and are at the same time very soluble in water, melt in their water of crystallization at comparatively low temperatures, producing solutions. If such a salt is said to have a melting-point, the limitations of the case it presents should be clearly understood. The temperature at which the salt melts will depend upon the rate of heating, for if heated slowly it will lose much of its water during the process, and will melt eventually at a higher temperature, or will not melt at all if too much water has been lost; and, further, if kept at its melting-point for a long enough time, it will solidify owing to the evaporation of the water. Soda crystals, $Na_2CO_3 \cdot 10H_2O$, and Glauber's salt, $Na_2SO_4 \cdot 10H_2O$, show a further peculiarity when heated. The former melts at 35·1°, forming not

[1] That is, excessively cooled.

[2] This condition is comparable with that of supersaturation (q.v.).

a clear but a turbid liquid, which consists of crystals of the monohydrate, $Na_2CO_3 \cdot H_2O$, suspended in a saturated solution of the salt; the latter melts at 33°, forming a solution in which crystals of the anhydrous salt, Na_2SO_4, are suspended.

If it does not sublime or decompose, a pure solid substance melts when sufficiently heated; i.e. it possesses a melting-point, viz. the temperature at which it remains during melting, so that the heat supplied, instead of raising the temperature of the substance, becomes its latent heat of fusion. So far as the chemical elements are concerned, few of them sublime, and there is no question of their decomposition; consequently they possess melting-points, which, however, range between wide limits.

MELTING-POINTS OF ELEMENTS

Element.	Melting-point, Centigrade.	Element.	Melting-point, Centigrade.
Helium	below −271°	Aluminium	658·7°
Hydrogen	−259°	Calcium	810°
Fluorine	−223°	Arsenic	850°
Oxygen	−218°		under pressure.
Nitrogen	−210°	Silver	960·5°
Argon	−188°	Gold	1063°
Chlorine	−101·5°	Copper	1083°
Mercury	− 38·87°	Manganese	1230°
Bromine	− 7·3°	Silicon	1420°
Phosphorus	44°	Nickel	1452°
Potassium	62·3°	Cobalt	1480°
Sodium	97·5°	Iron	1530°
Iodine	113·5°	Chromium	1615°
Sulphur (rhombic)	112·8°	Platinum	1755°
Sulphur (monoclinic)	119·2°	Titanium	1800°
Tin	231·9°	Boron	2200°–2500°
Bismuth	271°	Iridium	2350°
Cadmium	320·9°	Molybdenum	2550°
Lead	327·4°	Osmium	2700°
Zinc	419·4°	Tantalum	2900°
Antimony	630°	Tungsten	3400°
Magnesium	651°	Carbon	above 3600°

The melting-points of the principal elements given in the above table are interesting for several reasons.

First, it may be noticed that, with the exception of boron, carbon, and silicon, the non-metals have low melting-points; whilst the melting-points of the metals are higher, and cover a very wide range.

If the melting-points of the elements are plotted on a vertical axis against the atomic weights on a horizontal axis, a succession of curves is obtained which show that the melting-points are periodic functions of the atomic weights. Moreover, this melting-point curve, taken as a whole, is roughly an inversion of the atomic-volume curve, the elements with the highest melting-points, such as iron and chromium and the metals of the platinum group, having the smallest atomic volumes, and vice versa.

The useful applications of the various metals in the arts depend, among other properties, upon their melting-points. Especially, the employment of tantalum and tungsten for the metallic filaments of incandescent electric lamps is attributable to the great infusibility as well as electric resistance of these metals.

In the study of organic chemistry melting-points are of much importance. A large proportion of solid organic compounds melt at temperatures which can be registered by means of an ordinary mercurial thermometer, and the observation of melting-point is therefore frequently employed to characterize or identify an organic compound, as well as to ascertain its purity. Since the solution of a solid substance in a solvent lowers the freezing-point of the solvent, the presence of an impurity will generally lower the melting-point of a substance. The highest melting-point observed after successive recrystallizations of a substance is therefore regarded as the true melting-point of that substance.

There is a connection between the melting-point and chemical constitution of a compound, and in a homologous series increase in molecular weight involves rise in melting-point. For example, the primary alcohols have the following melting-points:

Alcohol.	Melting-point.	Difference for CH_2.
CH_3OH	− 94°	
		−18°
CH_3CH_2OH	−112°	
		−15°
$CH_3(CH_2)_2OH$	−127°	
		+ 5°
$CH_3(CH_2)_3OH$	−122°	
$CH_3(CH_2)_6OH$	− 36·5°	
		+18·6°
$CH_3(CH_2)_7OH$	− 17·9°	
		12·9°
$CH_3(CH_2)_8OH$	− 5°	
		12°
$CH_3(CH_2)_9OH$	+ 7°	
		12°
$CH_3(CH_2)_{10}OH$	19°	
		6°
$CH_3(CH_2)_{11}OH$	25°	
		5·5°
$CH_3(CH_2)_{12}OH$	30·5°	

The first few members of the series show exceptional relation-

ships; then a fairly regular melting-point difference for every increment of CH_2 appears, but this diminishes when the higher members of the series are reached.

(c) Formation of Solids from Solution—Crystalline and Amorphous States.

When aqueous solutions of silver nitrate and sodium chloride are mixed together, silver chloride is formed as a white precipitate which is apparently amorphous; nevertheless, silver chloride can occur crystalline. Again, if solutions of calcium chloride and ammonium carbonate are mixed, a white, flocculent precipitate of calcium carbonate is formed; but when this precipitate is heated in the liquid in which it has been produced, it becomes granular and denser, and is then found to have crystallized in forms identical to those exhibited by the mineral aragonite. Hydrated magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$, presents a similar phenomenon. When first precipitated from moderately concentrated solutions, this salt is flocculent, but on standing it becomes crystalline. If, however, an attempt is made to precipitate it from a quite dilute solution, no solid separates at once; but crystals of perceptible size are formed after a time. This case can hardly be distinguished from one of ordinary crystallization from aqueous solution; and from the other facts here mentioned it may be inferred that the amorphous state is not a permanent state, but a condition assumed when a solid is suddenly formed, so that the molecules have not had opportunity to marshal themselves in the order which pertains to crystals.

There is, however, another kind of precipitate, which is gelatinous, and never becomes crystalline. Examples of such precipitates are hydrated alumina and silica. These are colloidal substances, consisting of large and complex molecules, and are probably not true solids at all.

Another example of an amorphous substance is glass, which appears solid enough. When glass is melted, it consists of a solution of various oxides, and this solution solidifies as a whole, when cooled, without crystallizing. Glass may therefore be regarded as a solid solution. Since, however, glass is slightly flexible, and gradually becomes more flexible as it is heated, it may be questioned whether this substance should be regarded as a solid or a super-cooled liquid solution. Support is lent to the latter view by the tendency of glass to devitrify, that is, for crystals to

separate within it, just as crystals may separate within a liquid solution.

With regard to the general question of amorphous solids, the extreme view is sometimes taken that no pure chemical substance exists in the solid amorphous condition, but that all amorphous substances are in reality super-cooled liquids.

Solidification of Mixtures—Cryohydrates—Eutectic Mixtures.

Liquid mixtures are solutions, and when solutions are cooled sufficiently for solids to separate from them, a variety of phenomena may occur. It has already been seen that when a dilute aqueous solution of a substance is cooled, ice separates from that solution just below 0° C., and that the more concentrated the solution the lower is the temperature at which the water freezes. On the other hand, from a warm concentrated solution it is the dissolved solid, i.e. the solute, rather than the solvent that separates on cooling, provided the former is less soluble in cold than in hot water. Now since the separation of ice from an aqueous solution increases the concentration of the solution, and the separation of solute diminishes its concentration, it is clear that two solutions of the same substance from which ice and solute separate respectively on cooling continually approach each other in concentration, so as eventually to become identical. This condition of identity has been approached from either side by continuous cooling, and the curves connecting concentrations and temperatures at which solid, whether ice or solute, separates, approach each other and eventually meet in a point, shown in the case of sodium chloride in the accompanying figure.

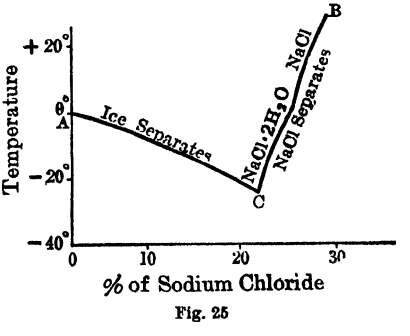


Fig. 25

The curve AC represents the temperatures at which ice separates according to the percentage of salt in the solution; similarly, the curve BC represents the temperatures at which salt separates from the cooling solution that it may remain saturated. Between + 0·15° C. and – 22° C. it is the hydrate $NaCl \cdot 2H_2O$ which is formed in the latter case. These two

approaching curves meet at the point C, which corresponds to −22° C. and 23·6 per cent of sodium chloride. Under these conditions the solution solidifies as a whole, for changes in concentration owing to separation either of ice or salt are at an end. This state, moreover, is reached whatever the concentration of the original solution may have been; for change in original concentration will affect only the point on either curve at which separation of solid begins. The solution in the state shown at C is a liquid with a definite solidifying-point, and the solid produced from it is one with a definite melting-point. These seem to be the properties of a chemical compound rather than of a mixture; but the solution is a mixture, for a 23·6 per cent salt solution cannot be regarded as a chemical compound; and the solid formed from this solution is a mixture of salt and ice, as may be revealed by the microscope.

The phenomena here described were first observed and studied by Guthrie, who called the solid produced when a solution solidifies as a whole a *cryohydrate*.[1] Since, however, the cryohydrate of a particular substance has a constant composition, Guthrie regarded such a product as a chemical compound. Clearly, however, he was wrong.

In the following table are given a few data regarding cryohydrates:

Salt.	Cryohydric Point, Centigrade.	Percentage of Anhydrous Salt in Cryohydrate.
Sodium chloride... ...	−22°	23·60
Potassium iodide ...	−22°	52·07
Sodium nitrate	−17·5°	40·80
Ammonium sulphate ...	−17°	41·70
Ammonium chloride ...	−15°	19·27
Magnesium sulphate ...	− 5°	21·86
Sodium sulphate ...	− 0·7°	4·55

The point C in the cryohydric diagram (fig. 25) marks the lowest temperature at which solidification takes place, and the solid mixture formed at that temperature is the easiest melted of any possible mixture. The point is therefore called the *eutectic*[2] *point*, and the mixture which solidifies is a *eutectic mixture*.

[1] I.e. ice-hydrate, because of the low temperature at which it is formed.
[2] Eutectic = easiest melted.

The phenomena here studied are characteristic of other mixtures besides aqueous solutions; they are of particular importance in the case of alloys which are mixtures of metals. First, it may be noted that, in accordance with principles with which the student is now familiar, mixtures of metals melt at lower temperatures than their constituents. A mixture of sodium and potassium may be made which is liquid at atmospheric temperature; and Wood's fusible metal is composed and melts as follows:

WOOD'S FUSIBLE METAL

1 part tin	M.-p.	232° C.	Alloy melts at 60·5° C.
2 parts lead	„	327° C.	
1 part cadmium ...	„	321° C.	
4 parts bismuth ...	„	271° C.	

A molten mixture of zinc (melting-point 419° C.) and cadmium (melting-point 321° C.) yields, by solidification of one or other metal during cooling, a eutectic mixture which solidifies at 270° C. and contains 73 per cent of cadmium. These facts are expressed diagrammatically thus:

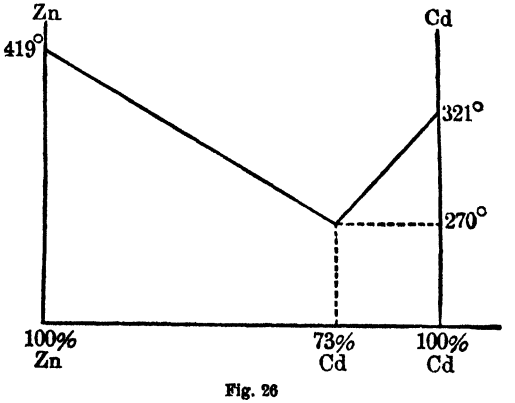


Fig. 26

Crystals and Crystallography.

According to popular ideas, a crystal is a clear and sparkling solid.[1] These ideas are true as far as they go. A well-formed crystal is transparent because its parts are packed in a close and orderly manner[2] without interspaces; and it often sparkles because

[1] Gr. κρύσταλλος, ice.

[2] The influence of close-packing is well seen by comparing together ice and snow. Both consist of crystals, but those of ice, which in small quantity is colourless and transparent, are close-packed without interspaces, whilst those of snow, which is opaque as well as white, lie loosely upon one another with air between.

its faces are flat, and reflect incident light without scattering it in innumerable directions.

To these ideas, however, must be added a third, also popularly recognized: that of geometrical form. Consequently **a crystal is a solid body, formed naturally from a state of vapour, liquid, or solution, which is bounded by plane surfaces, pairs of which intersect at edges which are straight lines, and three or more in solid angles or coigns.**

Whilst this definition serves for obvious crystals, it does not suffice to describe the crystalline state. A piece of rock-crystal,[1] for example, may plainly show a crystal form, but parts of it may be found which are irregular in shape; a lump of ice or rock-salt may be amorphous in external shape, whilst it is undoubtedly crystalline in internal structure. This may be shown in the case of rock-salt by breaking a lump with a hammer; among the fragments may be found almost perfect cubes, so the crystalline structure is revealed by fracture. When, however, a lump of rosin is broken by a hammer, or a pane of glass by means of a stone, the kind of fracture produced is dependent on the nature of the blow and not on the internal structure of the solid; for these are truly amorphous substances. Internal structure, however, as shown by fracture, is not alone a criterion of crystal nature; for slate and coal, for example, have a laminar fracture owing to being formed in strata by compression.

A fundamental distinction between crystalline and amorphous substances is well illustrated by the different behaviour of glass and rock-crystal towards light. Light travels through glass at the same rate in all directions; it is similarly refracted from whatever point it enters the glass. This, however, is not so with quartz; for if a ray of light enters a quartz-crystal in any direction except one it is doubly refracted, being thus divided into two plane-polarized rays; whilst in one direction only, parallel to what is called the optical axis, the ray is not doubly refracted.[2]

Thus crystals differ in optical as well as in other physical properties in different directions; and this fact is a criterion of crystal structure which is independent of external form.

It must be added, however, that crystals belonging to one system—the regular system—show similar properties in all directions.

[1] Rock-crystal, because of its icy appearance, was originally thought to have been formed by cold amid the Alps.

[2] Modern work on crystal structure is referred to on p. 128.

There are, on the other hand, liquids which differ in physical properties in different directions; and consequently the existence of liquid crystals has been recognized.

For the scientific classification and study of crystals there must be some system, and crystallographers have adopted the geometrical system of axes round which the crystal is supposed to be built up.

Consider, for example, a crystal such as that shown in fig. 27, which is the form in which the alums crystallize.

It is a double square pyramid, that is, a pyramid on a square base ABCD, together with what would appear as its image if it

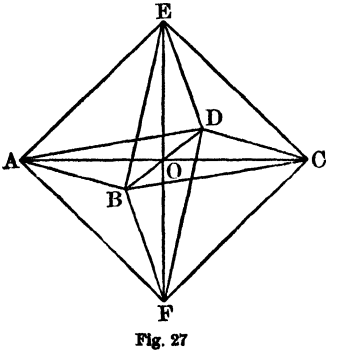


Fig. 27

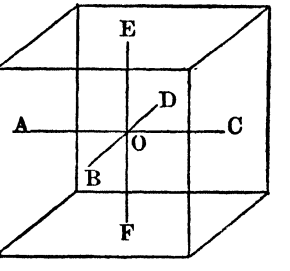


Fig. 28

stood upon a mirror. The equal diagonals of this square, AC and BD, bisect each other at O, and through this point, which is called the origin, passes the line EOF, which is equal to AC and BD, and is also bisected at O. The double-pyramid has eight faces, and is consequently called an octahedron. These faces are equilateral triangles, and they are all equal; moreover, the six angular points of the solid figure are equidistant from the centre or origin, O; consequently the figure is exceedingly symmetrical. Any of the other five angular points might take the place of the point F without altering the appearance of the figure. For instance, A might take the place of F; BEDF would then become the central plane, but this figure is also a square with the equal diagonals, BD and EF, bisecting one another at the point O. The lines AC, BD, EF are the crystallographic axes around which the regular octahedron appears to be built up.

It is possible, however, for a quite different figure to be constructed around the same crystallographic axes. This is the figure

of a cube (fig. 28). Here it is seen that the three equal axes emerge from the crystal at the centres of the six square faces of the cube.

These two forms, the *double-pyramid* and the *prism* (a cube is a square prism), are fundamental, and occur with modifications in other crystal systems.

Crystals are seldom as perfect as these figures represent them to be. Frequently some faces are developed by unequal growth at the expense of others, so that the form appears distorted. Thus alum may grow irregularly, and produce, instead of a regular octahedron, a form such as that shown in fig. 29, where the smaller faces are farther removed from the centre of the crystal than the larger ones. There can be no doubt, however, as to the type to which such a crystal belongs, for the existing faces are parallel to the corresponding faces of the perfect octahedron, being inclined to one another at the same angles.

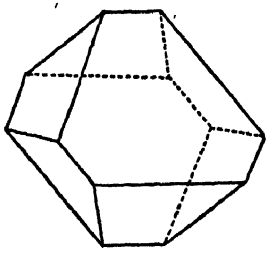


Fig. 29

Sometimes alternate faces are so developed as to obliterate the other faces; the crystal consequently possesses only half the number of faces of the original form. This is seen in the following illustration (fig. 30), which shows a regular tetrahedron, that is, a figure

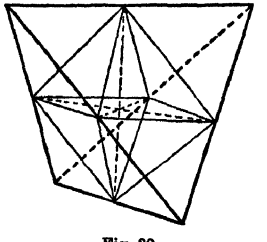


Fig. 30

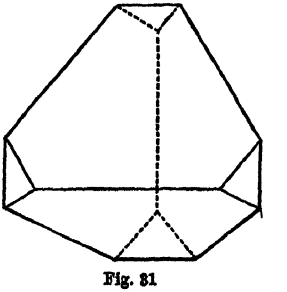


Fig. 31

with four equal faces in relation to the octahedron from which it is supposed to be derived.

Sometimes the other four faces of the octahedron begin to appear at the corners of the tetrahedron, as is shown in fig. 31. If these were so far developed as to yield faces equal to the faces of the tetrahedron reduced by their development, the octahedron would be regenerated.

The octahedron, with the full complement of faces, is said to be

a *holohedral* form, to which the tetrahedron is the corresponding *hemihedral*[1] form.

Very frequently, also, actual crystals are found to combine two forms, e.g. the pyramid and prism. The following figures show the ideal form of quartz, which combines the hexagonal prism and pyramid, and a form in which quartz more often occurs, showing distortion by unequal growths in different directions.

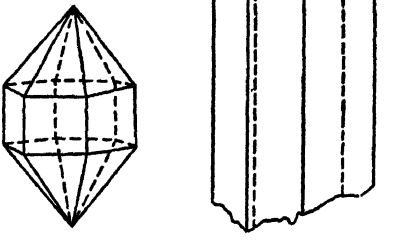


Fig. 32

The following crystallographic systems are recognized. Unfortunately one of several names may be employed for each system.

Crystal Systems.

i. REGULAR SYSTEM (Cubical, Isometric, Monometric, Tesseral). *3 axes, all equal, and at right angles* (fig. 33).

Examples.—Alum, salt, diamond, fluor-spar, various metals.

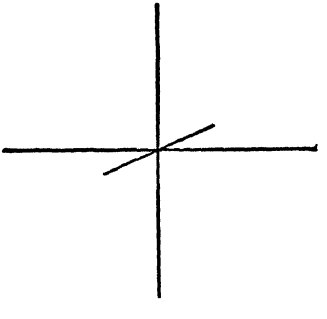


Fig 33

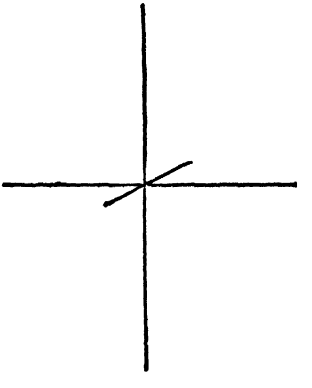


Fig. 34

ii. QUADRATIC SYSTEM (Square Prismatic, Dimetric, Tetragonal). *3 axes, 2 equal, all at right angles* (fig. 34).

Examples.—Zircon ($ZrSiO_4$), tin-stone (SnO_2), potassium dihydrogen phosphate, potassium ferrocyanide.

[1] Holohedral = full number of faces; hemihedral = half number of faces.

iii. RHOMBIC SYSTEM (Trimetric, Orthorhombic). *3 unequal axes, all at right angles* (fig. 35).

Examples. — Sulphur, nitre, potassium sulphate, magnesium sulphate, barium sulphate, potassium perchlorate, potassium permanganate.

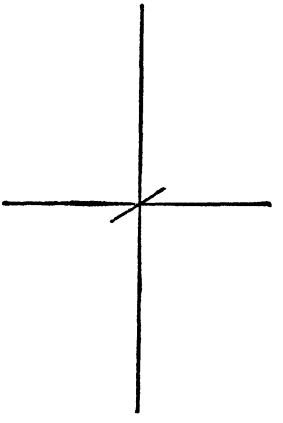


Fig. 35

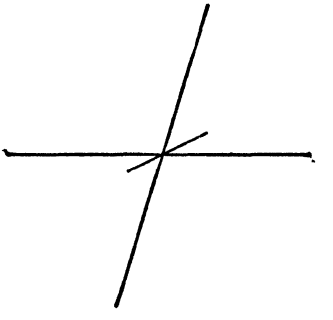


Fig. 36

iv. MONOCLINIC SYSTEM (Monometric, Monosymmetric, Clinorhombic). *3 unequal axes, 2 at right angles, the third inclined* (fig. 36).

Examples.—Gypsum, felspar, borax, soda crystals.

v. TRICLINIC SYSTEM (Asymmetric, Anorthic). *3 unequal axes, all inclined, there being no right angle between them* (fig. 37).

Examples.—Copper sulphate, potassium dichromate, boric acid.

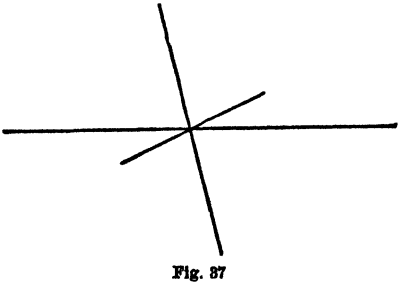


Fig. 37

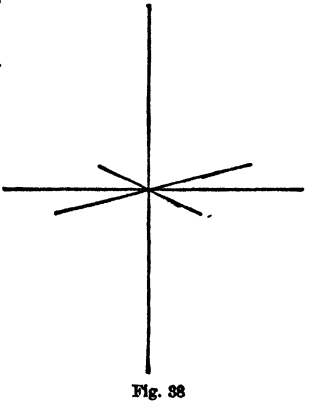


Fig. 38

vi. HEXAGONAL SYSTEM. *4 axes, 3 equal, in one plane, forming a regular hexagon; the fourth perpendicular to the plane of the other three* (fig. 38).

Examples.—Quartz, beryl, apatite, lead iodide.

Hemihedral forms: calcite, corundum, graphite.

NOTE.—The hemihedral forms of the hexagonal system are often classified as a separate system, the *Rhombohedral System* (Trigonal).

Crystallization.

It has already been seen that crystals may be produced from a substance in the state of vapour, as when snow is formed from water vapour, or iodine and naphthalene by the cooling of their respective vapours; also, that a pure liquid substance may solidify in the crystalline form, as when water freezes, or molten sulphur becomes solid. More frequently, however, crystals are obtained by the separation of a substance from solution in water or other solvent.

Inorganic salts are crystallized from aqueous solution; and if a salt is more soluble in hot water than cold, advantage is taken of this fact by preparing a hot saturated solution of the salt, and cooling the solution to atmospheric temperature. The excess of the salt, which can be dissolved in hot water over what can remain in solution at atmospheric temperature in contact with the solid salt, then separates in crystals, the size of which depends upon their rate of formation.

An experiment with copper sulphate will illustrate the formation of crystals. Suppose a hot saturated solution of this salt is rapidly cooled. As the solution approaches atmospheric temperature a mass of minute crystals separates, and if these are quickly filtered off, the nearly cold solution will slowly deposit more crystals as it stands. These crystals, moreover, will be larger, and will consequently appear deeper in colour than those which compose the crystal-meal that separated at first. Indeed, the more slowly a crystal forms the larger will it be; large crystals, like large trees, cannot be grown in a short space of time. On account of the long time available for the natural growth of crystals, mineral substances often occur in large crystals such as cannot possibly be made artificially. For example, calcium carbonate and barium sulphate occur naturally in very large transparent crystals, whilst artificially produced crystals of these substances are little more than microscopic in size.

The largest and most perfect crystals of a salt are best produced artificially by allowing its saturated solution to evaporate spon

taneously at atmospheric temperature in contact with some small, well-formed crystals of the salt. The rate of deposition of solid is commensurate with that of the evaporation of the water, since the solution must remain saturated; and if the growing crystals are turned over from time to time, to prevent disproportionate growth, large, well-formed crystals are eventually obtained. The mother-liquor, however, should not be allowed to evaporate completely, or the crystals will be contaminated with any impurity present in solution.

Recrystallization.

A crystalline salt may be purified by recrystallization, i.e. by dissolving it in hot water, filtering the solution if necessary, and allowing it to cool, so that crystals separate again. The soluble impurity will then probably remain in the mother-liquor, especially if it is present in relatively small amount, or is more soluble in water than the salt that is being recrystallized. Successive recrystallizations enhance the purity of the crystallized substance, but necessarily reduce its amount very seriously, since much of it remains in the successive mother-liquors. When salts are isomorphous, they tend to crystallize together, and their separation by recrystallization is therefore difficult. Copper sulphate and ferrous sulphate thus form isomorphous mixtures; but in this case the iron may be oxidized by means of a little nitric acid to non-crystallizable ferric sulphate, and the copper sulphate subsequently be obtained in crystals free from iron.

Polymorphism and Allotropy.

The phenomena of isomorphism have already been studied, and the law of isomorphism has been stated thus: the molecules of isomorphous substances contain equal numbers of atoms, which when not identical are analogous. Polymorphism has also been noticed, and it has been seen that polymorphous substances are those which, whilst preserving their chemical identity, can assume two or more crystalline forms under different conditions. Thus calcium carbonate is dimorphous, crystallizing as calc-spar in the hexagonal system, and as aragonite in the rhombic system. Titanic oxide, TiO_2, is trimorphous, crystallizing as rutile and anastase in two different forms of the quadratic system, and as brookite in the rhombic system. Ammonium nitrate is tetramorphous,

crystallizing in the regular system, the hexagonal system, and two forms of the rhombic system.

Conditions of temperature and state of solution determine which crystalline form is assumed; thus which of the two rhombic forms of ammonium nitrate separates from solution depends on whether the temperature is above or below 32° C.; and, moreover, crystals of sodium chloride, which are cubical when grown from water only, are octahedral when they separate from an alkaline liquid; and crystals of arsenious oxide consist of regular octahedra when formed by sublimation or from a solution in hydrochloric acid, and of rhombic prisms when produced from a caustic soda solution.

Various elements, and particularly some non-metals, resemble compounds in their polymorphism. Thus solid sulphur exists in two well-defined crystalline forms, belonging to the rhombic and monoclinic systems; carbon in two crystalline forms as well as in the amorphous state, and so on. Certain elements, however, exist in different forms in the liquid or gaseous state, and to these forms the term polymorphism cannot be applied. Thus there are two forms of liquid sulphur, one of which is yellow and mobile, and the other brown and viscous; these forms are observed successively when sulphur is carefully heated in a test-tube. And there are two forms of gaseous oxygen, ordinary oxygen, O_2, and ozone, O_3; and two forms of gaseous nitrogen, inactive and active respectively.

When an element can exist in more than one physical form, these forms are said to be allotropic[1]; they are allotropes, and the phenomenon is called allotropy or allotropism.

Thus ozone is said to be an allotropic form of oxygen; rhombic and monoclinic sulphur are allotropic forms of that element, and so forth. The term allotropy was given by Berzelius, in 1841, to the relation between different forms of an element to which it was thought the term isomerism could not well be applied. Since it includes such diverse phenomena as those presented by gaseous oxygen and liquid as well as solid sulphur, the term is in one sense an inclusive one, perhaps too inclusive to be scientific; and, moreover, since it excludes the phenomena presented by mercuric iodide, for example, because this substance is a compound, its scientific value is further discounted; for sulphur and mercuric

[1] ἄλλος, another; τροπός, habit.

iodide are dimorphous substances which, as will appear, closely resemble one another in their transformations.

On the other hand, since the term *polymerism* denotes atomic condensation within the molecule, so that substances which possess the same quantitative composition differ in molecular weight and chemical properties (e.g. C_2H_2 and C_6H_6), there is no valid scientific reason why the ozone-oxygen relationship should not be regarded as one of polymerism.

In view of these considerations, attempts to give a scientific definition of allotropy are not very successful. Ostwald directs attention to the energy aspect of the question in the following words: "Elements which by reason of different energy content possess different properties are allotropic". This conception is of value, and is particularly applicable to the ozone-oxygen relationship in connection with which it is developed, because individual and simple molecules are the units in which the phenomenon is displayed; but in the case of the dimorphism of sulphur the conception of the molecule is subsidiary to that of the crystal, and to refer the phenomenon to a difference of energy content alone, whether molecular or otherwise, is scarcely satisfying.

Again, a criticism has been passed on this definition that it would class as allotropic the physical states of solid, liquid, or vapour in which an element may exist, since the different properties of a substance in these states depend upon differences of energy content.

So that, whilst the term allotropy serves usefully to draw attention to the fact that various elements can exist in different forms, it cannot be defined with scientific accuracy, since the category it creates is imperfect by reason both of what it includes and of what it excludes.

It will now be profitable to study the conditions of change of one solid allotrope into another, or more properly of one form of a dimorphous substance into the other. The case of rhombic and monoclinic sulphur furnishes a useful example.

Rhombic or octahedral sulphur crystallizes from a solution of sulphur in carbon disulphide, and is otherwise formed at or near atmospheric temperature. Monoclinic or prismatic sulphur is produced at elevated temperature, as, for example, under the crust formed upon molten sulphur as it cools, and after some of the liquid has been drained away. It is significant, however, that

when kept at atmospheric temperature, prismatic sulphur gradually changes into the octahedral variety; and that naturally occurring sulphur is always octahedral. So it is concluded that whilst prismatic sulphur is the more stable form at certain elevated temperatures which favour its formation, octahedral sulphur is the more stable form at atmospheric temperature. Investigation has shown that a definite temperature exists above or below which the prismatic or octahedral form is respectively the more stable. This temperature is 95·5° C. Above 95·5° C. the prismatic form is the more stable, below this temperature the octahedral form; at this temperature both forms are equally stable. Consequently 95·5° C., which is the limiting temperature for the stabilities of the two forms of sulphur, is called the *transition temperature,* and the relationships with regard to this temperature are expressed thus:

$$\text{Octahedral sulphur} \underset{}{\overset{95\cdot5^\circ\text{ C.}}{\rightleftharpoons}} \text{prismatic sulphur.}$$

Across this temperature transition takes place from one form to the other, and the change, like many chemical reactions, is reversible. Such a change, with reference to dimorphous substances, is called an *enantiotropic change.*

Mercuric iodide presents phenomena closely analogous to those of sulphur. It exists in scarlet and yellow forms, the scarlet form consisting of quadratic (tetragonal), the yellow of rhombic crystals. When the scarlet crystals are gently heated, they turn yellow, melt, and yield a yellow sublimate, which, when cold, reverts to the red form, reversion being hastened by scratching. The transition temperature is 127° C., and the change is enantiotropic, thus:

$$\text{Scarlet (quadratic) mercuric iodide} \underset{}{\overset{127^\circ\text{ C.}}{\rightleftharpoons}} \text{yellow (rhombic) mercuric iodide.}$$

It is possible for yellow mercuric iodide to exist below 127°, though its existence is transitory. Thus, when formed by heating the red variety, it does not immediately become red when cooled below 127°; also, if the precipitation of mercuric iodide by the addition of potassium iodide to mercuric chloride solution is carefully observed, it will be seen that the precipitate, when first formed, is yellow, but that it quickly becomes red and eventually scarlet. And if mercuric iodide is dissolved in hot alcohol, and the

solution is then poured into water, the precipitate when first formed is pale yellow, but on keeping gradually turns red. When a substance persists in a state after the conditions for its stability have been exchanged for those under which another state of the substance is stable, the substance is said to be in a *meta-stable state.*

The relationship between yellow and red phosphorus is apparently different from the foregoing. Yellow phosphorus changes very slowly into the red variety when kept at atmospheric temperature, and the rate of change is accelerated by heating, becoming fairly rapid at 240°–250° C.

Evidently, then, the red variety is the more stable at comparatively low temperatures. It is formed from the white variety with the evolution of 27,300 calories per gramme-atom (= 31 grm.); thus

$$n\mathrm{P}_4 \longrightarrow 4\,\mathrm{P}_n + 27{,}300 \times 4n \text{ calories.}$$

If, however, red phosphorus is heated above 250°, out of contact with air, in order to reach a temperature at which it may pass into the yellow variety, it is found to sublime at about 290°, producing a vapour which condenses into yellow phosphorus. This phenomenon cannot, however, be regarded as the transformation of red into yellow phosphorus, since vapour intervenes; such transformation does not take place under ordinary conditions. Inasmuch as the change in the phosphorus takes place in one direction only, it is said to be *monotropic.*

It may be questioned, however, whether the failure to reverse the change in the case of phosphorus is not due to a failure to realize the right conditions. Chemical changes sometimes appear to be irreversible from this cause. That this is the case here is shown when red phosphorus is heated under pressure in a sealed tube.

Being unable to sublime, the red phosphorus forms a yellow liquid at 610°, from which, on cooling, red particles begin to separate at 580°, whilst the whole turns red at 570°. Thus the change from yellow to red phosphorus is seen to be reversible under pressure at about 600° C., which may be regarded as the transition temperature, so that under these conditions the change is enantiotropic.

In the following table are gathered together the chief examples of allotropy among the elements.

Element.	Forms.
Oxygen ...	Oxygen, O_2 $\rightleftharpoons$ Ozone, O_3.
Boron	Amorphous (brown powder), density 2·45 (impure[1]).
	Crystalline (adamantine), density 2·34.
Carbon ...	Amorphous, density 1·45–2·0.
	Graphite, density 2–2·25.
	Diamond, density 3·5.
Silicon ...	Amorphous, density 2·35.
	Crystalline, density 2·49.
Sulphur ...	Rhombic (octahedral) $\rightleftharpoons$ monoclinic (prismatic), 95·5°.
	density 2·06 density 1·96
	Also amorphous, colloidal, and liquid S (2 forms).
Phosphorus ...	Crystalline (yellow) $\rightarrow$ amorphous (red).
	density 1·83 density 2·106
	Reversible at 600° under pressure.
	"Metallic" phosphorus (impure).
Arsenic ...	"Metallic" (steel grey), density 5·727.
	Black or mirror arsenic, density 4·713.
	Yellow arsenic, density 3·88.
Antimony ...	Metallic, black and yellow forms, comparable with those of arsenic.
Tin	Grey tin $\rightleftharpoons$ tetragonal tin, 20° C.
	Tetragonal tin $\rightleftharpoons$ rhombic tin, 161° C.?
Iron	α-iron $\rightarrow$ β-iron, 770°.
	β-iron $\rightarrow$ γ-iron, 890°.

The following compounds present analogous phenomena:

Ammonium nitrate ...	α-rhombic $\rightleftharpoons$ β-rhombic, 32·2°.
	β-rhombic $\rightleftharpoons$ rhombohedral, 83°.
	rhombohedral $\rightleftharpoons$ regular, 125·6°.
Mercuric iodide	tetragonal $\rightleftharpoons$ rhombic, 127°.
Potassium nitrate ...	rhombic $\rightleftharpoons$ rhombohedral, 129·5°.
Silver iodide	hexagonal $\rightleftharpoons$ regular, 146°–147°.

There are certain metallic oxides which are well known to undergo temporary change of colours when heated. Amongst these are HgO, ZnO, Pb_3O_4. Such changes are enantiotropic, though the transition temperatures are not in all cases known. Red lead, for example, blackens when heated sufficiently, but, if the compound is not decomposed, the original colour is restored on cooling. The transition temperature has in this case been found to be 580° C.

[1] Since "amorphous boron" contains 4 to 5 per cent of oxygen as suboxide, it can hardly be regarded as an allotropic form of the element.

SUMMARY

CRYOHYDRATE; EUTECTIC.—A cryohydrate is a solidified mixture of solute and solvent (water), having the same composition as the solution.

A eutectic mixture, or eutectic, is a solidified mixture of solute and solvent which has the lowest melting-point. A cryohydrate is a special case of a eutectic.

A eutectic point is the point on a graph where the curves representing separation of solute and solvent intersect. The temperature thus represented, being the lowest temperature at which solid can be formed, is the eutectic temperature, and the mixture, the composition of which is also represented, is the eutectic mixture.

CRYSTALLOGRAPHY.—A crystal is a solid body, formed naturally from a state of vapour, liquid, or solution, which is bounded by plane surfaces, pairs of which intersect at edges which are straight lines, and three or more in solid angles or coigns.

CRYSTALLOGRAPHIC SYSTEMS.—1. *Regular System.*—3 axes, all equal, and all at right angles.

2 *Quadratic System.*—3 axes, 2 equal, and all at right angles.

3. *Rhombic System.*—3 unequal axes, all at right angles.

4. *Monoclinic System.*—3 unequal axes, 2 at right angles, the third inclined.

5. *Triclinic System.*—3 unequal axes, all inclined, there being no right angle between them.

6. *Hexagonal System.*—4 axes, 3 equal, in one plane, forming a regular hexagon, the fourth perpendicular to the plane of the other three.

ALLOTROPY.—When an element can exist in more than one physical form, these forms are said to be allotropic, i.e. they are allotropes, and the phenomenon is called *allotropy* or *allotropism.*

CHAPTER X

SOLUTIONS

In the broadest sense a solution is a homogeneous mixture of two or more substances; it may therefore be a gaseous, liquid, or solid mixture. Thus a mixture of gases such as the atmosphere is a gaseous solution; a mixture of solids such as an alloy or a glass is a solid solution. The term solution is, however, frequently restricted to liquid mixtures, and in this sense it will be employed here.

A solution, then, is a homogeneous mixture of a liquid with a gas, another liquid, or a solid. The dissolving liquid is called the *solvent*, and the dissolved gas, liquid, or solid the *solute*, the mixture of solvent and solute thus becoming the *solution*.

That a solution is merely a mixture may not be credited without demur, for there are numerous examples of chemical change accompanying the act of solution. A solution of sulphur dioxide gas in water, for example, is a solution containing sulphurous acid, and not merely a mixture of sulphur dioxide and water; and a solution of calcium phosphate in hydrochloric acid contains calcium chloride and phosphoric acid rather than the original salt. It is not, however, the process of solution that is being considered, but the product; not the change necessary to produce the mixture, but the mixture produced.

There is, however, a further objection to the idea that a solution is only a mixture. Is there no chemical union between the solvent and the solute? The act of solution of a substance in water is generally accompanied by lowering of temperature, due to the absorption of heat of solution incident upon the change in the physical state of the solute; but when sulphuric acid is mixed with water, much heat is evolved, and this probably results from some kind of chemical union between the acid and the water. Again, from a concentrated solution of copper sulphate, crystals of the hydrated salt $CuSO_4 \cdot 5H_2O$ separate. It may be believed that this compound

exists in solution just previous to its separation as crystals, but a different view of the nature of a dilute solution of copper sulphate appears justified by the properties of such a solution. Therefore some kind of chemical change seems to take place during the making of a dilute solution of this salt from the solid and water. The further consideration of the phenomena presented by the dilute solutions of salts may, however, be deferred till a little later.

Solutions of Gases in Liquids

Aqueous solutions of gases are familiar. Drinking-water contains dissolved air; effervescing beverages contain dissolved carbon dioxide; chlorine, ammonia, and hydrogen sulphide solutions are common in the laboratory.

A gas does not dissolve to an unlimited degree in a liquid, and the extent to which it dissolves depends upon four conditions:

i. The nature of the solvent.
ii. The nature of the gas.
iii. The temperature of the solvent.
iv. The pressure of the gas.

The **solubility** or **coefficient of solubility** of a gas in a liquid is defined as **the volume of the gas which is dissolved by unit volume of the liquid.** The temperature must be stated, since this influences the amount of gas dissolved, but the question of pressure does not enter into the definition for a reason which will appear later.

i. THE NATURE OF THE SOLVENT.

The influence of the solvent is illustrated by the following figures relating to carbon dioxide:

Solvent.	Vol. CO_2 dissolved by 1 vol. Solvent at 25° C.
Water	0·8256
Ethyl alcohol, 97 %	2·706
Chloroform	3·430
Methyl alcohol	3·837
Acetone	6·295

ii. THE NATURE OF THE GAS.

Gases differ widely in their solubility in water or other solvent.

The solubility of a gas may be measured by the apparatus known as an absorptiometer, and shown in the accompanying figure.

The pure, dry gas is contained over mercury in the graduated

tube A, and its pressure is regulated by means of the tube B connected with A by thick rubber tubing. At the top of A is a 3-way tap leading to the atmosphere, or to the flexible tube C made of lead, and connecting the measuring-tube with the absorption vessel D. This vessel is at first completely filled with air-free water or other solvent for the gas. Some of this solvent is then made to flow out through the tap F, whilst an equal volume of gas enters the absorption vessel from the top, until the liquid level stands at E, the known volume of the remaining solvent being that which is to be saturated with the gas. The gas is agitated with the liquid repeatedly until no further diminution of volume in A is observed. The remaining gas is then taken back into A by opening the tap F under mercury, and so adjusting the pressure as to cause mercury to enter, and the liquid consequently to rise to the top of D, so as to displace all the gas. The volume of gas which has been dissolved by the known volume of liquid in D is then ascertained by observing the volume remaining in A at atmospheric pressure. If desired, the absorption vessel may be surrounded by a water-jacket to keep its temperature constant.

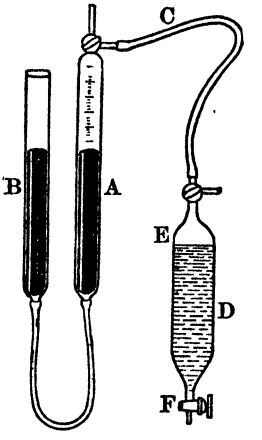


Fig. 39

In the following table are given the solubilities in water of some of the commoner gases, together with their boiling-points:

Gas.	Volume of Gas dissolved by 1 volume of Water at 0° C.	B.-p. of Liquefied Gas under Atmospheric Pressure.
Hydrogen	0·021	−252·8°
Nitrogen	0·0235	−195·7°
Carbon monoxide ...	0·0328	−190°
Oxygen	0·0489	−182·9°
Nitrous oxide ...	1·305	− 89·8°
Carbon dioxide ...	1·713	− 80°
Hydrogen sulphide ...	4·37	− 61·8°
Chlorine	4·610	− 33·7°
Sulphur dioxide ...	79·789	− 10·1°
Hydrogen chloride ...	503·0	− 83°
Ammonia	1148·0	− 33·5°

It will be noticed that these gases fall conveniently into three

categories. First, there are the gases hydrogen, nitrogen, carbon monoxide, and oxygen, which are but slightly soluble in water, so that they may be collected over water without appreciable loss, whilst for rough experimental purposes their solubility may be ignored. Secondly, there are nitrous oxide, carbon dioxide, chlorine and hydrogen sulphide, the solubilities of which need to be taken account of in the ordinary experiments of the laboratory. Nitrous oxide is generally collected over warm water to reduce the amount lost by solution; carbon dioxide is generally collected by air displacement, although it may be collected conveniently over warm water; chlorine and hydrogen sulphide are rather too soluble in water to be collected over that medium without serious loss. There remain sulphur dioxide, hydrogen chloride, and ammonia, which are very soluble in water, and must always be collected by air displacement, or over mercury or some other liquid in which they do not dissolve.

Two interesting questions arise from the consideration of these figures. The first is as to how far solubility in water is connected with the condensibility of the gas; and the second is as to the connection between solubility and power to combine chemically with water.

A consideration of the boiling-points of the liquefied gases shown in the table reveals some connection between solubility and condensibility. The least soluble gases are the least condensible; but there is no quantitative connection between the two properties, for chlorine and ammonia, for example, have practically the same boiling-point, but widely different solubilities.

No doubt chemical union between the gas and water will have some influence on solubility, though the precise nature of this influence is not apparent. Of the above gases carbon dioxide, sulphur dioxide, and ammonia combine with water to form carbonic acid, sulphurous acid, and ammonium hydroxide respectively, but the proportion of combined to uncombined gas is in each case relatively small; in the case of carbon dioxide it is less than 1 per cent.

iii. The Temperature of the Solvent.

It is the temperature of the solvent, rather than that of the gas, which needs to be considered here. If the temperatures of the liquid and gaseous phases are initially different that of the gaseous will soon become adjusted to that of the liquid phase, so that the only

question concerns the condition of equilibrium between a liquid and a gas, both at the same temperature.

The solubility of a gas in water or other solvent invariably diminishes with rising temperature, though there is no simple connection between temperature and solubility. As a rule, when a gas has been dissolved in water, boiling the water serves to expel from solution all the dissolved gas. Thus dissolved air is completely expelled from water by boiling the water for a short time.

The following figures and accompanying curve (fig. 40) show the solubility of carbon dioxide in water, volume for volume, at different temperatures:

CARBON DIOXIDE

Temperature, Centigrade.	Solubility.	Temperature, Centigrade.	Solubility.
0°	1·713	30°	0·665
5°	1·424	35°	0·592
10°	1·194	40°	0·530
15°	1·019	45°	0·479
20°	0·878	50°	0·436
25°	0·759	60°	0·359

There is a notable difference between hydrogen chloride and ammonia as regards effect of temperature on solubility.

HYDROGEN CHLORIDE		AMMONIA	
Temperature, Centigrade.	Solubility.	Temperature, Centigrade.	Solubility.
0°	0·825	0°	0·875
8°	0·783	8°	0·713
16°	0·742	16°	0·582
24°	0·700	24°	0·474
32°	0·665	32°	0·382
40°	0·633	40°	0·307
48°	0·603	48°	0·244
56°	0·575	56°	0·186

This difference is seen when concentrated solutions of the two gases are boiled. Whilst ammonia is completely expelled from water by boiling, this is not the case with hydrogen chloride.

When a concentrated aqueous solution of hydrogen chloride is boiled under atmospheric pressure, it loses hydrogen chloride faster than water vapour; when a dilute solution is boiled, it loses water vapour faster than hydrogen chloride. Since, therefore, a concentrated solution becomes weaker by boiling, and a dilute solution more concentrated, the two solutions approach each other in strength

when boiled, and eventually become identical. The solution obtained by continued evaporation of any aqueous solution of hydrogen chloride contains 20·24 per cent of hydrogen chloride, and distils unchanged at 110° C. under a pressure of one atmosphere.

A constant boiling-point at a certain pressure is characteristic of a chemical compound, and the constant boiling solution might on

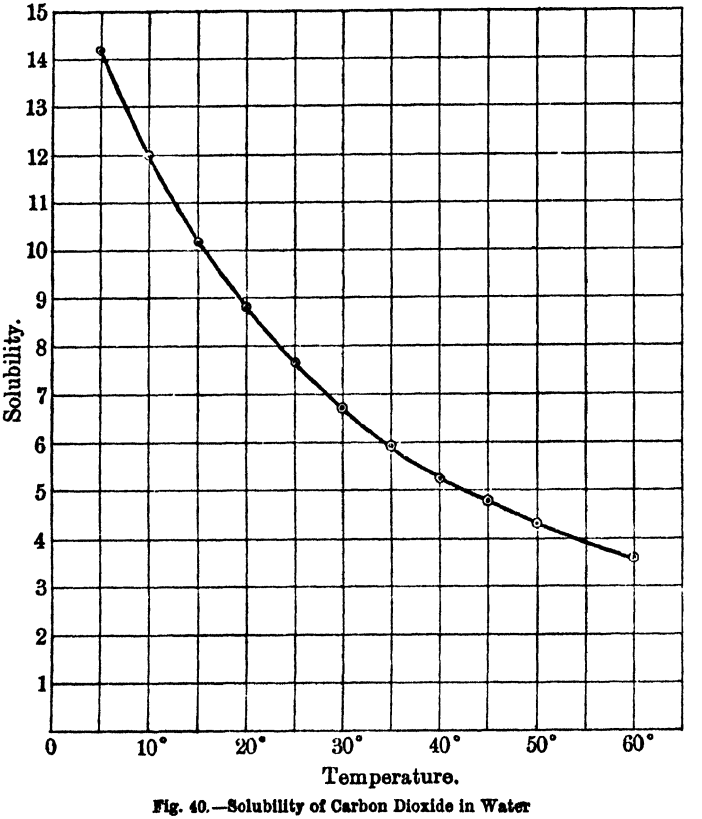


Fig. 40.—Solubility of Carbon Dioxide in Water

this account be supposed to be a chemical compound of hydrogen chloride and water. A chemical compound, however, whilst it distils at temperatures which vary with varying pressures, yields always the same distillate. But this is not the case with hydrochloric acid, for the composition of the distillate from a constant-boiling acid depends upon the pressure under which the boiling-point is reached. For example, the distillate from a constant-boiling acid under 100 mm. pressure contains 22·9 per cent of hydrogen chloride,

whilst that obtained under 2500 mm. contains only 18·0 per cent of this substance.

It must be remembered that when heat is continuously applied to a liquid or solution, the temperature must rise until it becomes constant or all the liquid has evaporated. In the case of hydrochloric acid, owing probably to chemical union (see p. 192) between hydrogen chloride and water, the gas is retained in quantity sufficient to cause the boiling-point of the solution to rise to 110° C., whilst in the case of ammonia all the gas has left the water by the time the temperature reaches 100° C., so that eventually, instead of a constant boiling mixture, only water distils.

iv. THE PRESSURE OF THE GAS.

That increase of pressure increases the amount of a gas dissolved by a liquid is well known. Soda-water, for example, contains carbon dioxide dissolved under pressure, and the escape of this gas from solution when the pressure is released is the cause of effervescence.

The following is the *law of Henry*:

The quantity of a gas dissolved by a given volume of a liquid is proportional to the pressure of the gas.

Since, according to Boyle's law, the volume of a gas is inversely proportional to its pressure, it follows that

The volume of a gas dissolved by a given volume of a liquid is independent of the pressure.

The law may be otherwise stated as follows:

The ratio of the concentration of the gas dissolved in the liquid to its concentration in the atmosphere above is constant. Since this constant depends upon the nature of the gas and of the solvent, it expresses the solubility of the gas.

Now, there are deviations from Boyle's law, which are the greater the higher the pressure and more condensible the gas. And there are similar deviations from Henry's law, which are the greater the higher the pressure and the more soluble the gas.

Hydrogen chloride, for example, departs widely from Henry's law; for 1 grm. of water at 0° C. dissolves 0·856 grm. of hydrogen chloride when under 1000 mm. pressure, and 0·657 grm. instead of 0·0856 grm. of the same gas under 100 mm. pressure.

The law is approximately true, not only for slightly soluble gases, but also for more soluble gases at high temperatures. For example, the law is true for ammonia at 100° C. and for sulphur dioxide above 40° C.

Solubilities of Gaseous Mixtures.

Henry's law applies to the solution of the constituents of gaseous mixtures, the pressures of the individual gases being exercised according to Dalton's law of partial pressures, which has already been expressed as follows: The total pressure of a gaseous mixture is the sum of the partial pressures of the individual gases.

A combination of these two laws sets forth the behaviour of a gaseous mixture in contact with a solvent. It is *Dalton and Henry's law.*

The quantities of the various gases dissolved from a gaseous mixture by a given volume of liquid are proportional to the solubilities and partial pressures of the gases.

Consequently these quantities are expressed relatively by the products of the partial pressures and solubilities, as the following example shows.

To find the composition of the gas dissolved from air by water at 0° C.

Air.	Percentage Composition.	Solubilities	Product.	Percentage Composition of Gas Dissolved.
Nitrogen	79	0·024	1·896	63·3
Oxygen	21	0·049	1·029	34·4
Carbon dioxide ...	0·04	1·71	0·0684	2·3

The products of the partial pressures, as indicated by percentage composition, and solubilities show the relative amounts of nitrogen, oxygen, and carbon dioxide dissolved in the water, and recoverable from it by boiling. These may be regarded as the partial pressures of the recovered gases at the same volume, or, what is equivalent, the partial volumes at the same pressure. The figures in the fourth column, which are those in the third column brought to a percentage, thus give the percentage composition by volume of air boiled out of water. The greater solubility of oxygen, and particularly of carbon dioxide, as compared with nitrogen, accounts for the enrichment of air by these gases through the process of solution in water; and it will be seen that if carbon dioxide were first removed it would be possible to obtain a small quantity of practically pure oxygen by repeating the processes of solution and boiling a number of times.

Solutions of Liquids in Liquids

Pairs of liquids may be divided into three categories, according to their mutual solvent action.

i. LIQUIDS WHICH MIX IN ALL PROPORTIONS. — Water and alcohol, alcohol and ether, ether and olive oil, are examples of such pairs of liquids. There is no limit to the mutual solubility of these pairs of liquids; there is no question of a coefficient of solubility. Changes of volume as well as changes of temperature occur during such admixture. For example, 53·9 volumes of ethyl alcohol at 0° C. mixed with 49·8 volumes of water, produce 100 volumes of mixture instead of 103·7 volumes.

Similia similibus solvuntur: like are dissolved by like. Thus water, H·OH, dissolves alcohol, C_2H_5·OH, and acetic acid, CH_3CO·OH; a hydroxylic solvent dissolves hydroxylic compounds. When, however, the radicle, combined with the hydroxyl (OH), group is large, the alcohol or acid is not soluble. For example, cetyl alcohol, $C_{16}H_{33}OH$, and stearic acid, $C_{17}H_{35}COOH$, do not dissolve in water.

Further, one hydrocarbon will dissolve another; natural petroleum is a mixture of open-chain and other hydrocarbons; the products of tar distillation are a mixture of closed-chain hydrocarbons. Acquaintance with organic chemistry will reveal other examples to the student.

ii. LIQUIDS THE MUTUAL SOLUBILITY OF WHICH IS LIMITED.— When ether is added little by little to water, and the mixture is shaken, at first the liquids mix, but soon the limit of solubility is reached, and ether is seen to form a separate layer on the surface of the water. When this takes place, the liquids are saturated solutions of water in ether and ether in water respectively. At 15° C., 8·2 grm. of ether dissolve in 100 grm. of water, whilst 1·16 grm. of water dissolve in 100 grm. of ether. The consequence of this is that ether which has been washed with water is "wet", and if it needs to be dried must stand in contact with anhydrous calcium chloride, phosphoric oxide, or metallic sodium, and then be redistilled. The presence of ether in the water can be shown by freezing the latter, and then attempting to set fire to the ice. The ether will vaporize from the surface of the ice and burn.

A distinction must be drawn between a solution of two liquids and an emulsion. The former is necessarily clear, the latter turbid

or opaque, since it consists of minute drops of one liquid suffused through the other. When aniline or other organic liquid is distilled in presence of water, the distillate may be turbid owing to the presence of a little water which forms an emulsion with it. Contact with a drying agent removes the water, and clarifies the distillate.

The distribution of a substance between two solvents is an interesting case which sometimes arises; and in this case the available material is distributed throughout the two solvents in contact according to its relative solubilities in them. Thus the ratios of the concentrations of the dissolved substance in the solvents remains the same at a given temperature, whatever the relative volumes of the solvents and the consequent states of dilution of the solutions may be.

In three experiments the amounts of succinic acid found dissolved in unit volumes of water and ether respectively were as follows:

Succinic acid per unit volume of

Water.		Ether.		Ratio = Constant.
0·024 grm.	.....	0·0046 grm.	.....	5·2
0·070 „	.....	0·013 „	.....	5·2
0·121 „	.....	0·022 „	.....	5·4

This constant ratio is called the *coefficient of distribution*, or *partition coefficient.*

There is a close analogy between this case and that of a gas dissolving in a solvent; for in the latter case the ratio between the concentration of the gas in the solvent and in the space above it is constant when equilibrium has been reached. Indeed, the solubility of a gas in a liquid may be regarded as a partition coefficient.

An illustration of the distribution of a substance between two solvents arises in qualitative analysis, when bromine or iodine, liberated from a bromide or iodide by chlorine, is removed from water by means of carbon disulphide. The halogen is so much more soluble in carbon disulphide at ordinary temperature than in water that nearly all of it passes into the former solvent, leaving little in the water. A complication arises as regards the partition coefficient in the case of iodine, since the molecular state of this substance differs in the two solvents.

iii. LIQUIDS WHICH ARE IMMISCIBLE.—Under this category are

included water and hydrocarbons such as petroleum and benzene, and water and oils.

A practical advantage in the use of petroleum or benzene as a solvent over ether is the fact that the former is essentially anhydrous, whilst ether may be "wet". Even oils, however, are not absolutely insoluble in water, for essential oils, when shaken with water, impart their odour to the water.

The Distillation of Mixed Liquids—Fractional Distillation.

A liquid boils when its vapour pressure has attained to the pressure of the superincumbent atmosphere, and this is true whether the liquid is a single substance or a mixture. Consider the case of a mixture of ethyl alcohol boiling at 78° C., and water boiling at 100° C.

Ethyl alcohol alone would exert a pressure of 760 mm. at 78°, whilst the vapour pressure of water at 78° would be 327 mm. Neither of these liquids, however, can exert its full vapour pressure in the mixture, for the vapour pressure of a solvent at any temperature is lowered by a dissolved substance; and so alcohol and water mutually lower each other's vapour pressure. If the proportion of water to alcohol is small its effect in lowering the vapour pressure of the alcohol will be proportionately small, whilst the larger proportion of alcohol with which it is mixed will have a proportionately great effect in reducing the vapour pressure of the water. Consequently the mixture will begin to boil slightly above the boiling-point of alcohol, and the first portions of the distillate will be nearly pure alcohol. The boiling-point, however, will gradually rise, and the proportion of water in the distillate correspondingly increase until the boiling-point is practically 100° and the distillate nearly pure water. If, however, the distillation is stopped before the alcoholic distillate becomes much diluted with water, and if the residue is then rejected and the distillate partially redistilled, a distillate still richer in alcohol will be obtained. So by repeated distillations the alcohol, though reduced in quantity, may be nearly freed from water.

The process of fractional distillation is generally carried out as follows: Fractions A, B, C, D, &c., are collected at small temperature intervals, and the residue is put on one side. A is then redistilled up to, say, 1° above the boiling-point of the more volatile constituent, thus yielding a distillate A_1; to the residue of A, B is

then added, and the distillation continued up to the same temperature, the distillate B_1 being collected. By a similar procedure distillates C_1 and D_1 may be obtained, and the process repeated if desired with A_1, B_1, C_1, D_1. Thus a fairly efficient separation of the more from the less volatile constituent of the mixture is effected. The residues from the successive distillations, if mixed and distilled, will yield the less volatile constituent nearly pure after the rejection of a small intermediate fraction containing what remains of the more volatile constituent.

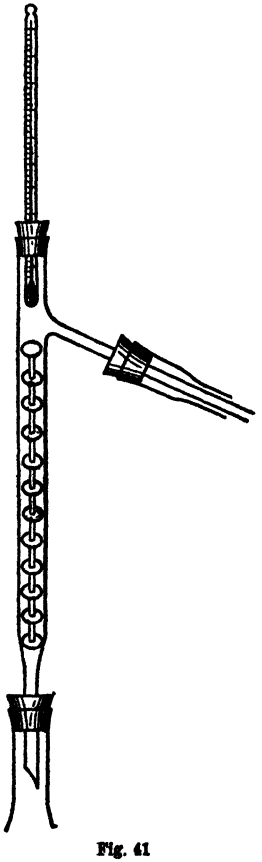


Fig. 41

A more perfect separation results if a *dephlegmator* or *fractionating-column* is employed. This consists of a tube fixed between the distilling-flask and the condenser, in which, by means of disks and rods or other means, a large surface is provided on which the vapour may be cooled. Some of the vapour of the less volatile constituent is thus continuously condensed, and runs back into the distilling-flask, the ascending vapour passing through a certain amount of liquid in the column; consequently only the most volatile part of the vapour passes forward into the condenser.

The difficulty of obtaining pure alcohol from a mixture of alcohol and water is increased when the proportion of alcohol to water is small. The vapour of the alcohol is held back by the water, and at the same time the alcohol has only a small effect on the vapour pressure of the water. Hence the temperature at which the liquid first boils is considerably above the boiling-point of alcohol, and the distillate at once contains much water. On the other hand, if it is desired to get rid of the alcohol, leaving behind only water, this may be effected by heating the mixture on the steam bath for a time.

Solutions of Solids in Liquids

Water is the solvent almost invariably used for inorganic substances; for organic substances alcohol, ether, petroleum-ether,

ethyl acetate, chloroform, benzene, and other solvents may be employed. *Similia similibus solvuntur* again applies. Water dissolves acids, bases, and many salts, with or without water of crystallization, as well as some organic compounds containing OH groups, such as the lower alcohols, acids, glycerine, and sugars; petroleum dissolves other hydrocarbons, ether other neutral organic substances, and so forth.

In dealing with the solution of solid substances, the specifically chemical action of the solvent may be disregarded for the present. For instance, the hydrolysis of phosphorus pentachloride by water and the consequent solution of the hydrolytic products is irrelevant to the present study. Attention will here be confined to the action of water as a solvent.

Solubility.

The solubility of a substance in water is defined as **the number of grams of the substance which will dissolve in 100 grm. of water.**

This definition involves the idea of *saturation.* When a substance is brought into contact with water it gradually dissolves up to a certain point, beyond which no further increase in concentration of the solution takes place. A solution is said to be *saturated* when it contains as much dissolved substance (solute) as possible, and remains in equilibrium with some of the solid substance; i.e. no spontaneous change takes place under constant conditions in the concentration of the solution or the amount of substance remaining undissolved. A solution is *unsaturated* when it contains less of the solute than a saturated solution under the same conditions; that is to say, when the act of solution is incomplete because either sufficient of the substance is unavailable, or there has not been sufficient opportunity for the state of saturation to be reached. Consequently an unsaturated solution will always dissolve more of the substance when opportunity occurs.

In contrast to the unsaturated state is the *supersaturated* state. A solution is supersaturated when it contains more of the solute than a saturated solution in contact with the solid could contain under the same conditions. A supersaturated solution can exist only in the absence of solid matter; it is in a *meta-stable* state which is disturbed by a slight impetus from without. Its production depends upon the fact that most substances are more soluble in hot water than cold, and that if a hot, saturated solution, free from

solid, is cooled, the separation of crystals may be postponed until a fragment of crystal enters the solution. Then rapid separation of crystals takes place until equilibrium in contact with the solid is secured, that is, the solution becomes saturated. The phenomenon illustrates the inertia of matter, that is, the tendency of a substance or mixture to persist in the same physical state, although the conditions for the stable existence of that state have ceased, until an external stimulus causes a rapid adjustment to the conditions of true equilibrium. The supercooling of a liquid, i.e. its persistence in the liquid state at a temperature below that at which solidification normally occurs, is an analogous phenomenon.

Supersaturation is well illustrated by sodium sulphate solution. If a hot, saturated solution of this salt is prepared and filtered into a flask, the neck of which is then plugged with cotton-wool, the solution may be cooled to atmospheric temperature without separation of solid. If the cotton-wool is then removed and a fragment of the crystallized salt dropped into the flask, rapid crystallization takes place with evolution of heat, until a solid cake of crystals is produced.

Whether a solution of a solid substance is unsaturated, saturated, or supersaturated at a given temperature is properly determined with reference to the substance, as follows: If the solid is added to an unsaturated solution, solid will dissolve, and the solution become more concentrated; if it is added to a saturated solution the solution will remain unaltered; if it is added to a supersaturated solution solid will separate, and the solution become more dilute. All three solutions will attain to the same concentration, because they attain to a state of true equilibrium in contact with the solid. Moreover, the state of equilibrium is dynamic rather than static. The concentration of the solution remains constant, not because nothing is taking place, but because molecules of the solute are entering and leaving the solution at the same rate. The three states may be represented graphically as follows:

Unsaturation: solid $\overset{\text{solute}}{\longrightarrow}$ solution.

Supersaturation: solid $\overset{\text{solute}}{\longleftarrow}$ solution.

Saturation: solid $\overset{\text{solute}}{\rightleftharpoons}$ solution.

The state of equilibrium between a solid and a solution is thus analogous to the state of chemical equilibrium between the

factors and products of a reversible chemical reaction, and to the state of thermal equilibrium between two bodies at the same temperature.

The Process of Solution.

A readily soluble solid is easily dissolved by being stirred or shaken with the solvent. A saturated solution may be prepared either by keeping the solid in contact with the unsaturated solvent until saturation is attained, or, more rapidly, by heating the solvent with excess of the solid, and then cooling the solution to the desired temperature in contact with the solid. The more finely divided a solid is the more rapidly will it dissolve, on account of the larger surface exposed. It is therefore wise to pulverize a solid before attempting to dissolve it, unless it is quite easily soluble.

The physical state of a solid, apart from mere fineness of subdivision, also determines its solubility. Thus yellow mercuric oxide is about 14 per cent more soluble in water, and at the same time more active chemically than the red, crystalline form of this compound; this difference is probably due to an allotropic difference in the two forms. Again, precipitated calcium carbonate is more soluble in ammonium salt solutions than the crystalline form (aragonite) produced by heating the precipitate with the liquid. Thus, when calcium carbonate is precipitated by ammonium carbonate added to calcium chloride solution in presence of ammonium chloride, the precipitate is at first flocculent and amorphous, but becomes crystalline and less bulky when the liquid containing it is boiled; and, further, boiling serves to precipitate in the crystalline form of aragonite traces of calcium carbonate that remain in solution in the cold liquid. These phenomena illustrate the influence of physical state on solubility.

Influence of Temperature on Solubility.

Rise of temperature generally, but not always, increases the solubility of a solid in water.

The solubility of potassium chlorate, for example, is much increased by rise of temperature, that of potassium chloride shows a less increase, whilst that of sodium chloride is little affected by change of temperature. On the other hand the solubility of calcium hydroxide, as well as that of certain organic salts of calcium such as the acetate, decreases with rise of temperature, so that from a cold

saturated solution solid separates on warming; whilst the solubility of gypsum, $CaSO_4 \cdot 2H_2O$, reaches a maximum at about 40° C. and then diminishes again.

TABLE OF SOLUBILITIES

Temperature.	$KClO_3$.	KCl.	NaCl.	$Ca(OH)_2$.	Temperature.	$CaSO_4 \cdot 2H_2O$.
10°	4·45	31·0	35·7	0·176	10°	0·2439
20°	7·22	34·0	35·8	0·165	18°	0·2550
30°	9·26	37·0	36·0	0·153	25°	0·2631
40°	13·31	40·0	36·3	0·141	30°	0·2644
50°	17·95	42·6	36·7	0·128	35°	0·2651
60°	23·42	45·5	37·1	0·116	40°	0·2653
70°	29·16	48·3	37·5	0·106	55°	0·2541
80°	36·93	51·1	38·0	0·094	65·3°	0·2444
90°	46·11	54·0	38·5	0·085	75°	0·2337
100°	55·54	56·7	39·1	0·077	100°	0·2048

These results are shown more clearly when expressed as curves in which solubilities are ordinates and temperatures are abscissæ (fig. 42.) The values for $Ca(OH)_2$ and $CaSO_4 \cdot 2H_2O$ are multiplied by 100 to bring them into the figure according to scale.

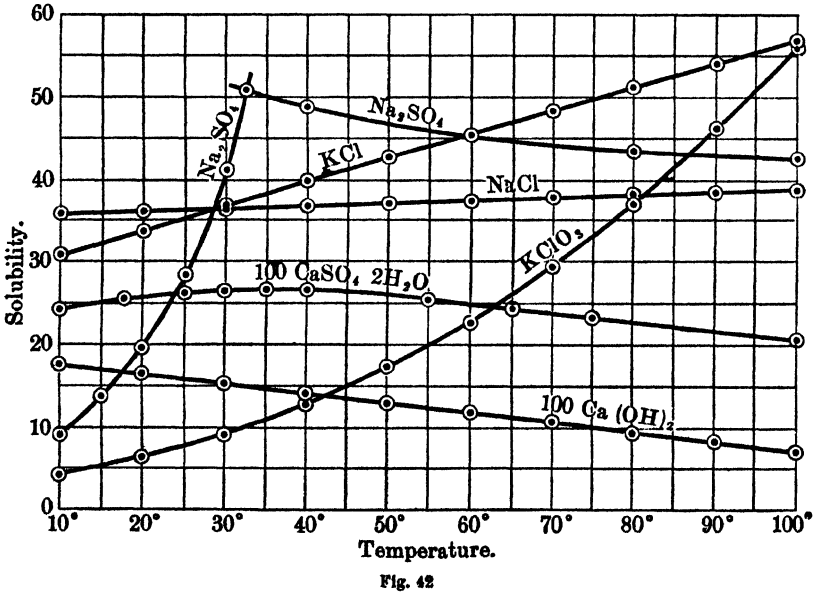


Fig. 42

The solubilities of crystallized sodium sulphate appear to be anomalous. They are as follow:

SOLUBILITIES OF SODIUM SULPHATE

Temperature.	Solubility.	Temperature.	Solubility.
10°	9·0	33°	50·6
15°	13·4	40°	48·8
20°	19·4	60°	45·3
25°	28·0	80°	43·7
30°	40·8	100°	42·5
32·75°	50·65		

The curve (fig. 42) shows a sharp break at 32·5°, and indeed it is clear that the solubility is represented by two curves which intersect at that point. These curves must correspond to two distinct states, either solid or in solution, the point of intersection indicating an abrupt change from one state to the other. It must be remembered that the numerical values represented by the curve are the amounts of the anhydrous salt found in the saturated solutions at the corresponding temperatures. Why does the power of water to dissolve sodium sulphate so suddenly change at the indicated temperature? Inquiry shows that the nature of the solution does not change; it is the nature of the solid in contact with the solution that changes. The fact is that the decahydrate $Na_2SO_4 \cdot 10H_2O$ exists in contact with the solution only up to 32·5°; above that temperature this hydrate loses all its water, so that it is the anhydrous salt that remains in contact with the solution. Thus the first part of the curve represents the solubility of $Na_2SO_4 \cdot 10H_2O$ in terms of Na_2SO_4, the second part that of anhydrous Na_2SO_4. The change from the crystallohydrate to the anhydrous salt at 32·5° C. may be seen if the solid hydrate is gently heated. It will melt at this temperature, which is the transition temperature, and give rise to a meal of anhydrous crystals in contact with a saturated solution of the salt in the available water derived from the hydrated crystals. It follows from this that if a solution of sodium sulphate is made to crystallize above 32·5° C. the anhydrous salt will separate, whilst below this temperature the decahydrate will be formed.

Sodium carbonate shows analogous phenomena, but in this case it is $Na_2CO_3 \cdot H_2O$ which is formed from $Na_2CO_3 \cdot 10H_2O$, not the anhydrous salt.

Relation between Chemical Composition and Solubility.

The relationship between chemical composition and solubility is a large question of much interest and importance. The operations of qualitative analysis familiarize the student with parts of the

subject, and a thoughtful study of a table of solubilities leads to certain generalizations.

For example, all nitrates and chlorates, and nearly all chlorides and sulphates, are readily soluble in water; all carbonates and phosphates, except those of the alkalis, are practically insoluble; moreover, the solubilities of sulphides in water and dilute acids and alkalis are important for analytical separations.

The solubilities of metallic compounds in relation to the periodic system are significant. Thus it is only the most powerfully basic hydroxides that dissolve in water; and the alkaline earth hydroxides which follow those of the alkalis in basic strength increase in solubility with increase of basic strength from calcium to barium. Thus 100 parts of water at 10° C. dissolve

$Ca(OH)_2$	$Sr(OH)_2$	$Ba(OH)_2$
0·176	0·566	2·48

Gradations of solubility of related compounds in a natural group are shown particularly in the case of almost insoluble salts. The sulphates of the alkali metals, the sulphides of zinc and cadmium, which differ sufficiently in solubility in dilute acid to be precipitated in different analytic groups, and the chloride, bromide, and iodide of silver furnish examples.

SOLUBILITIES OF SLIGHTLY-SOLUBLE SALTS

Grams per litre:*

At 18° C.	$CaSO_4$	2·016	$SrSO_4$	0·114		$BaSO_4$	0·0023
At 20° C.	AgCl	0·0016	AgBr	0·000084		AgI	0·0000028

It is interesting to note that on account of solubility differences bromide solution converts precipitated AgCl into AgBr, and iodide solution AgCl and AgBr into AgI. A similar phenomenon is observed in the titration of neutral chloride solution by standard silver nitrate in presence of chromate. Owing to the greater solubility of chromate there is no permanent precipitation of silver chromate until all the chloride in solution has been precipitated. The relationships of solubility between simple and double or complex salts are worthy of notice. Compare, for example, the alkali sulphates and the alums:

	K.	Rb.	Cs.
Sulphates	9·22	42·6	173·1
Alums	7·60	1·81	0·49

grams per 100 grm. water at 10° C.;

as well as the simple chlorides and platinichlorides:

	K.	Rb.	Cs.
Chloride	31·0	84·4	174·7
Platinichloride	0·90	0·154	0·050

grams per 100 grm. water at 10° C.

These figures strikingly illustrate the fact that the solubilities of double and complex salts of the alkali metals stand in a reverse relation to those of the corresponding simple salts. It will be remembered, moreover, that sodium alum and sodium platinichloride are freely soluble in water.

SUMMARY

SOLUBILITY OF A GAS.—The solubility, or coefficient of solubility, of a gas in a liquid is defined as the volume of the gas which is dissolved by unit volume of the liquid.

LAW OF HENRY.—The quantity of a gas dissolved by a given volume of a liquid is proportional to the pressure of the gas. Or (from Boyle's law) the volume of a gas dissolved by a given volume of a liquid is independent of the pressure.

LAW OF DALTON AND HENRY.—The quantities of the various gases dissolved from a gaseous mixture by a given volume of liquid are proportional to the solubilities and partial pressures of the gases.

SOLUBILITY OF A SUBSTANCE.—The solubility of a substance in water is defined as the number of grams of the substance which will dissolve in 100 grm. of water.

CHAPTER XI

THE PROPERTIES OF DILUTE SOLUTIONS

The properties of solutions, and particularly of dilute solutions, have been studied in great detail during recent years, and the facts and theories connected with this subject have aroused keen interest.

An aqueous solution of silver nitrate yields a precipitate of silver chloride with a similar solution of hydrogen chloride, or any metallic chloride, but not with an aqueous solution of chloroform, $CHCl_3$, in spite of the large proportion of chlorine this compound contains. What is the reason for this difference? A plain answer, correct, so far as it goes, would be that silver nitrate solution is a reagent, not for chlorine, but for a chloride, and chloroform is not a chloride. A further difference, however, between solutions of a chloride and of chloroform relates to electrolysis, that is, the decomposition of a substance in aqueous solution by means of a current of electricity. A chloride solution is capable of electrolysis, a solution of chloroform is not. Consequently the former is an *electrolyte*, the latter not. Since the properties of dilute solutions are elucidated by the phenomena of electrolysis, that subject will first receive attention.[1]

Electrolysis.

The beaker shown in fig. 43 contains a solution of copper sulphate into which dip two pieces of platinum foil. These are connected by lengths of copper wire—preferably silk-coated, except at the ends, for the purpose of insulation—with an electric battery of, say, three cells, shown at the bottom of the figure. An electric current flows from the positive pole of the battery through the wire to one platinum plate, then through the solution and back to the battery through the other platinum plate and wire; so the circuit is completed. The platinum plates are called the *electrodes*,

[1] The contents of this chapter were partly anticipated when the modern view of the molecule was discussed. Nevertheless the chapter stands in proper sequence here.

i.e. the ways of the current, the entrance to and exit from the solution undergoing electrolysis; they are named, rather picturesquely, the *anode* and the *cathode*, i.e. the way up and the way down; the positive (+) electrode is the *anode*, the negative (−) electrode the *cathode*. The electric current, generated in the battery by chemical action, travels in two modes throughout this circuit—through the wires without chemical change, through the solution with chemical change. For *electrolysis* takes place when a current passes through a solution of copper sulphate, which is an electrolyte; metallic copper is deposited on the cathode, which thus becomes electroplated, and a quantity of oxygen chemically equivalent to the copper is evolved from the anode, whilst round about the anode the solution develops acidity, such as would be derived from the reaction:

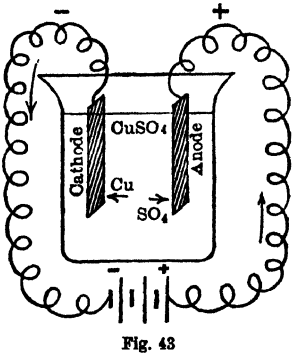


Fig. 43

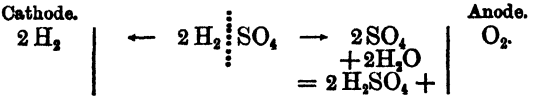
$$SO_4 + H_2O = H_2SO_4 + O.$$

It is believed, therefore, that atoms of copper charged with + electricity travel to the cathode, and that there they give up their charges, which pass back through the wire to the battery, whilst the copper remains behind on the cathode; and that similarly SO_4 radicles, with corresponding charges of negative electricity, travel to the anode, there causing oxygen to be evolved from water in the manner shown above. The charged Cu atoms and SO_4 radicles are called *ions*, because they *go* to the electrodes; the former are *cations*, because they travel to the cathode, the latter *anions*, because they travel to the anode. The SO_4 ion is also sometimes called the *sulphion*.

If the anode is of copper instead of platinum, there is no evolution of oxygen gas, but copper is dissolved by the influence of SO_4, so that the concentration of the solution remains unchanged, while copper is in effect transferred from the anode to the cathode. This kind of action takes place in silver-plating. The article to be plated is made the cathode and a bar of pure silver the anode, the electrolyte being a solution of potassium silver cyanide, $KAg(CN)_2$. Metallic silver then dissolves from the anodic bar at

the same rate as it is deposited on the article forming the cathode.

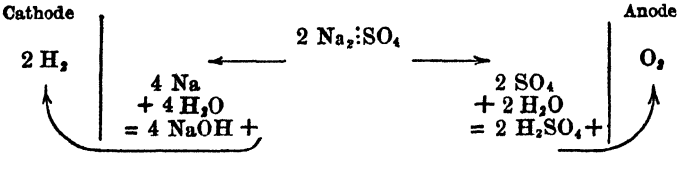
If dilute sulphuric acid is electrolyzed, hydrogen appears at the cathode, and an equivalent quantity of oxygen at the anode, whilst the acidic strength of the solution remains unchanged. The action may be represented thus:



Since the water alone undergoes permanent change, being decomposed into its constituent gases, 2 volumes of hydrogen and 1 volume of oxygen, it is customary to call this process the electrolysis of water, the acid being added to enable the water to conduct the current. If the current is led into pure water no action is observed to take place, for the water is practically a non-conductor, a *non-electrolyte.*

Why diluted sulphuric acid should be an electrolyte, and water not, is a question which may well be asked—a question to which an answer must be found.

One further example of electrolysis may, however, first be noticed. The electrolysis of sodium sulphate gives sodium ions at the cathode and SO_4 ions at the anode. The SO_4, reacting with water, produces sulphuric acid and oxygen as before, but the sodium at the cathode causes hydrogen to be evolved from the water and sodium hydroxide to be formed in solution, thus:



So in this case acid and alkali appear in equivalent quantities at the anode and cathode respectively, together with hydrogen and oxygen gases respectively.

If wires from the terminals of a battery are laid side by side on a piece of porous paper soaked in a solution of sodium sulphate, with phenol-phthalein as an indicator, a crimson stain will appear beneath the wire attached to the negative pole of the battery. The cathode is thus indicated through the development of alkali by electrolysis. Such paper is called pole-finding paper.

Electrolytic Dissociation.

There now remains the question as to the nature of electrolysis and the constitution of electrolytes; why, for example, hydrogen chloride solution is an electrolyte and not chloroform, and why pure water is not an electrolyte.

And it is a gain at once to recognize that it is only substances reactive in aqueous solution, which are capable of reactions of neutralization or double decomposition, that are electrolytes; in a word, it is acids, bases, and salts that belong to this category.

In connection with electrolysis there are three points to be considered:

i. The separation of the electrolyte into its constituent ions.
ii. The migration of these ions to the electrodes.
iii. The separation of the electrolytic products at the electrodes.

Now ii and iii are plainly connected with the passage of the current; the ions are conveyed by the current to the electrodes, and there appear as or give rise to the products of electrolysis. But upon the question as to whether the current separates the electrolyte into its ions before directing them to the electrodes further light is needed.

A priori, it would appear that when a substance like sodium chloride dissolves in water its molecules dissolve entire. The alternative is to suppose that they decompose or dissociate into sodium and chlorine; and this seems absurd to anyone acquainted with the properties of these two elements. But then the question recurs: What is the difference between the chlorine in sodium chloride and in chloroform, which accounts for the different behaviour of these substances towards silver nitrate? or why are the component parts of electrolytes also reactive in other ways, whilst the components of non-electrolytes are inert? Evidence apart altogether from electrolysis can be found in answer to this question.

The student will remember that the molecular weights of dissolved substances can be determined by cryoscopic and ebulliscopic methods; i.e. by observing the depression of freezing-point or rise of boiling-point of a solvent caused by a known weight of dissolved substance. He may also have noticed that the substances generally chosen to illustrate these methods are non-electrolytes; sugar, for example, in aqueous solution, or some organic substance in an

organic solvent. The reason for this choice is that electrolytes give anomalous results which are best avoided in an elementary consideration of the subject. These anomalous results, however, throw much light on the matter now in hand. A given weight of sodium chloride in dilute solution, for example, causes practically twice the depression of freezing-point or rise of boiling-point caused by an equimolecular proportion of cane-sugar. Therefore there are twice as many molecules, or of what behave as molecules, in a solution of sodium chloride as in a solution of sugar calculated to be equimolecular. This fact supports the apparently impossible conclusion as to the dissociation of sodium chloride molecules into sodium and chlorine atoms; and further support for this conclusion is derived from the phenomena of osmotic pressure.

The *osmotic pressure* of a substance in solution is the pressure which causes it to diffuse into the pure solvent. It is an expression of the motions of the molecules of the solute, and is measured by means of a "semi-permeable membrane" through which the solvent can pass but not the solute.[1] Now, there is a close analogy between osmotic pressure and gas pressure. The osmotic pressure of a dissolved substance varies directly as its concentration, or inversely as its volume (cf. Boyle's law); it also varies directly as the absolute temperature (cf. Charles's law); and the numerical value of the constant R in the equation $pv = RT$ is the same whether p stands for gaseous pressure or osmotic pressure. Further, equimolecular solutions of different substances have the same osmotic pressure (cf. Avogadro's theory).

Now, when a gaseous substance, such as N_2O_4, undergoes dissociation without increase of volume its pressure increases, and is doubled when every molecule has produced two molecules. Similarly, the osmotic pressure of dilute sodium chloride solution is double what might have been expected when it is compared with that of a non-electrolyte such as sugar. So, again, there is direct evidence of the dissociation in aqueous solution of sodium chloride molecules into the only possible parts, sodium and chlorine.

The student is now prepared for the theory of *electrolytic dissociation* or *ionization*. This theory, originated by the Swedish physicist Arrhenius, in 1887, has revolutionized modern thinking upon a vast number of chemical phenomena. It asserts that when

[1] More will be said about semi-permeable membranes and dialysis under the subject of colloids.

an electrolyte, such as sodium chloride, is dissolved in a suitable solvent, such as water, it undergoes spontaneous dissociation into its ions, sodium and chlorine, but that these ions have upon them charges of electricity; the sodium ion, for example, consists of an atom of sodium with a certain positive charge, and the chlorine ion, or more properly chloride ion, of an atom of chlorine with an equal negative charge. It is these charges which differentiate the ions from the free elements. It is free sodium, for example, which reacts with water, not sodium ions; free chlorine which has a characteristic colour and smell, not chloride ions. So when sodium chloride dissolves in water it undergoes the following reversible change:

$$NaCl \rightleftharpoons \overset{+}{Na} + \overset{-}{Cl} \quad \text{or} \quad NaCl \rightleftharpoons Na^{\cdot} + Cl',$$

these being alternative methods of representing electrolytic dissociation, or, more briefly, ionization.[1]

Only, therefore, as a substance is ionized can it be reactive; only then is it capable of electrolysis or chemical reactions in solution.

When hydrogen chloride is dissolved in water it is ionized thus:

$$HCl \rightleftharpoons H^{\cdot} + Cl',$$

and sodium hydroxide thus:

$$NaOH \rightleftharpoons Na^{\cdot} + OH'.$$

Water, however, which is not an electrolyte, is ionized thus:

$$H_2O \rightleftharpoons H^{\cdot} + OH',$$

to the minutest extent; only, indeed, to the extent of 1 grm.-molecule in 10 million litres. Since, therefore, $H^{\cdot}$ and OH' ions cannot coexist in the same solution, they will combine when solutions which separately contain these ions are mixed. Now a solution which contains $H^{\cdot}$ ions contains an acid; indeed, according to the theory of ionization, degree of acidity depends essentially upon the concentration of hydrogen ions; whilst a solution containing OH' ions is a solution of a base, that is of an alkali, the strength of which depends similarly on the concentration of OH' ions. When, therefore, solutions of an acid and an alkali are brought together, e.g. solutions of HCl and NaOH, a reaction such as the following takes place:

$$H^{\cdot} + Cl' + Na^{\cdot} + OH' = HOH + Na^{\cdot} + Cl'.$$

[1] If the student has mastered Chapter VI he will know that, according to modern views, sodium chloride becomes ionized as it is formed, so that solution in water but causes dissociation of already existing ions.

The process of neutralization is the reaction:

$$H^{\cdot} + OH' = HOH,$$

and there is no other reaction. Neutralization is but the synthesis of water molecules from their constituent ions; the sodium and chlorine in the above case are no more united after neutralization than before, for they remain as separate ions throughout the process.

This theory of the process of neutralization, now nearly a generation old, was revolutionary enough at the time of its inception, but it has now become an integral part of physico-chemical theory; it is a fundamental idea of modern chemistry which has stimulated innumerable researches and greatly extended the boundaries of scientific knowledge.

The first point in connection with electrolysis, cited on p. 211—the separation of the electrolyte into its constituent ions—has now been duly considered; and the conclusion is that this separation is a spontaneous process accompanying the act of solution; it is neither a part of the process of electrolysis, nor in any way dependent upon the introduction of an electric current into the solution; but it is a necessary precursor alike of electrolysis and every kind of chemical activity of which the substance in solution is capable. The student must therefore most carefully avoid the fallacy of supposing that electrolytic dissociation is a part of electrolysis.

Nevertheless, since electrolytic dissociation involves the separation of the ions with electric charges upon them, it is seen how closely chemical and electrical phenomena are connected.

With these ideas in mind the process of electrolysis may again be reviewed.

Ions of $Na^{\cdot}$ and Cl', for example, stand free in every part of a solution of NaCl, and are directed by the current to the cathode and anode respectively. The electric charges of these ions are equal and opposite, and their magnitude is connected with valency. Thus Na and OH, being univalent, carry each a unit charge; Cu and SO_4, however, both being bivalent, carry double charges. If the same current passes successively through two electrolytic cells containing solutions of NaOH and $CuSO_4$ respectively, the number of bivalent Cu ions, carrying double charges, conveyed to the cathode will be half the number of univalent Na ions which are similarly conveyed, or in other words sodium and copper will be conveyed in equivalent quantities by the current in its course.

These conclusions are expressed in Faraday's *laws of electrolysis*, discovered experimentally long before electrolytic dissociation was thought of.

LAWS OF ELECTROLYSIS.—I. The amount of chemical action in an electrolytic cell is proportional to the current that passes.

II. The quantities of substances liberated at the electrodes when the same current passes successively through different electrolytic solutions are chemically equivalent.

From the second law it is apparent that chemical equivalents may be found by means of electrolysis. For example, the same current may be passed successively through solutions of sulphuric acid and copper sulphate; the evolved hydrogen may be measured and the deposited copper weighed. The weights of hydrogen and copper will be found to be in the ratio of their equivalent weights. The electro-chemical equivalent of copper, for example, is of course simply its chemical equivalent determined by electrolysis.

It is possible now to fill a little more detail into the mental picture of electrolysis of, say, sodium chloride. $Na^{\cdot}$ and Cl' ions react at the electrodes in equal numbers, but they need not have travelled there at the same rate. Suppose a number of people within an enclosure seek to leave it at two opposite exits. They must pass through the exits at the same rate, let it be supposed, but that does not influence the rate at which each individual may approach the exit that he chooses. The quicker he reaches the exit the longer must he wait there; that is all. In other words, unequal approach to the exits will involve unequal crowding around them. That is what happens in electrolysis. For example, in the electrolysis of sodium chloride solution the chloride ions travel faster than the sodium ions, with consequent increase in concentration of the chloride ions in the neighbourhood of the anode.

A simple model, roughly illustrating electrolysis, may be made in the following way. Two equal strips of plain cardboard, say 8 in. long and $\frac{1}{2}$ in. wide, are taken, and a similar scale, say with $\frac{1}{2}$-in. divisions, is marked out on each. A plus sign is then made in the centre of each division on one card, and a minus sign on the other. The two cards are then held together by rubber bands, with the scales face to face. This represents the state of a solution previous to electrolysis. The process of electrolysis is shown by moving the cards relatively to each other. An equal number of plus and minus signs must necessarily be exposed at either end,

independently of the question whether the cards are moved at equal or unequal rates, or whether one card even remains stationary. It is the relative motion of the cards which determines the exposure of the signs; similarly it is the relative motion of the ions which determines the extent of electrolysis. The process of electrolysis is illustrated similarly in the following diagram:

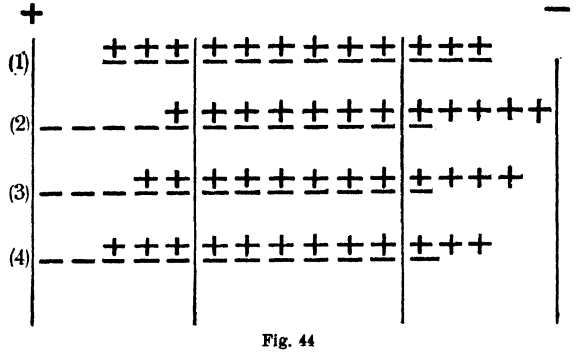


Fig. 44

In (1) the state before electrolysis is represented; (2) represents electrolysis with ions migrating at equal rates; (3) shows the cations migrating more slowly than the anions; (4) shows the cations stationary whilst the anions move at the same rate as before. The extent of electrolysis is influenced by the speed of each ion, but the separated products are always equivalent. The superior speed of the anions in (3) and (4) results in the solution becoming more concentrated towards the anode.

What actually happens at the electrodes, however, requires elucidation. When the electrolytic product is identical in composition with the ion there is no question; for example, in the electrolysis of copper sulphate the cupric ion loses its charge at the cathode, becomes an atom of copper, and is deposited as metal. When, however, secondary products appear, as when, for example, hydrogen and oxygen gases are obtained by the electrolysis of dilute caustic soda solution, the matter is not so simple. What then is the mechanism by which sodium ions at the cathode give rise to hydrogen gas? The older explanation was that the ion lost its charge and became an atom of sodium, which then reacted with the water, evolving hydrogen, and thereby returned to its former state. Why, however, should such a cycle of change be assumed, why should sodium leave the solution only to re-enter it?

There is certainly no evidence of the appearance of metallic sodium.

Here must be introduced the idea of *solution pressure*. When zinc dissolves in dilute sulphuric acid, evolving hydrogen, it is because it has a solution pressure greater than hydrogen, and by reason of this pressure displaces hydrogen. This amounts to the same thing as saying that zinc is more electro-positive than hydrogen. Similarly, when sodium dissolves in water, displacing hydrogen, it does so by its superior solution pressure.

Now, since hydrogen appears in the electrolysis of sodium hydroxide solution it is displaced from water in preference to sodium, which will never appear in the elementary state so long as the less electro-positive hydrogen can take its place. And the hydrogen that comes from water, whether by the action of metallic sodium or during electrolysis, is the hydrogen formed by the ionization of water thus:

$$H_2O \rightleftharpoons H^{\cdot} + OH',$$

although this ionization is so very slight; for molecular water, according to the conception of the theory, would be inert.

The following, then, is what happens at the cathode during the electrolysis of dilute sodium hydroxide solution. Sodium ions arrive there, each with its positive charge. They do not leave the solution, but instead displace the weaker hydrogen from the ionized water. So these hydrogen ions lose their charges, which were equal to those of the sodium ions that have displaced them, and become molecules of gas, while the current flows on through the cathode. More water is ionized in consequence of the disturbance of equilibrium, its hydrogen being in turn displaced by the arriving sodium ions, so that $Na^{\cdot}$ and OH' may be present at the cathode in equivalent amounts.

Meanwhile OH' ions arriving and giving up their charges at the anode react with one another thus:

$$4OH' = 2H_2O + O_2.$$

This is because they cannot remain in the solution unbalanced by cations. Consequently whilst hydrogen and oxygen appear in equivalent quantities at the electrodes, the solution remains unchanged in composition, the only effect being the displacement of the alkali (NaOH) towards the cathode.

It may be noted that in the electrolysis of nearly anhydrous

fused sodium hydroxide, as in the original experiment of Davy, metallic sodium appears instead of hydrogen at the cathode; this is because there is no water whose hydrogen can be displaced by the accumulating sodium ions.

The student should now be able to express the facts of electrolysis of other solutions that come under his notice in terms of the ionization theory.

Chemical Reactions in Solution.

The properties of acids, bases, and salts in dilute aqueous solution are the properties of their ions, and reactions between them are reactions between their ions.

This applies, for example, to the *Colours of Salt Solutions*. Thus, the yellow colour of potassium chromate solution is the colour of the chromate ion, the blue colour of copper sulphate the colour of the cupric ion, and so forth. Certain ions are essentially coloured, others essentially colourless.

The following basic and acidic ions are coloured:

Basic Ions	Acidic Ions
Cations.	Anions.
$Cu^{\cdot\cdot}$, blue.	CrO_4'', bright yellow.
$Co^{\cdot\cdot}$, pink.	Cr_2O_7'', orange red.
$Ni^{\cdot\cdot}$, bright green.	MnO_4'', deep green.
$Cr^{\cdot\cdot\cdot}$, purple.	MnO_4', crimson.
$Mn^{\cdot\cdot}$, pale pink.	$[Fe(CN)_6]''''$, yellow.
$Fe^{\cdot\cdot}$, green.	$[Fe(CN)_6]'''$, yellow.

Since cupric ions, for example, are blue, and cobaltous ions pink, dilute solutions of cupric and cobaltous salts are blue and pink respectively, because their salts are ionized. Probably, however, these ions are hydrated.

Anhydrous cupric chloride is brown, and if dissolved in water without ionization would probably give a yellow solution. A concentrated aqueous solution of this salt is in fact green, but becomes blue on dilution. The green colour is believed to be due to admixture of yellow, non-ionized cupric chloride with blue cupric ions. Since dilution promotes ionization it changes the yellow colour of the non-ionized salt into the blue colour of cupric ions; consequently the green colour of the mixture of $CuCl_2$ and $Cu^{\cdot\cdot}$ gradually gives place to the blue colour of the latter.

Again, a pink solution of cobaltous chloride of moderate con-

centration is turned blue by the addition of concentrated hydrochloric acid, and also by heating.

In this case the blue colour is probably due not to the presence of non-ionized $CoCl_2$, but to the formation of $HCoCl_3$ or H_2CoCl_4, the anions of which $[CoCl_3]'$ or $[CoCl_4]''$ are blue.

If ammonia is added to a solution of a cupric salt there is produced first a bluish-green precipitate, and then a deep-blue solution. The colour of this solution is too intense for that of cupric ions; from the solution, indeed, the compound $CuSO_4 \cdot 4NH_3 \cdot H_2O$, cuprammonium sulphate, will crystallize after the addition of alcohol. The deep-blue colour has been shown to be due to the cuprammonium cation $[Cu(NH_3)_4]''$.

Now, if potassium cyanide is added to the deep-blue cuprammonium solution the colour fades and the solution eventually becomes colourless. This solution still contains copper, but plainly the metal is now present neither as cupric nor cuprammonium ions; for apart from its colour it fails to react with hydrogen sulphide. From this colourless solution potassium cuprocyanide, $K_3Cu(CN)_4$, can be isolated as a colourless salt; thus the copper is present in solution as the colourless anion $[Cu(CN)_4]'''$.

Similarly, if potassium cyanide is added to cobaltous chloride solution cobaltous cyanide is precipitated, and then dissolves in excess of the cyanide to produce potassium cobaltocyanide, $K_4Co(CN)_6$, which readily passes by oxidation into the cobalticyanide, $K_3Co(CN)_6$. In this case the anions $[Co(CN)_6]''''$ and $[Co(CN)_6]'''$ are formed in turn; these are pale yellow in colour, and differ entirely in chemical reactions from cobaltous ions. Thus the formation of cobalticyanide prevents the precipitation of hydrated, black, cobaltic oxide by means of alkali and bromine water, the corresponding oxide of nickel being precipitated by these reagents in spite of the presence of cyanide, since it forms no stable anions like cobalt.

The more familiar potassium ferro- and ferri-cyanide furnish examples of anions containing iron, with reactions entirely different from those of either ferrous or ferric salts.

These illustrations suffice to show the importance of the conception of ions in analytical chemistry. The phenomena of precipitation and of hydrolysis which play so important a part in analytical work will be dealt with later. There remains, however, to be considered here:

The Theory of Indicators.

The indicators used in acidimetry and alkalimetry are natural or synthetic colours which undergo a sharp colour change in a liquid which changes from acid to alkaline or vice versa.

It has been stated above that an acid is a compound which separates hydrogen ions in solution, and that acidic intensity depends upon the concentration of these ions. Thus, different acids differ in acidic strength because they are ionized to different extents in equivalent aqueous solutions. Hydrochloric and nitric acids are acids of maximum strength, being completely ionized in dilute solution; sulphuric acid is about half, oxalic acid a fifth, as strong as hydrochloric and nitric acids; whilst acetic acid has a strength less than 1 per cent that of the strongest acids. A possible misunderstanding may here be guarded against. Although oxalic acid, for example, is only partially ionized in, say, decinormal solution, it does not follow that it cannot be completely neutralized, i.e. converted into sodium oxalate by titration with decinormal soda. Experience shows that it can. The partial ionization is a state of equilibrium reached when the acid is dissolved alone in water. That state is disturbed when alkali is added and further ionization takes place, so that the whole of the acid eventually provides hydrogen ions to react with the hydroxide ions of the alkali and complete neutralization.

Indicators are feeble acids or bases, the salts of which differ in colour from the free acids or bases themselves. The common indicators—litmus, methyl orange, phenol-phthalein—are acidic substances.

The acid of litmus is red, the alkali salt blue; the acid of methyl orange is pink, the alkali salt yellow; the acid of phenol-phthalein is colourless, the alkali salt crimson. Now the alkali salt of a feeble, scarcely ionized acid undergoes much more ionization than the acid itself, and so the above facts may be expressed thus: The undissociated litmus acid is red, its anion is blue; the undissociated methyl orange acid is pink, its anion yellow; the undissociated phenol-phthalein acid is colourless, its anion crimson. It seems extraordinary, however, that ionization should produce such remarkable colour changes, and it is generally believed that these changes depend upon intra-molecular rearrangement, i.e. the shuffling of the atoms within the complicated molecules of the indicators during neutralization.

Now it is well known that the three above-named indicators differ in their behaviour towards certain acids and bases. The facts are these:

Litmus is turned bluish-red by carbonic acid, but becomes blue again on boiling the solution containing it, on account of the dissipation of the carbonic acid. Litmus may be used as an indicator for oxalic acid as well as mineral acids, and for ammonia.

Methyl orange is practically unaffected by carbonic and boric acids, so that solutions of sodium carbonate and borax may be titrated by mineral acid with the aid of methyl orange, as if they were sodium hydroxide. Oxalic acid, however, produces a gradual instead of a sharp colour change with methyl orange. This indicator is therefore useless for titrations with oxalic acid.

Phenol-phthalein is sensitive to the weakest acids, even carbonic acid; it is indeed more sensitive than litmus. This indicator gives no sharp end point, however, with ammonia, and is therefore useless in titrating this alkali.

The ionic theory explains these facts satisfactorily as follows: The acids of the indicators stand in this order of diminishing strength:

Methyl orange, litmus, phenol-phthalein.

The acid of methyl orange is sufficiently weak to be displaced sharply from its alkali salt by mineral acids, but it is sufficiently strong to compete with oxalic acid, and therefore to be displaced but gradually by the latter; moreover, it is sufficiently strong to form a salt with the feebly basic ammonia which is ionized, so as to show sharp colour change.

The acid of litmus is weak enough to be displaced to some extent by carbonic acid,[1] and completely by oxalic acid; but it is also strong enough to form an ionizable salt with ammonia.

Phenol-phthalein is so weak an acid that it reacts sharply even with carbonic acid; but, owing to its feebleness, it cannot form a non-hydrolyzable salt with ammonia. Therefore its colour change with ammonia is gradual, because the coloured ions derived from the ionized ammonium salt do not at once appear, owing to the hydrolysis of this salt.

[1] It is said that the pure colouring-matter of litmus gives a full red colour with water saturated with CO_2.

SUMMARY

ELECTROLYTE.—An electrolyte is a substance which conducts an electric current whilst undergoing chemical decomposition which is electrolysis.

An electrolyte, when dissolved in a suitable solvent, undergoes spontaneous dissociation into ions. This is electrolytic dissociation or ionization.

LAWS OF ELECTROLYSIS OF FARADAY.

i. The amount of chemical action in an electrolytic cell is proportional to the current that passes.

ii. The quantities of substances liberated at the electrodes when the same current passes successively through different electrolytic solutions are chemically equivalent.

CHAPTER XII

THE COLLOIDAL STATE

When a finely-divided solid is mixed with water or other solvent, either it may dissolve completely or some or all of it may remain undissolved. These two conditions are easily distinguished. If the solid dissolves completely the resulting liquid, whether coloured or not, is clear or transparent. If the solid does not dissolve completely, the liquid when shaken will appear turbid or opaque, and if the mixture is allowed to stand undisturbed the solid in suspension will in time settle, leaving the supernatant liquid clear.

The distinction between a substance in solution and one in suspension appears fundamental; for a liquid containing suspended matter may be filtered to be made clear, but it is needless to filter a solution. Yet suspended solids differ in the fineness of their subdivision, and in the ease with which they are removed by subsidence or filtration. Sand, for example, will settle more quickly than precipitated chalk, and both of these can be filtered more easily than precipitated barium sulphate or calcium oxalate. And the student is familiar with substances even more difficult to filter than the last named. The sulphur which separates when hydrogen sulphide gas is passed through an oxidizing solution, or when acid is added to a polysulphide, cannot be removed completely by means of ordinary filter-paper, the pores of which are evidently too large to retain the minute particles of which the precipitate consists.

Indeed, although the solution may become practically transparent, yet the presence of suspended sulphur is revealed by a slight opalescence. Precipitated silver chloride presents a similar phenomenon; whilst copper sulphide, imperfectly precipitated from cold solution, may yield a brown filtrate, which, although transparent, contains the sulphide in a very fine state of subdivision. It appears, therefore, that a liquid may contain suspended matter so finely

divided as not to produce opacity or to be removable by subsidence or ordinary filtration. It is pertinent to ask, therefore, how such a suspension differs from a true solution.

Meanwhile the subject may be approached from a different point of view.

When an aqueous solution of sodium silicate, or soluble glass, is acidified with dilute hydrochloric acid, silicic acid is liberated, and, if the solution is in a concentrated state, will separate from it in the form of "gelatinous silica". If, however, the solution is sufficiently dilute, there is no precipitate, the liquid remaining clear. It might be supposed that the difference between these two conditions depended simply on the amount of water present, there being enough water to hold the silicic acid in solution in the one case, but not in the other. If this were so, the gelatinous silica separated in the former case would be in equilibrium with a saturated solution of the same substance. This, however, is not so; the phenomenon here exhibited is indeed quite different from an ordinary case of precipitation, as will appear in the sequel.

This and kindred phenomena were first investigated by Graham in 1849 in connection with experiments on liquid diffusion. Graham found that the rates of diffusion into pure water of different substances in aqueous solution were various, and that simple salts and acids passed rapidly through an animal membrane or parchment paper, whilst complex substances like gelatine or glue in aqueous solution did not penetrate these membranes. These latter substances Graham called *colloids* (κόλλα, glue), whilst acids and salts, being crystallizable or related to crystallizable substances, he called *crystalloids*. So crystalloids and colloids can be separated from one another by aqueous diffusion through a parchment or other suitable membrane, fixed on a frame like a drum and floating on water, crystalloids passing through the membrane into the external water, whilst colloids remain behind in the drum. The process is called *dialysis*, because it involves separation of one substance from another by passing it through a membrane, through which crystalloids in solution, but not colloids, can pass.

A diluted acidified solution of sodium silicate may be submitted to dialysis. The sodium chloride formed in the reaction,

$$Na_2SiO_3 + 2\,HCl = H_2SiO_3 + 2\,NaCl,$$

and excess of hydrochloric acid pass through the membrane of the

dialyser, leaving the silicic acid behind in pure aqueous solution. Such a solution may be concentrated by evaporation to a strength of about 14 per cent. After this it changes to a jelly, similar to that obtained by acidifying a concentrated solution of soluble glass. Not only does concentration cause dialysed silicic acid to coagulate, but a trace of hydrochloric acid, or some simple salt, acting catalytically, produces the same effect. It thus appears that there are two forms of aqueous colloidal silicic acid; the clear form, which seems to be a solution, and the gelatinous form, which evidently is not. These two forms, in which colloids in general may occur, are called respectively the *hydrosol* and *hydrogel*, or simply *sol* and *gel*.

Besides silicic acid and organic substances such as gums and resins, glue and gelatine, various inorganic substances occur or can be obtained in the colloidal state.

Graham prepared the sols of ferric, chromic, and aluminium hydroxides by dialysis; the sols of arsenious and antimonious sulphides may be prepared by boiling arsenious oxide and tartar emetic respectively with water, and adding hydrogen sulphide to the solutions: the liquids become yellow and red respectively because of the formation of the sulphides in the sol condition. A drop of hydrochloric acid added to either solution precipitates the yellow arsenious or orange-red antimonious sulphide, the sulphides thus assuming the gel condition.

It will now be understood that the above-mentioned brown liquid obtained in precipitating copper sulphide contained the sol of this sulphide, whilst the opalescent liquid containing sulphur held this element also in the colloidal state.

The sols of certain metals are interesting, and often display remarkable colours. Thus gold and silver may be separated from their salts by hydrazine, formaldehyde, &c. Faraday produced blue, violet, and rose-coloured liquids by reducing gold chloride by means of an ethereal solution of phosphorus floating on the surface of the solution; and Bredig obtained sols of gold, silver, platinum, &c., by an electric discharge through water between poles of the metal.

It is easy to understand that colloids have been regarded by chemists with much interest from the time of their discovery to the present day. They are of practical importance because they embrace many common non-crystallizable organic substances such as gum,

resin, glue, starch paste, egg-albumin, casein, and gelatine; but they are particularly interesting from the physico-chemical standpoint because they present a fresh phase of the great subject of molecular physics. Indeed, a transparent dialysed liquid, consisting of silicic acid and water for example, which on the addition of a suitable catalyst becomes a jelly that can be inverted without flowing, presents to the scientific mind a subject for investigation full of an interest that can scarcely be surpassed.

What is this transparent liquid? Is it a solution like a mixture of sodium chloride and water? If it is, why does the silicic acid remain in the dialyser whilst the sodium chloride passes through it? It has already been suggested that the process of dialysis is a kind of filtration, i.e. that the silicic acid molecules are too large to pass through the pores of the parchment paper. But filtration is applied to something in suspension. Is the silicic acid in this apparently clear liquid really in suspension?

An answer to this question as regards colloids in general has been gained by the use of the ultra-microscope invented by Siedentopf and Zsigmondy in 1903. The principle underlying the use of this instrument is that illustrated by the vision of the "mote in the sunbeam". It is well known that the moving dust of the air, which cannot ordinarily be seen, is made visible in a beam of sunlight entering a darkened room through a chink in a shutter. At the same time the track of the beam itself is clearly outlined; but if the air is free from dust the sunbeam disappears.

This effect, studied by Professor Tyndall, is applicable also to liquids, and will reveal the presence of suspended particles within them in the same way that it shows aerial dust.

Moreover, the lesson to be learned is that very intense and localized light, by increasing the intensity of reflection, greatly enhances our powers of vision. And if the dust of the air, otherwise quite invisible, thus becomes apparent to the naked eye, particles too small for microscopic vision under ordinary illumination may be seen under illumination analogous to that of the sunbeam. This is the principle of the ultra-microscope, in which a beam of sunlight, or from the electric arc, passes through a slit horizontally, or is focused into a liquid which is examined by the microscope vertically. Any light which enters the microscope must then have been reflected from the surface of particles suspended in the liquid.

Particles having a diameter only one-hundredth that of the smallest particles visible under ordinary illumination can then be seen as spots of light like planets in the darkness. And so colloidal liquids have been seen to be suspensions, and the size of the suspended particles has been estimated by counting the number of them in a volume of the liquid containing a known weight of material. Thus the particles of platinum, gold, and silver seen in colloidal suspensions of these metals have been discovered to have diameters ranging from 2×10^{-4} to 6×10^{-4} mm. The smallest particles detectable by this method, when illuminated by bright sunlight, have a diameter of 4×10^{-6} mm., whilst the individual molecules of substances like chloroform and alcohol have diameters of $0{\cdot}4\times10^{-6}$ to $0{\cdot}8\times10^{-6}$ mm., and of hydrogen $0{\cdot}1\times10^{-6}$ mm.

Thus the particles of colloidal metals in aqueous suspension have diameters about a thousand times as great as those of molecules which form mixtures with water regarded as true solutions; whilst the smallest particles that can be rendered visible have only about ten times the diameter of gaseous and other simple molecules.

These metallic suspended particles are not, however, molecules, but rather minute fragments of solid metal; since molecules of solid metals, consisting of definite aggregates of atoms, can scarcely be said to exist. Thus, they differ from silicic acid and complex organic substances which are known to consist of very large molecules. The molecule of egg-albumin is estimated to have a molecular weight of 17,000, and the molecules of the enzymes emulsin and invertin have molecular weights of about 45,000 and 54,000 respectively, with molecular diameters of about 6×10^{-6} mm. Such molecules can be seen by the ultra-microscope, but there seems no hope that the simpler inorganic molecules will ever be revealed to the eye of man, although they lie but a little way below his range of vision aided by this powerful instrument.

Finally, although colloids cannot ordinarily be filtered, the fact that parchment paper retains them suggests that special methods of filtration might effect their separation as parchment paper does. Special filters have in fact been prepared by treating ordinary filter-paper with collodion or gelatine, which have pores varying in diameter between 930×10^{-6} mm. and 21×10^{-6} mm. By means of these filters various colloids have been differentiated and

classified according to the sizes of their particles, with the following results:

Suspensions of non-colloids.
Colloidal platinum.
Colloidal ferric hydroxide.
Colloidal arsenious sulphide
Colloidal gold.
1 per cent gelatin.
Colloidal silicic acid.
Litmus.
Dextrin.
Solutions of crystalloids.

Thus it is seen that colloids afford a gradation between what are commonly regarded as suspensions and solutions; and so it is evident that the idea of a colloid as a glue-like substance has been extended so as to include all kinds of matter in a state between that of molecules and that of gross particles which are ordinarily perceptible. Therefore such natural products as clay and lime are regarded as colloids, and many precipitates formed in analysis are believed also to pass through the colloidal state before separating as particles that can be filtered. Indeed it appears that there are two ways in which a precipitate may be formed and pass into a state of equilibrium with the liquid phase with which it is in contact. These are either by direct crystallization, as in the case of magnesium ammonium phosphate, as well as calcium carbonate at elevated temperature; or the formation and coagulation of a colloid, as in the case of many sulphide and hydroxide precipitates. Silver chloride and calcium oxalate are also examples of this kind of precipitate, and barium sulphate is probably a limiting case between the two kinds.

The coagulation of colloids is a subject which has received much attention. It has already been pointed out that a colloidal substance such as silicic acid can exist in two conditions, those of "sol" and "gel"; and that an electrolyte has the power of coagulating a sol, thus converting it into a gel. It is now recognized that the particles of a sol are electrically charged; in some cases such as metallic hydroxides positively, in others such as metallic sulphides, silver chloride, and silicic acid, negatively. Consequently a colloidal sol is capable of a kind of electrolysis, the colloidal matter travelling either to the cathode or the anode when a current is

passed through the liquid. This motion of colloidal particles in an electric field is called *cataphoresis.*

The coagulation of a sol by means of an electrolyte, as, for instance, that of arsenious sulphide sol by means of hydrochloric acid, with formation of a flocculent precipitate, is probably an electrical phenomenon, in which the particles lose their charges and consequently coalesce. The reverse process may, however, take place in too concentrated solution. For example, precipitated basic ferric acetate is prone to pass into the sol condition, chiefly as hydroxide owing to hydrolysis, and so form a slimy mass impossible to filter. The formation of a sol from a gel, which is the opposite of coagulation, is called *peptization.*

Connected with peptization is the subject of *protective colloids.* Certain organic colloids have the power of hindering the coagulation of inorganic colloids with which they are associated. The persistence of the sol condition is the result of the mutual repulsions of similarly charged particles; and when from any cause these repulsions cease to operate coalescence of particles may take place with coagulation of the colloid. If, however, the individual particles of the sol are protected by an envelope of any material which hinders their electric discharge, the sol condition will persist even in presence of an electrolyte which would otherwise cause coagulation. Thus, as was found by Faraday, gold sol, formed by the reduction of auric chloride solution by phosphorus, is stabilized by gelatin, and the precipitation of silver chloride is prevented by the same colloid, the less stable silver chloride sol being protected against the electrolyte present by the more stable gelatin sol.

So far the study of colloids in this chapter has been restricted to phenomena of the liquid state. In the original and narrower sense in which the term was employed colloids necessarily contained a liquid phase, but just as the term "solution", which is generally applied to liquid mixtures, may be extended to include gaseous and solid mixtures, so the term colloid is now extended to include certain phenomena of the gaseous and solid states.

The distinctive property, however, of the colloidal state, which differentiates it from the state of solution, is heterogeneity; that is to say, the colloid is dispersed through the medium, there is a *disperse phase* and a *dispersion medium.* So far the disperse phase has been regarded as solid, and the dispersion medium as liquid. When, however, the conception is extended to gaseous and

solid systems, a comprehensive scheme results in which a variety of interesting phenomena are included. Thus Wo. Ostwald has proposed the following classification of colloids:

Disperse Phase.	Dispersion Medium.	Examples.
Solid	Solid	Carbon particles in iron. Gold in ruby glass.
Solid	Liquid	Colloidal solutions of metals, gelatin, starch, &c.
Solid	Gas	Smoke. Fine dust. Fumes.
Liquid	Solid	Certain minerals.
Liquid	Liquid	Emulsions.
Liquid	Gas	Fog. Mist. Clouds.
Gas	Solid	Solidified froths, e.g. pumice.
Gas	Liquid	Froths and foams.

The only system excluded from this scheme is that of a gas dispersed in a gas. This system, however, is homogeneous, like a true solution, there being no distinction as regards molecular dimensions between its different components; therefore it is not colloidal.

It is evident from a consideration of the table that a very large number of phenomena encountered in nature and employed in the arts come under the category of colloids. Indeed, as Ostwald has said: "It is simply a fact that colloids constitute the most universal and the commonest of all things we know. We need only to look at the sky, at the earth, or at ourselves to discover colloids or substances closely allied to them. . . . We have only recently come to learn that every structure assumes special properties and a special behaviour when its particles are so small that they can no longer be recognized microscopically, while they are still too large to be called molecules. Only now has the true significance of this region of the colloid dimensions—The World of Neglected Dimensions—become manifest to us."

SUMMARY

DIALYSIS is the separation of substances in solution by the use of a *membrane*, through which *crystalloids* in solution will pass but not *colloids*.

COLLOIDS, e.g. silicic acid, can exist in two states, the *hydrosol* (or sol) state, and the *hydrogel* (or gel) state.

Sols are converted into gels by catalysis.

By means of the *ultra-microscope* colloidal liquids have been seen to be suspensions.

Colloids have been separated by the use of special filters, and a gradation has been established between colloids in suspension and crystalloids in solution.

Colloids consist of electrically charged particles which can be separated by an electric current, the process being called *cataphoresis.*

A sol passes into a gel by *coagulation,* a gel into a sol by *peptization.*

More stable colloids can act as *protective colloids* to less stable colloids, thus preventing their coagulation by electrolytes.

A colloidal system includes a *disperse phase* and a *dispersion medium.* The system may be gaseous, liquid, or solid.

PART III—CHEMICAL COMPOUNDS AND CHEMICAL CHANGES

CHAPTER XIII

TYPES OF CHEMICAL COMPOUNDS

The chemical elements are divided broadly into metals and non-metals. The metals form only a limited number of compounds among themselves, these being chiefly crystalline products that separate from molten alloys. The non-metals, taken alone, however, form a considerable number of prominent compounds, amongst which are important hydrides, chlorides, oxides, and oxyacids. Excepting carbon compounds, which for the most part form a category by themselves, the largest number of compounds contain both metal and non-metal, for amongst these are all the metallic oxides, sulphides, halides, and oxy-salts.

There is no doubt that oxygen, and to a less degree hydrogen, is a key-element; so that the study of oxides, and to a less extent hydrides, yields a deep insight into the properties of the elements and their compounds. From oxides there is an easy transition on the one hand to hydroxides and oxy-salts, and on the other to halides, sulphides, &c., and so the chief regions of inorganic chemistry may be traversed systematically.

Therefore, these various compounds will be studied in the following sequence: hydrides, oxides and hydroxides, halides, sulphides, oxy-salts.

Hydrides.

Except for cuprous hydride $(CuH)_n$, which seems to be unique, the hydrides of the elements fall into two classes: (*a*) non-volatile hydrides of powerful metals, (*b*) volatile, generally gaseous, hydrides of non-metals and metalloids.

(*a*) *Metallic Hydrides.*—The following metallic hydrides, in addition to $(CuH)_n$, are known:

LiH, NaH, KH, RbH, CsH, CaH_2, SrH_2, BaH_2.

The metals forming them are those of the alkalis and alkaline

earths, the most intense of all the metals, which themselves are able to decompose water at atmospheric temperature.

The hydrides are crystalline solids formed by the combination of the respective metals with hydrogen, and are decomposed by water with the evolution of twice the volume of hydrogen which is evolved when the metal alone reacts with water. Thus calcium hydride, known technically as "hydrolith", reacts in the following way with water:

$$CaH_2 + 2\,H_2O = Ca(OH)_2 + 2\,H_2.$$

These hydrides stand in great contrast to the volatile hydrides of the non-metals next to be enumerated.

(*b*) *Non-metallic Hydrides.*—The following non-metallic hydrides are typical:

(B_2H_6, &c.)	CH_4	NH_3	OH_2	FH
	SiH_4	PH_3	SH_2	ClH
	GeH_4	AsH_3	SeH_2	BrH
	(SnH_4)	SbH_3	TeH_2	IH
		(BiH_3)		

These compounds, and the relationships between them, have, however, been fully studied in the chapter on the periodic system, to which the student is referred.

Oxides and Hydroxides.

The following classes of oxides can be distinguished:

Neutral oxides, including *suboxides.*
Basic oxides.
Acidic oxides, including *mixed anhydrides.*
Saline oxides.
Peroxides, divided into *poly-* and *super-oxides.*

Neutral oxides include the following:

$$H_2O,\ CO,\ N_2O,\ NO,$$

as well as the *sub-oxides*

$$Cu_4O,\ Ag_4O,\ Pb_2O.$$

Water is a truly neutral oxide, or, more strictly, it is equally basic and acidic, since by the minute degree of ionization that takes place within it hydrogen and hydroxide ions are necessarily produced in equivalent quantities.

Carbon monoxide is very slightly soluble in water, but the

solution is neutral. Nevertheless this oxide is related to formic acid, H·COOH; thus, adopting conventional formulæ:

$$CO + H_2O \leftarrow H\cdot C\overset{O}{\overset{\|}{\underset{OH}{}}};$$

that is to say, CO is produced from HCOOH by dehydration, but HCOOH is not produced from CO by hydration. The explanation appears to be that hydroxylation of CO thus:

$$C{=}O + H_2O \rightarrow C\overset{OH}{\underset{OH}{<}}$$

does not take place; for even when another oxygen atom is present in CO_2, to fortify the first oxygen atom, the acid produced, viz. carbonic acid, is unstable:

$$O{=}C{=}O + H_2O \rightleftharpoons O{=}C\overset{OH}{\underset{OH}{<}}.$$

If CO is brought into contact with KOH at 100° C., however, the case is different; CO is slowly absorbed to produce formate, thus:

$$C{=}O + KOH \rightarrow H{-}C\overset{O}{\overset{\|}{\underset{OK}{}}}.$$

This reaction involves rearrangement of the atoms concerned, i.e. intra-molecular rearrangement, probably in the following way:

$$C{=}O + KOH \rightarrow C\overset{OH}{\underset{OK}{<}} \rightarrow HC\overset{O}{\overset{\|}{\underset{OK}{}}};$$

but the reaction is possible owing to the basic power of the potash, and the stability of the salt produced.

Nitrous oxide, N_2O, whilst distinctly soluble in cold water, produces no acid. It is nevertheless derived from hyponitrous acid, $H_2N_2O_2$, by loss of water, thus:

$$\begin{matrix} N{=}N \\ | \quad | \\ OH\ HO \end{matrix} \rightarrow \begin{matrix} N{=}N \\ \diagdown\ \diagup \\ O \end{matrix} + H_2O.$$

Like carbon monoxide, nitrous oxide is an acidic anhydride from one side only; it is produced from an acid by loss of water, but does not combine with water to form that acid. A true acidic anhydride must produce an acid by combining with water; nitrous oxide is regarded as a neutral oxide because its aqueous solution is neutral.

Nitric oxide, NO, is also classed as a neutral oxide, because so far as it dissolves in water it yields a neutral solution. There is,

however, an uncommon acid, nitrohydroxylamic acid, from which this oxide is derived by loss of water:

$$HO—N(H)—NO_2 \longrightarrow H_2O + 2\,NO.$$

The *suboxides* Cu_4O, Ag_4O, Pb_2O,[1] contain less oxygen than the lowest basic oxides Cu_2O, Ag_2O, PbO, and they do not dissolve in water. Thus they form a small category by themselves, and since they are neither basic nor acidic they may be regarded as neutral.

Basic oxides are numerous, and differ much in basic power. The oxides of the alkali metals slake very vigorously, producing hydroxides which are caustic alkalis. The oxides of the alkaline earth metals also slake, producing hydroxides which increase in solubility from calcium to barium. A few other metallic oxides, e.g. MgO and Ag_2O, dissolve very slightly in water, giving faintly alkaline solutions.

Metallic hydroxides may be produced either by the direct combination of the corresponding oxide with water, or by precipitation from a corresponding salt solution by an alkali. Occasionally both methods of preparation are possible; e.g. calcium hydroxide may be produced either by the slaking of lime thus:

$$CaO + H_2O = Ca(OH)_2$$

or, on account of its slight solubility in water, by precipitation from a salt solution by means of alkali, thus:

$$CaCl_2 + 2\,NaOH = Ca(OH)_2 + 2\,NaCl.$$

Of these two methods of preparation the first is alone available for the alkali hydroxides on account of their solubility, the second can alone be employed for such hydroxides as those of copper, zinc, iron, and aluminium, on account of the inertness towards water of the corresponding oxides.

Note on Acids, Bases, and Salts.

A base is generally defined as a compound which neutralizes an acid to form a salt, water being eliminated in the process of neutralization.

Originally the formation of water was overlooked, bases and acids being considered oxides which combined to form a salt, e.g.:

$$CaO + SO_3 = CaO \cdot SO_3.$$

[1] Pb_2O appears to be basic, since halides corresponding to it are known.—Denham, *Trans. Chem. Soc.*, 1917, *111*, 29; 1918, *113*, 249.

Then it was discovered that hydrogen chloride is an acid which forms a salt with a base with elimination of water, thus:

$$CaO + 2\,HCl = CaCl_2 + H_2O,$$

and so two kinds of acids were recognized: oxyacids such as H_2SO_4 derived from acidic oxides such as SO_3, and the so-called hydracids, which, containing no oxygen, are not derived from acidic oxides. And since acidic oxides were found to combine with water to form acidic hydroxides or oxyacids, they were called acidic anhydrides, or simply anhydrides. Thus the nomenclature on the acidic side became definite; an acid was recognized as a compound containing hydrogen replaceable by a metal, and acidic oxides were no more called acids. The dualism which divides an oxysalt into basic and acidic oxides is sometimes retained for convenience, however, especially in tabulating analytical data. A carbonate such as dolomite, for example, will be said to contain so much CaO, so much MgO, and so much CO_2.

It must be recognized, nevertheless, that so far as reactions depending on specifically acidic properties are concerned, no distinction is to be drawn between oxyacids and hydracids. Each kind of acid consists of hydrion combined by electrovalency with anion, and whether the anion of an acid contains oxygen or not is of secondary importance.

It has been usual to represent sulphuric acid as if it were sulphuryl hydroxide, $SO_2(OH)_2$, because it is related to sulphuryl chloride, SO_2Cl_2, from which it can be derived by hydrolysis. Such a method of formulation, however, is not to be commended, since it shows two of the oxygen atoms in the sulphate radicle differently placed from the other two; and, moreover, no acid is a hydroxide in the same sense as a base is a hydroxide. The modern method of formulating sulphuric acid has been shown on p. 126.

The essential characteristic of an acid, then, is that it contains loosely bound hydrogen ions which it easily parts with; and the simplest conception of a base is that it is complementary to an acid, and receives the hydrogen ions which the acid so easily gives away. Thus *an acid is a donor, and a base an acceptor of hydrogen ions.*[1]

There is, however, more than one way in which a base can accept hydrogen ions. The way most generally recognized is that of providing hydroxide ions to form water, as in the reaction:

$$Na^{\cdot} + OH' + H^{\cdot} + Cl' = H_2O + Na^{\cdot} + Cl';$$

[1] Lowry, *Chemistry and Industry*, 1923, 46.

and when a base thus provides hydroxide ions in solution, it is an alkali as well as a base.

An anhydrous oxide can, however, behave as a base in the sense of accepting hydrogen ions; for example, zinc oxide will dissolve in an acid producing a salt, and thus neutralize the acid by accepting its hydrogen ions and converting them into water:

$$Zn^{\cdot\cdot}O'' + 2H^{\cdot} + SO_4'' = H_2O + Zn^{\cdot\cdot} + SO_4''.$$

In both these cases water is produced by the neutralization of an acid; ammonia, NH_3, however, probably acts directly as a hydrogen ion acceptor thus:

$$NH_3 + H^{\cdot} + Cl' = NH_4^{\cdot} + Cl'.$$

There is no need for the assumption which is generally made that the ammonia first necessarily reacts with water to produce ammonium hydroxide, NH_4OH, before it can neutralize an acid. It is true that NH_3 does react with water to form an alkaline solution containing ammonium and hydroxide ions; but it is more likely when added to dilute hydrochloric acid solution to react with the hydrogen ions of the acid than with similar ions derived from the water.

Acidic Oxides.

The oxides of non-metals are generally acidic oxides, and combine more or less readily with water to form oxyacids. Thus N_2O_5, P_2O_5, SO_3, have a great affinity for water, and can with difficulty be separated from it; in this respect they resemble the oxides of the alkali metals, which combine with water with great vigour to form hydroxides. Other non-metallic oxides, such as CO_2, SO_2, B_2O_3, As_4O_6, do not so vigorously combine with water, and are more easily separated from it; SiO_2, probably because it consists of polymerized molecules, does not directly combine with water. The strongest acidic oxides, like the strongest basic oxides, are those which combine most readily with water; and the feeblest are those which, like silica, have very little attraction for water.

If the basic hydroxides are arranged roughly in order of diminishing basic strength, and the acidic hydroxides similarly in order of diminishing acidic strength, the interesting observation is made that the two series overlap in the centre thus:

$$\underset{\text{Diminishing basic strength.}}{\xrightarrow{\quad}} \quad NaOH \quad Ca(OH)_2 \quad Mg(OH)_2 \quad | \quad Al(OH)_3 \quad | \quad HAlO(OH)_2 \quad | \quad H_3PO_4 \quad H_2SO_4 \quad HNO_3 \quad \underset{\text{Diminishing acidic strength.}}{\xleftarrow{\quad}}$$

Thus $Al(OH)_3$ is both a feeble base and a feeble monobasic acid, and is said to be *amphoteric*.[1] This is shown by the fact that this hydroxide dissolves in acid to form an aluminium salt, and in alkali to form an aluminate. That it is both a base and an acid is shown by the following series of reactions which can easily be carried out:

i. $\underset{\text{(salt)}}{AlCl_3} + 3\,\underset{\text{(base)}}{NaOH} = \underset{\text{(base)}}{Al(OH)_3} + 3\,\underset{\text{(salt)}}{NaCl}$

ii. $\underset{\text{(acid)}}{HAlO(OH)_2} + \underset{\text{(base)}}{NaOH} = \underset{\text{(salt)}}{NaAlO(OH)_2} + \underset{\text{(water)}}{H_2O}$

iii. $\underset{\text{(salt)}}{NaAlO(OH)_2} + \underset{\text{(acid)}}{HCl} = \underset{\text{(acid)}}{HAlO(OH)_2} + \underset{\text{(salt)}}{NaCl}$

iv. $\underset{\text{(base)}}{Al(OH)_3} + 3\,\underset{\text{(acid)}}{HCl} = \underset{\text{(salt)}}{AlCl_3} + 3\,\underset{\text{(water).}}{H_2O}$

Thus $Al(OH)_3$ completes the cycle:

base; acid; acid; base.

The mineral known as spinel, $MgO \cdot Al_2O_3$ or $MgAl_2O_4$, contains alumina as aluminate; and analogous to this is chrome ironstone, which is ferrous chromite, $FeO \cdot Cr_2O_3$. Other amphoteric hydroxides are: $Sn(OH)_2$, $Sn(OH)_4$, $Sb(OH)_3$, and perhaps $Zn(OH)_2$; though the existence of $Zn(ONa)_2$ is improbable, and of $Zn(OH)(ONa)$ doubtful.

It may here be recorded that certain of the less electro-positive metals form both basic and acidic oxides, the lower oxides being basic, the higher acidic. The best-known examples of such metals are chromium and manganese, to which may be added uranium on account of an interesting point in connection with the trioxide of this metal. The facts are set forth in the following table.

Cr.	Mn.	U.
CrO, wholly basic. Cr_2O_3, basic, feebly acidic, e.g. in $FeCr_2O_4$. CrO_3, wholly acidic. (CrO_2Cl_2 is not a salt, but an acidic chloride).	MnO, wholly basic. MnO_2, possibly basic, feebly acidic. MnO_3, wholly acidic. Mn_2O_7, acidic. $(MnO_3)_2SO_4$ suggests basic property.	UO_2, wholly basic. UO_3, acidic; basic with regard to one oxygen atom in the uranyl salts, e.g. $UO_2(NO_3)_2$

These examples illustrate the acid-producing tendency of added oxygen; they justify the name oxygen (acid-producing). The

[1] I.e. facing both ways.

compound $(MnO_3)_2SO_4$, permanganyl sulphate, formed by dissolving potassium permanganate in concentrated sulphuric acid, is rather unaccountable; the uranyl salts, e.g. the nitrate, $UO_2(NO_3)_2$, are interesting for the following reason. Uranium is the highest member of the sixth group of the periodic system; therefore its oxides should be more basic than those of any other member of the group. This is so, and basic power here extends even to the trioxide, although it does not in the case of the less-basic chromium trioxide. It is only one of the three oxygen atoms, however, which can be replaced by acidic radicles so that basic salts, the uranyl salts, are formed. These are nevertheless true salts; the nitrate, for example, dissolves freely in water.

Mixed Anhydrides.—There are a few non-metallic oxides which combine with water or bases to produce two acids or salts. The chief of these are nitrogen and chlorine peroxides.

Nitrogen peroxide, NO_2 or N_2O_4, readily dissolves in cold water, producing an equimolecular mixture of nitrous and nitric acids, thus:

$$2NO_2 + H_2O = HNO_2 + HNO_3;$$

it is therefore regarded as the mixed anhydride of these two acids.

Chlorine peroxide or *dioxide,* ClO_2, does not form any acid with water, although it yields a yellow solution from which the hydrate $ClO_2 \cdot 8H_2O$ can be crystallized. With alkali, however, a mixture of chlorite and chlorate is formed, thus:

$$2ClO_2 + 2NaOH = NaClO_2 + NaClO_3 + H_2O.$$

In this limited sense, therefore, ClO_2 is a mixed anhydride.

Saline Oxides.—It has been remarked above that the higher oxides of certain metals are acidic whilst the lower are basic. For example, CrO_3 is acidic whilst Cr_2O_3 is basic. If potassium chromate is added to a chromic salt solution, a dingy, yellow precipitate is obtained which has the empirical composition CrO_2.

This is basic chromic chromate, $Cr_2O_3 \cdot CrO_3$ or $(CrO)_2CrO_4$, formed thus:

$$2CrCl_3 + K_2CrO_4 + 2H_2O = Cr_2O_3 \cdot CrO_3 + 2KCl + 4HCl;$$

it is therefore a saline oxide, composed of a basic and an acidic oxide of the same metal.

The following are other examples of saline oxides:

$$Fe_3O_4,\ Mn_3O_4,\ Pb_2O_3,\ Pb_3O_4.$$

Fe_3O_4, ferroso-ferric oxide, is a compound of FeO and Fe_2O_3. If a mixture of ferrous and ferric salts is precipitated by alkali, black hydrated Fe_3O_4 is produced. *Mn_3O_4* may be regarded as $MnO \cdot Mn_2O_3$, or perhaps $2MnO \cdot MnO_2$. The former constitution is suggested by the behaviour of this oxide with concentrated sulphuric acid, in which it dissolves, forming a mixture of manganous and manganic sulphates, thus:

$$Mn_3O_4 + 4H_2SO_4 = MnSO_4 + Mn_2(SO_4)_3 + 4H_2O.$$

So Mn_2O_3, acidic relatively to MnO, is really also a basic oxide.

Pb_2O_3 and *Pb_3O_4* are $PbO \cdot PbO_2$ and $2PbO \cdot PbO_2$ respectively, i.e. they are lead meta- and ortho-plumbate, related to the hypothetical acids:

$$O = Pb\langle^{OH}_{OH} \quad \text{and} \quad {}^{HO}_{HO}\rangle Pb\langle^{OH}_{OH}$$

thus:

$$O = Pb\langle^{O}_{O}\rangle Pb \quad \text{and} \quad Pb\langle^{O}_{O}\rangle Pb\langle^{O}_{O}\rangle Pb.$$

It might be expected that tin, in the same group of the periodic system as lead, would form similar saline oxides. That it does not is probably due to the fact that SnO is not basic enough to combine with SnO_2, for SnO and SnO_2 are undoubtedly more acidic than PbO and PbO_2 respectively.

Peroxides.

A peroxide is an oxide which readily yields some of its oxygen either as a gas or by behaving as an oxidizing agent. Thus PbO_2, besides being an acidic oxide, is a peroxide which behaves as follows when heated alone (i) or with hydrochloric acid (ii):

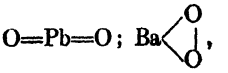
i. $2PbO_2 = 2PbO + O_2$.
ii. $PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2$.

This description, however, is not precise enough; for BaO_2 behaves like PbO_2 in regard to these two reactions, but is also capable of a third reaction, with dilute acid, viz.:

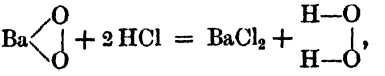
$$BaO_2 + 2HCl = BaCl_2 + H_2O_2.$$

Now the difference between BaO_2 and PbO_2 thus revealed is fundamental, for lead belongs to the fourth periodic group, and is quadrivalent in PbO_2, whilst barium, belonging to the second

group, is only bivalent. The constitutions of these two oxides are therefore ordinarily represented thus:



and so BaO_2 yields H_2O_2 with dilute acid thus:



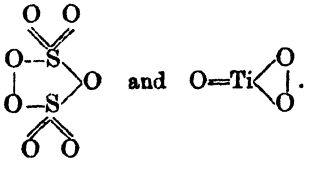
a reaction of which PbO_2 is plainly incapable.

Peroxides are divided into two classes, of which the above are examples. These are sometimes known as poly- and superoxides respectively (Mendeléeff):

Polyoxides.	Superoxides.
PbO_2.	BaO_2.
MnO_2.	Na_2O_2.
ClO_2.	S_2O_7.
NO_2.	TiO_3.

The term peroxide is applied to a particular oxide, irrespective of any other property it may possess. Thus, amongst the polyoxides are ClO_2 and NO_2, which are also mixed anhydrides; and amongst the superoxides are those which are basic: BaO_2 and Na_2O_2; and those which are acidic: S_2O_7 and TiO_3.

The acidic, like the basic superoxides, contain a chain of 2 oxygen atoms in lieu of an increased valency of the nuclear atom. Thus the constitutions of the two latter oxides are generally represented thus:



Halides.

The binary compounds of the halogens fluorine, chlorine, bromine, and iodine differ much in character, according to the diversity of the elements which form them. Attention may be confined to the chlorides, and those of silicon and sodium may be chosen first of all as typical of non-metallic and metallic chlorides respectively.

Silicon tetrachloride, $SiCl_4$, the chloride of a non-metal, may be

prepared by the union of its elements, or more usually by passing chlorine over a heated mixture of silica and carbon, thus:

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$

It is formed as a vapour, and may be condensed as a colourless liquid which is soluble in such a solvent as benzene. It cannot be prepared by the action of aqueous hydrochloric acid on silica, for it is instantly decomposed, i.e. hydrolyzed, by water, thus:

$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl.$$

It is not, however, decomposed by concentrated sulphuric acid, for silicon forms no sulphate.

Sodium chloride, NaCl, presents an extreme contrast to silicon chloride in mode of preparation and properties. It is obtained by neutralizing base by acid in aqueous solution, thus:

$$NaOH + HCl \rightarrow NaCl + H_2O,$$

and is consequently not decomposed by water. It is a crystalline solid, insoluble in a solvent like benzene, which dissolves silicon chloride; it is not volatile, except at high temperature, but it is decomposed by concentrated sulphuric acid, because sodium forms a sulphate, and HCl is more volatile than H_2SO_4.

Now consider *aluminium chloride*, $AlCl_3$. Alumina, Al_2O_3, is amphoteric, and the chloride also is intermediate in character. Thus it is prepared anhydrous as a sublimate by passing either chlorine or hydrogen chloride over the heated metal, and it may also be obtained in aqueous solution by dissolving the hydroxide in excess of hydrochloric acid, and then crystallized as $AlCl_3 \cdot 6H_2O$. If, however, the anhydrous or hydrated chloride is heated with water, hydrolysis takes place and hydrated alumina separates.

So the following reaction is reversible:

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3HCl.$$

Contrast with this:

$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl,$$

and

$$NaCl + H_2O \leftarrow NaOH + HCl.$$

Thus it is seen that, as with oxides, there are chlorides in which basic and acidic characters predominate respectively, and chlorides of intermediate or amphoteric character.

Sulphides.

In the course of qualitative analysis the student becomes acquainted with various types of metallic and metalloidal sulphides. Non-metallic sulphides are not very important; carbon disulphide will serve as an example of these.

Since oxygen and sulphur are in the same group of the periodic system, a comparatively close analogy between oxides and sulphides may be expected. Thus, for example, members of the following pairs of compounds may be expected to show somewhat close relationships to each other:

$$CO_2, CS_2;\ As_2O_3, As_2S_3;\ K_2O, K_2S;$$

and they do.

Carbon dioxide and carbon disulphide differ in physical properties no more than oxygen and sulphur differ; and they are distinctly analogous to each other in chemical properties. Thus, as carbon dioxide combines with basic oxides to form carbonates, so carbon disulphide combines with basic sulphides to form thio- or sulpho-carbonates:

$$CO_2 + 2\,NaOH = Na_2CO_3 + H_2O.$$
$$CS_2 + 2\,NaSH = Na_2CS_3 + H_2S.$$

These oxy- and thio-salts are respectively decomposed by acids, thus:

$$Na_2CO_3 + 2\,HCl = 2\,NaCl + H_2CO_3.$$
$$Na_2CS_3 + 2\,HCl = 2\,NaCl + H_2CS_3.$$

Thiocarbonic acid, H_2CS_3, separates in the latter case as a liquid, and is thus more stable than carbonic acid, H_2CO_3, which exists only in dilute solution. These acids, however, readily decompose into H_2O and CO_2 and H_2S and CS_2 respectively.

Practice in qualitative analysis teaches the student the relation between As_2O_3 and As_2S_3. Thus As_2O_3—or more correctly As_4O_6—is an acidic oxide, dissolving in alkali hydroxide to form arsenite, and similarly As_2S_3 is an acidic sulphide dissolving in alkali hydrosulphide to form thioarsenite;

$$As_2O_3 + 2\,NaOH = 2\,NaAsO_2 + H_2O.$$
$$As_2S_3 + 2\,NaSH = 2\,NaAsS_2 + H_2S.$$

Frequently, however, As_2S_3 is dissolved in NaOH, and then the reaction is:

$$2\,As_2S_3 + 4\,NaOH = 3\,NaAsS_3 + NaAsO_2 + 2\,H_2O.$$

When, however, the solution formed in this way is acidified, As_2S_3 is reprecipitated on account of its insolubility:

$$3\,NaAsS_2 + NaAsO_2 + 4\,HCl = 2\,As_2S_3 + 4\,NaCl + 2\,H_2O.$$

Basic sulphides resemble basic oxides, thus:

$$Na_2O + H_2O = 2\,NaOH$$
$$Na_2S + H_2S = 2\,NaSH;$$

hydrosulphide being analogous to hydroxide. When an alkali sulphide is dissolved in water, as might be expected, it reacts with water in this way:

$$Na_2S + H_2O = NaSH + NaOH,$$

and is strongly alkaline on account of the hydroxide formed.

Calcium sulphide, formed in the dry way as in the black-ash process, is scarcely soluble in water; nevertheless it is slowly hydrolyzed by water, thus:

$$2\,CaS + 2\,H_2O = Ca(SH)_2 + Ca(OH)_2.$$

Consequently it is not formed in presence of water; and calcium is not precipitated from solution as sulphide.

A characteristic of many metallic sulphides is their exceeding insolubility in water; and in consequence they are unacted upon by this substance, and the corresponding metals are quantitatively precipitated from aqueous solutions of their salts by hydrogen sulphide, as in the well-known analytical reactions. The sulphides of some metals, however, whose oxides are feebly basic or amphoteric, cannot be precipitated in presence of water, so that the hydroxides appear in place of the sulphides.

Thus when ammonium hydrosulphide is added to an aluminium salt solution, $Al(OH)_3$ is precipitated, owing presumably to hydrolysis of the hydrosulphide:

$$AlCl_3 + 3\,NH_4SH = Al(SH)_3 + 3\,NH_4Cl.$$
$$Al(SH)_3 + 3\,H_2O = Al(OH)_3 + 3\,H_2S.$$

A similar reaction occurs with chromium.

Oxy-salts.

The formation of oxy-salts, such as sulphates, is a criterion of a metal. A chloride may or may not be a salt, a sulphate necessarily

is. Consider, for example, the following series of chlorides and sulphates:

Chlorides:	PCl_5	$SiCl_4$	$AlCl_3$	$MgCl_2$	NaCl
Sulphates:	—	—	$Al_2(SO_4)_3$	$MgSO_4$	Na_2SO_4.

PCl_5 and $SiCl_4$ are certainly not salts, and phosphorus and silicon form no sulphates; $AlCl_3$ is a chloride of intermediate character possessing some saline qualities, and $Al_2(SO_4)_3$ is an imperfect salt somewhat hydrolyzed by water; $MgCl_2$ is also hydrolyzed when heated with water, $MgSO_4$ scarcely so; NaCl and Na_2SO_4 are true salts yielding neutral solutions in which there is no hydrolysis. That the chlorides $AlCl_3$ and $MgCl_2$ appear more hydrolyzable than the corresponding sulphates is probably due to the volatility of hydrogen chloride, which escapes with the steam when solutions of these salts are evaporated.

It appears that an element must possess a certain minimum metallic strength in order to form a sulphate; to form an acid sulphate a metal must be of the strongest character. Thus it is only the sulphates of the alkali metals which combine with sulphuric acid to form solid acid sulphates, e.g. $NaHSO_4$ and $KHSO_4$; though a few other metals appear to form such sulphates in solution. The study of carbonates is very instructive. The elements fall into five categories as regards power to form carbonates:

i. No carbonates.
ii. Basic carbonates only.
iii. Normal as well as basic carbonates.
iv. Normal carbonates only.
v. Acid as well as normal carbonates.

Non-metals form no carbonates, and power to form basic carbonates emerges amongst the metalloids. Thus, of the fifth-group elements, nitrogen, phosphorus, arsenic, antimony, bismuth, the last alone forms a carbonate, which however is basic, and so reveals itself as more metallic than any other of these five elements.

The elements of the fourth group, carbon, silicon, germanium, tin, and lead, show similar relationships. Lead is the only member of these five that forms a carbonate, and this metal appears to be more metallic than bismuth, because in presence of excess of carbonic acid to prevent hydrolysis it yields the normal carbonate $PbCO_3$.

A number of other metals more readily form basic than normal carbonates; amongst these are copper, mercury, zinc, magnesium,

Undoubtedly the failure to form a normal carbonate is due not only to the weakness of a metal but to the feebleness of carbonic acid. Thus magnesium, which is prone to form a basic instead of a normal carbonate by precipitation, shows no tendency to form a basic sulphate, because sulphuric acid is sufficiently powerful to enable its salts to resist hydrolysis.

Incidentally it may be supposed that a normal carbonate is first formed in the act of precipitation, and that the basic carbonate which actually appears is due to subsequent hydrolysis. For example, in the case of lead, the basic carbonate may be supposed formed from the normal carbonate, thus:

$$3\,PbCO_3 + 2\,H_2O \longrightarrow 2\,PbCO_3 \cdot Pb(OH)_2 + H_2CO_3.$$

Sometimes this process of hydrolysis may actually be observed. For example, when sodium hydrogen carbonate is added to mercurous nitrate solution the precipitate first formed is almost white, and consists of the normal carbonate, the hydrolysis of which is prevented by the bicarbonate present. On dilution and warming, however, the precipitate darkens, and basic carbonate, and finally oxide, is formed, because of the decomposition of the alkali bicarbonate in solution, and the consequent hydrolysis of the precipitated mercurous carbonate.

The series of the metals must be traversed far in the upward direction before those metals are reached which form normal but not basic carbonates. Such are the metals of the alkaline earths and the alkalis. Calcium carbonate, for example, is normal when precipitated, and never becomes basic. This salt is soluble to a minute extent in pure water, to which it imparts a faintly alkaline reaction. It is true that hydrolysis of the dissolved salt takes place, but this results in the formation of hydroxide and bicarbonate, thus:

$$2\,CaCO_3 + 2\,H_2O \rightleftharpoons Ca(HCO_3)_2 + Ca(OH)_2,$$

OH' ions showing alkalinity being due to the ionization of $Ca(OH)_2$. The same phenomenon appears more markedly in the case of alkali carbonates, which show a strongly alkaline reaction. Thus, sodium carbonate reacts with water in this way:

$$Na_2CO_3 + H_2O \rightleftharpoons NaHCO_3 + NaOH,$$

and so its strongly alkaline reaction is explained; for, according to the ionization theory, a salt producing basic and acidic ions only, e.g. $2Na^{\cdot}$ and CO_3'', would be neutral in reaction.

It has been seen above that only the most powerful metals form hydrogen or acid sulphates; the same is true in regard to hydrogen or acid carbonates. Thus it is only the alkali metals that form solid hydrogen carbonates, and these increase in stability from sodium to cæsium in the series:

$$NaHCO_3,\ KHCO_3,\ RbHCO_3,\ CsHCO_3.$$

The alkaline earth metals, with ferrous iron and magnesium, form unstable hydrogen-carbonates in solution however, e.g. $Ca(HCO_3)_2$, and these hydrogen-carbonates, existing only in solution, differ from the solid hydrogen-carbonates of the alkali metals by being more soluble than the corresponding normal carbonates. Whilst, therefore, $CaCO_3$ is dissolved by passing carbon dioxide through its suspension in water, $NaHCO_3$ is precipitated when the same gas is passed through a cold saturated solution of Na_2CO_3.

The superior solubility of calcium carbonate in water containing carbon dioxide in solution over its solubility in pure water is of profound importance in nature; for it is the cause, not only of the temporary hardness of water, but of the disintegration of calcareous rocks, as well as of their original formation through the agency of marine organisms, which form their shells from calcium carbonate held in aqueous solution by carbonic acid. These facts are represented by the following reversible reaction:

$$CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2.$$

Hydrated Salts.

Water of crystallization is of common occurrence in crystallized salts, and since its presence has a great influence on physical properties, the student must on no account ignore it in formulating a salt. The influence of temperature and atmospheric conditions on hydrated salts will be dealt with in another place; it may here be remarked, however, that when such salts are coloured the corresponding anhydrous compounds are invariably of a different colour. Thus, for example:

$CuSO_4 \cdot 5H_2O$	is blue;	$CuSO_4$	is white.
$FeSO_4 \cdot 7H_2O$	„ green;	$FeSO_4$	„ white.
$NiSO_4 \cdot 7H_2O$	„ deep green;	$NiSO_4$	„ yellow.
$CuCl_2 \cdot 2H_2O$	„ bluish green;	$CuCl_2$	„ brown.
$FeCl_3 \cdot 6H_2O$	„ yellow;	$FeCl_3$	„ iron-black.
$CoCl_2 \cdot 6H_2O$	„ crimson;	$CoCl_2$	„ blue.
$CoBr_2 \cdot 6H_2O$	„ dark red;	$CoBr_2$	„ green.
$CoI_2 \cdot 6H_2O$	„ dark red;	CoI_2	„ violet

The proportion of water varies much in different hydrated salts; ammonium oxalate, for example, has 1 molecule of water to 1 molecule of salt, ordinary sodium phosphate has 12, and the alums have 24; whilst between these extremes there are salts containing 2, 5, 6, 7, and 10, and less frequently 3, 4, and 8 molecules of water. Occasionally, too, the same salt will crystallize with varying proportions of water according to the temperature of its formation. Thus, for example, manganous sulphate, $MnSO_4$, forms crystallo-hydrates with 1, 4, 5, and 7 molecules of water at different temperatures.

The way in which water is combined chemically in crystallo-hydrates constitutes a problem the discussion of which is beyond the scope of the present work; nevertheless it will be well to tabulate here the commonest hydrated salts according to the molecular proportions of water they contain:

$\frac{1}{2}H_2O$	.....	$2\,CaSO_4 \cdot H_2O$.
H_2O	.....	$Na_2CO_3 \cdot H_2O$; $(NH_4)_2C_2O_4 \cdot H_2O$.
$2\,H_2O$	.....	$BaCl_2 \cdot 2\,H_2O$; $CuCl_2 \cdot 2\,H_2O$; $CaSO_4 \cdot 2\,H_2O$.
$3\,H_2O$	.....	$K_4Fe(CN)_6 \cdot 3\,H_2O$.
$4\,H_2O$	.....	$NaNH_4HPO_4 \cdot 4\,H_2O$.
$5\,H_2O$	.....	$Na_2S_2O_3 \cdot 5\,H_2O$; $CuSO_4 \cdot 5\,H_2O$; $Bi(NO_3)_3 \cdot 5\,H_2O$.
$6\,H_2O$	.....	$CaCl_2 \cdot 6\,H_2O$; $MgCl_2 \cdot 6\,H_2O$; $CoCl_2 \cdot 6\,H_2O$; $FeCl_3 \cdot 6\,H_2O$; $CrCl_3 \cdot 6\,H_2O$; $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6\,H_2O$, and similar double sulphates.
$7\,H_2O$	.....	$MgSO_4 \cdot 7\,H_2O$; $ZnSO_4 \cdot 7\,H_2O$; $FeSO_4 \cdot 7\,H_2O$; $NiSO_4 \cdot 7\,H_2O$; $CoSO_4 \cdot 7\,H_2O$.
$8\,H_2O$	.....	$Ba(OH)_2 \cdot 8H_2O$; $BaO_2 \cdot 8H_2O$.
$10\,H_2O$	.....	$Na_2CO_3 \cdot 10\,H_2O$; $Na_2SO_4 \cdot 10\,H_2O$; $Na_2B_4O_7 \cdot 10\,H_2O$.
$12\,H_2O$	.....	$Na_2HPO_4 \cdot 12\,H_2O$; $Na_2HAsO_4 \cdot 12\,H_2O$.
$18\,H_2O$	.....	$Al_2(SO_4)_3 \cdot 18\,H_2O$.
$24\,H_2O$	.....	$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O$, and other alums.

Double and Complex Salts.

DOUBLE SALTS are those which have a definite chemical individuality in the solid state, but break up more or less completely in aqueous solution into their constituent single salts. Crystallized potassium alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\,H_2O$, for example, is undoubtedly a chemical compound, and not a mixture of its two constituent salts; but when dissolved in water it gives the separate reactions of aluminium and potassium sulphates, so that its solution contains a mixture of these two salts, the process of solution having been accompanied evidently by disintegration of the double salt.

The formula for alum is sometimes halved, thus:

$$KAl(SO_4)_2 \cdot 12\,H_2O.$$

Now it is always wise to accept the simplest available formula in default of evidence to the contrary; but it may be objected that the above formula suggests a complex rather than a double salt, since it does not show complete molecules of the two constituent sulphates. This objection would perhaps have little weight were it not for a peculiar change which solid chromic alum undergoes when heated to 90° C. The violet crystals then turn green, with loss of water, changing into a salt which contains no free sulphate, since its solution gives no precipitate with barium chloride. The change is thus formulated:

$$K_2SO_4 \cdot Cr_2(SO_4)_3 \longrightarrow K_2[Cr_2(SO_4)_4] \text{ or } 2\,K[Cr(SO_4)_2].$$

So a double salt becomes a complex salt; potassium chromic sulphate becomes potassium chromisulphate, the potassium salt of chromisulphuric acid, $HCr(SO_4)_2$, a compound which is actually formed when chromic sulphate is warmed with sulphuric acid.

That $K[Cr(SO_4)_2]$ is so different from $K_2SO_4 \cdot Cr(SO_4)_3 \cdot 24\,H_2O$ is a good reason for not writing the formula for any alum in a way to suggest relationship to the former of these compounds.

Nevertheless there is evidence that saturated solutions of double salts contain complex ions, and probably chromic alum solution is no exception.

Double salts are very numerous. Besides the double sulphates and isomorphous selenates there are double chlorides, bromides, and iodides, and less frequently double carbonates and nitrates.

Double Sulphates.—The alums, and salts of which ferrous ammonium sulphate is a well-known example, may be mentioned.

Alums are isomorphous salts of the type

$$M_2 \cdot SO_4 \cdot X_2''' (SO_4)_3 \cdot 24\,H_2O,$$

where M = Na, K, NH_4, Rb, Cs, Tl, Ag (?),
and X = Al, Fe, Cr, Mn, Ga, Ti, Rh.

They are formed by mixing the constituent salts in aqueous solution, in proportions approximating to theoretical requirements, and crystallizing. The alums are less soluble than their constituent salts, and this is particularly the case with those of the extremely electropositive metals rubidium and cæsium.

Double sulphates of the ferrous ammonium sulphate type are the salt $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$ and others in which Mg'', Zn'', Cu'', Mn'', Co'', Ni'' may take the place of Fe'', and other alkali metals that of NH_4'. The relation between these double sulphates and the heptahydrated sulphates, e.g. $FeSO_4 \cdot 7H_2O$, is interesting.

It was found by Graham that one of the seven molecules of water in this salt required a higher temperature for its expulsion than the other six. This seventh molecule Graham called *constitutional water*, because it appeared to enter into the constitution of the salt more intimately than the other six molecules. It is this molecule which seems to be displaced by ammonium or other alkali sulphate in the formation of the double salt. The relationship may be thus shown:

$$FeSO_4 \cdot H_2O \cdot 6H_2O : FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O.$$

It should be remarked that the ammonium sulphate in the double salt exerts a protective influence over the ferrous sulphate, for ferrous ammonium sulphate is less oxidizable by the air than ferrous sulphate, and for this reason is preferred for the purpose of volumetric analysis.

DOUBLE CHLORIDES.—The mineral carnallite is $KCl \cdot MgCl_2 \cdot 6H_2O$, to which there corresponds the ammonium salt $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$. The solubility of magnesium and manganous hydroxides in ammonium chloride solution, with the corresponding fact that the hydroxides of these metals are not precipitated by ammonia in presence of ammonium chloride, is sometimes attributed to the formation in solution of complex ions, such as $(MgCl_3)'$, derived from $NH_4Cl \cdot MgCl_2$. The salts themselves, however, are usually regarded as double rather than complex salts. The double chloride $NaCl \cdot AlCl_3$ is a volatile compound, the formation of which was a part of an early process for the preparation of metallic aluminium.

Examples of double salts of another type are sodium potassium tartrate (Rochelle salt), $NaKC_4H_4O_6 \cdot 4H_2O$, microcosmic salt, $NaNH_4HPO_4 \cdot 4H_2O$, and magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$.

These are formulated differently from the alums and other double salts, as containing two or more metallic radicles within the same molecule. Since, however, these salts show no complex ions in dilute solution, and their molecular magnitudes are unknown, it may be that they should be put in the same category as other double salts.

COMPLEX SALTS are those which, derived originally from single salts, are so stable as to maintain their individuality in solution, one of the metals appearing as a basic ion, whilst the other has become part of a complex acidic ion, so that its metallic nature is

masked. Potassium ferrocyanide, $K_4Fe(CN)_6$, is a familiar example of a complex salt. It appears to be composed of $4KCN + Fe(CN)_2$, and is indeed formed by adding potassium cyanide to ferrous sulphate solution until the precipitated cyanide has been redissolved, and then boiling the solution. Thus a remarkable change takes place; the iron ceases to behave as a basic radicle and becomes part of an acidic complex, so that it gives no ferrous reactions in solution. No ferrous salt is present, only a potassium salt—potassium ferrocyanide—which ionizes in solution thus:

$$K_4Fe(CN)_6 \rightleftharpoons 4K^{\cdot} + [Fe(CN)_6]''''.$$

So profound is this change, and so stable the complex salt, that from its concentrated solution sulphuric acid separates hydroferrocyanic acid, $H_4Fe(CN)_6$, as a white solid.

Alum and potassium ferrocyanide, as representatives of double and complex salts respectively, present extremes, but there are gradations between them. The behaviour of nickel and cobalt salts with potassium cyanide furnishes a case in point. The following reactions take place:

$$NiSO_4 + 2KCN = Ni(CN)_2 + K_2SO_4; \quad Ni(CN)_2 + 2KCN = K_2Ni(CN)_4.$$
$$CoSO_4 + 2KCN = Co(CN)_2 + K_2SO_4; \quad Co(CN)_2 + 4KCN = K_4Fe(CN)_6.$$

Both $K_2Ni(CN)_4$ and $K_4Co(CN)_6$ are complex rather than double salts, for they do not contain nickelous and cobaltous ions; moreover, $K_4Co(CN)_6$ is plainly analogous to $K_4Fe(CN)_6$. From each of these solutions, however, the simple cyanide $Ni(CN)_2$ or $Co(CN)_2$ is reprecipitated by dilute acid. These are examples of complex salts, therefore, which are less stable than ferrocyanide. When a solution of potassium cobaltocyanide is boiled in presence of air it undergoes oxidation to cobalticyanide thus:

$$2K_4Co(CN)_6 + H_2O + O = 2K_3Co(CN)_6 + 2KOH,$$

and this latter salt is much more stable than cobaltocyanide, in this respect resembling ferro- or ferricyanide. The fact that nickel forms no such stable complex salt, nickelic salts being unknown, underlies the well-known separation of these two metals.

The student meets with other examples of complex acids and salts in the course of chemical analysis. Hydrofluosilicic acid, H_2SiF_6, is evidently composed of $2HF + SiF_4$, but it contains the complex ion $[SiF_6]''$. Potassium platinichloride, or chloroplatinate,

K_2PtCl_6, and the corresponding acid H_2PtCl_6, formed when platinum is dissolved in aqua regia, are of the same type, and so is the corresponding stannichloride, K_2SnCl_6. Potassium cobaltinitrite, $K_3Co(NO_2)_6$, formed as a yellow crystalline precipitate when potassium nitrite is added to a cobaltous solution acidified with acetic acid, is of the same type as $K_3Co(CN)_6$ and $K_3Fe(CN)_6$.

Ammonium phospho-molybdate is a complex salt of a different kind, in which 12 molecules of MoO_3 are combined with $(NH_4)_3PO_4$. It is formed in presence of nitric acid, and when dissolved by ammonia suffers hydrolysis into simple phosphate and molybdate. Potassium antimonyl tartrate, or tartar emetic, $[KSbOC_4H_4O_6]_2H_2O$, is a complex rather than a double salt, for it dissolves in water without hydrolysis; which antimonious salts will not do. It is therefore best regarded as the potassium salt of antimonyl-tartaric acid, $[K(SbOC_4H_4O_6)]_2H_2O$.

SUMMARY

Types of Chemical Compounds

HYDRIDES.—Metallic and non-metallic.

OXIDES AND HYDROXIDES.

Neutral oxides, including suboxides.
Basic oxides.
Acidic oxides, including mixed anhydrides.
Saline oxides.
Peroxides divided into poly- and superoxides.

HALIDES.—Metallic and non-metallic.

SULPHIDES.—Metallic, metalloidal, and non-metallic.

OXYSALTS.—Sulphates, carbonates, &c.

HYDRATED SALTS.

DOUBLE AND COMPLEX SALTS.

CHAPTER XIV

CHEMICAL CHANGE IN GENERAL

A classical illustration of chemical change, at once simple and valuable, is furnished by the work of Priestley and Lavoisier on mercuric oxide. Priestley heated mercuric oxide by concentrating the sun's rays upon it with a lens, so as to decompose it into mercury and oxygen. The reaction is represented thus:

$$2\,HgO \longrightarrow 2\,Hg + O_2.$$

This mercuric oxide could previously be obtained, as was shown by Geber, by gently heating mercury for a long time in the air, when atmospheric oxygen united with the metal, thus:

$$2\,Hg + O_2 \longrightarrow 2\,HgO.$$

Lavoisier combined these two operations by first heating mercury at a moderate temperature in a confined space, and noting the volume of air absorbed, and then collecting the mercuric oxide formed and heating it more strongly; this resulted in the evolution of a volume of oxygen equal to that of the air which was previously absorbed. So the possibility of reversing a chemical reaction was established, a fact now represented thus:

$$2\,Hg + O_2 \rightleftharpoons 2\,HgO.$$

This simple illustration has been chosen because it gives rise to various questionings, the consideration of which leads far into the subject of chemical change in general.

Thus it is a surprising thing that the compound of mercury and oxygen should be a red, crystalline powder, so different from its constituent elements, and the question at once occurs whether the whole of chemistry is full of surprises like that. The elementary student is rather led to suppose that it is. At least there are many such surprises which lend to chemical science a fantastic charm for the youthful mind. For example, the vapour of sulphur is led over

red-hot charcoal, and, instead of yellow crystals and black lumps, there appears a colourless liquid with a quite extraordinary smell; or ammonia and hydrogen chloride gases are brought together, and instead of a neutral gas resulting from the combination of an acid and an alkaline gas, there is dense white smoke which settles down as solid sal ammoniac.

"It is the unexpected that happens" might apparently be said of chemical change. Indeed, the difference between physical mixture and chemical combination often appears to be this—the properties of a mixture are what might be expected, they are the mean of those of the constituent parts of the mixture, whilst the properties of a chemical compound often could not be expected, for they are unrelated to those of the constituent elements.

Yet, if the impression gained from the facts above considered were true, and if the above epigram were a generalization of chemistry then there would be no chemical science; chemistry would be but a catalogue of curious material phenomena.

The scientific thinker is thus met with the fundamental question of the relation between the properties of compounds and those of their constituent elements; he is led, indeed, to the threshold of a field of inquiry as broad as chemistry itself.

This particular inquiry may, however, be carried a little further. The greatest differences in properties are seen between elements and their simplest compounds. When a compound is converted into another compound by the addition or substitution of other elements, the physical differences brought about are not so great. Consider, for example, the series of paraffin hydrocarbons C_nH_{2n+2} (see p. 164). An increment of CH_2 causes no surprising change in the properties of a hydrocarbon; on the contrary it causes an almost constant alteration of boiling-point and other physical properties. Or, consider the influence of the substitution of chlorine for hydrogen in the CH_3 group of acetic acid, $CH_3 \cdot COOH$. The chloracetic acids $CH_2Cl \cdot COOH$, $CHCl_2 \cdot COOH$, $CCl_3 \cdot COOH$, stand in order of increasing strength; thus the electronegative element chlorine has had a specific influence in increasing the strength of the acid.

The colour, also, of a complex chemical compound is definitely related to its constitution, and is modified by the substitution of one element or group for another within the molecule. The art of producing synthetic dyes depends among other things on a

knowledge of the influence of certain substituents on the colour of the compound formed. The same is true regarding the therapeutic properties of synthetic drugs.

But, more generally, if, according to the periodic law, the properties of the elements and their compounds are periodic functions of the atomic numbers, then this law should at least relate the properties of a particular compound to those of a similar compound of an analogous element. That it does this is shown by a systematic study of oxides, chlorides, and other simple compounds. Our present knowledge of the law, however, fails to account completely for the properties of a particular compound. It is known, for example, that the solid iodides of imperfect metals are brightly coloured, although the constituent ions are colourless; such iodides are: PbI_2, Hg_2I_2, HgI_2, SnI_4, SbI_3; but why PbI_2 is yellow, for instance, and SnI_4 scarlet, is not known, though probably it is referable to the electronic constitution of the iodine atom, as well as to the intimate mode of union of iodine with the metallic atom in the solid state, which prohibits ionization. The colours of ions such as green manganate and crimson permanganate may be connected with the different modes of distribution of electrons in the several external layers of the central atom.

These are examples of the questionings to which a consideration of the superficial properties of a simple chemical compound gives rise. The human mind desires an explanation of the unexpected. Why is mercuric oxide red? Why is permanganate solution crimson? These questions cannot at present be answered fully, though their answer is bound up with the problems of atomic constitution.

Reversible Reactions.

A second question suggested by the reaction between mercury and oxygen is that of the reversibility of a chemical change. Are all reactions reversible? If not, why not?

Speaking generally, the possibility of reversing a chemical reaction depends on the realization of suitable conditions. Some chemical changes brought about by heat are so profound that their reversal in the narrower sense is not possible. Sugar, for example, is destroyed if heated strongly; it is commonly said to be burnt, and the final products of the burning of sugar in air are carbon dioxide and water. Can such a change be reversed?

Growing plants can reconvert the carbon of carbon dioxide

and water into sugar, and the chemist can laboriously synthesize a kind of sugar; but that is not a true reversal of the chemical reaction of decomposition, because the synthetic changes do not follow the same route as the changes of decomposition.

Now, reverting to the reaction between mercury and oxygen, it would appear from Lavoisier's experiment that there is a certain minimum temperature at which visible combination between the elements takes place, and a somewhat higher temperature at which visible decomposition of the compound formed sets in. These temperatures cannot be stated because they are conditioned, but it may be judged that below or above a limited range of temperature oxygen and mercury do not combine or remain in combination respectively.

Such a statement, however, is not very satisfactory, because, whilst it recognizes the increased activity of mercury and oxygen molecules, due to rise of temperature, which first promotes combination between the two elements, and subsequently causes disruption of the compound formed, it takes no account of the physical state or concentration of the combining elements; or otherwise, since oxygen is a gas, that it may escape from the mercury altogether when evolved and so render a reversal of the reaction impossible.

It is worth while to attempt to gain a clear mental picture of this reversible reaction, since it illustrates fundamental principles which underlie chemical reactions in general.

Chemical Equilibrium.

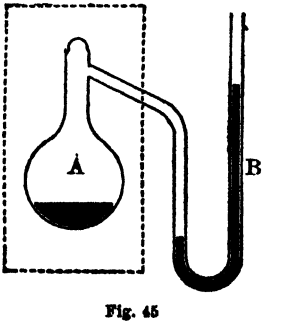


Fig. 45

Suppose the flask A in the figure contains mercury and mercuric oxide in contact with oxygen gas, the pressure of the latter being indicated by the manometer B, consisting of a U-tube containing mercury; and suppose that the flask is heated in a chamber, the outline of which is shown by the dotted line, to a temperature $t°$ C., within the limits between which a reaction between mercury and oxygen is known to take place. Then the manometer will show in which direction the reaction is proceeding. If combination is taking place, the mercury will rise in the limb nearer the flask, owing to diminution of gas

pressure; if decomposition, the mercury in the nearer limb will be depressed because of increase of pressure. But in either case equilibrium will eventually result, and the mercury in the manometer will become and remain stationary, registering a certain gas pressure; this is not because nothing is taking place, but because the two opposite reactions are proceeding at equal rates, and a state of dynamic equilibrium has been attained, which is suitably represented by the equation:

$$2\,Hg + O_2 \rightleftharpoons 2\,HgO.$$

If the temperature is altered the pressure will likewise alter. If, for instance, the temperature is raised, further decomposition will begin, but the accumulating oxygen will soon bring it to a standstill and a higher constant pressure will be registered corresponding to the higher temperature.

This reversible chemical reaction, depending upon temperature, is an example of *thermal dissociation*; and the pressure at which equilibrium is reached at a given temperature is called the *dissociation pressure* for that temperature.

The following dissociation pressures have been measured for the reaction under discussion.[1]

Temperature.	Millimetres Hg Pressure.
360° C.	90
380°	141
400°	231
420°	387
440°	642
460°	1017
480°	1581

If the temperatures are represented graphically by abscissæ, and the corresponding pressures by ordinates, the relation between them is given by a curve which takes the form shown in fig. 46.

The curve may be thus interpreted: at the lower temperatures there is little increase of pressure as the temperature rises, tendency to dissociation is small, and a small pressure suffices to prevent it, whilst a pressure greater than that necessary to prevent dissociation promotes absorption of the gas with formation of more of the oxide. At the higher temperatures, as shown by the steepness of the curve, there is a great increase of pressure with small rise of temperature, or, otherwise expressed, great pressure of oxygen

[1] Taylor and Hulett, *J. Physikal Chem.*, 1913, *17*, 565.

is necessary to prevent dissociation, and combination apart from such great pressure is impossible. Although this thermal dissociation is a chemical change it closely resembles the physical change involved in the evaporation of water, and the vapour-pressure curve of water takes a similar form.

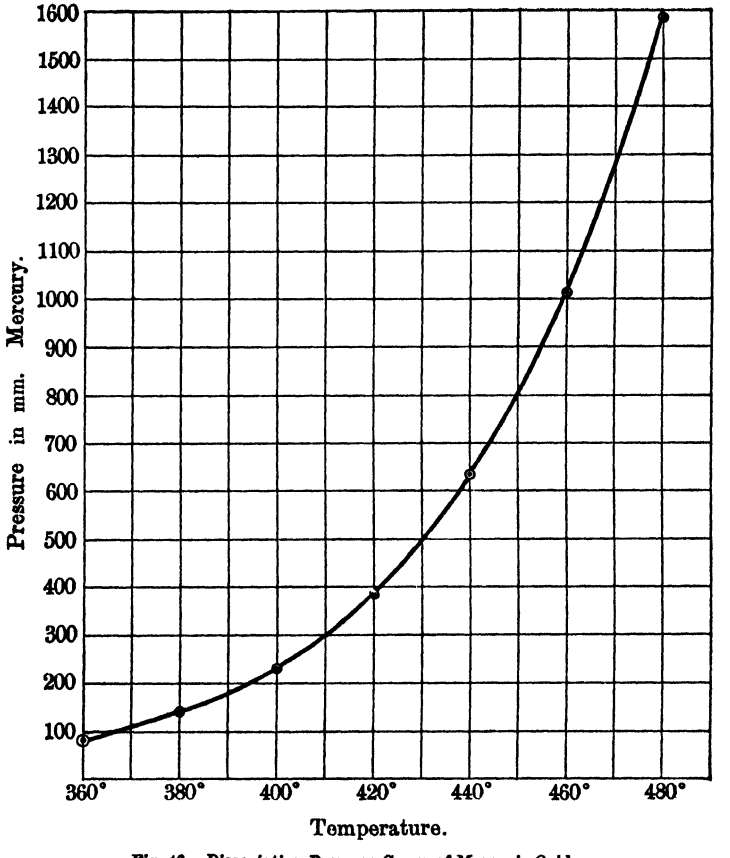


Fig. 46.—Dissociation Pressure Curve of Mercuric Oxide

If the student has followed the exposition of this simple chemical reaction thus far he will be prepared for the conclusion that the reaction depends on three determining factors. First, there is the specific power of combination between mercury and oxygen. Compared with other elements, mercury has little intrinsic attraction for oxygen; if, for example, copper were substituted for mercury, the result would be very different. The quality of mercury thus mani-

fested may be called its *chemical affinity*, a convenient but originally rather vague term.

Second, there is the *effect of temperature*. The power of mercury to combine with oxygen remains latent until by rise of temperature the molecules of metal and gas are made sufficiently active. Chemical change is always confined within certain temperature limits. At very low temperatures matter is inert and incapable of chemical change; at very high temperatures matter is too active, its atoms are too restless to enter into chemical union.

Third, there is the *effect of pressure*, that is of the concentration of oxygen molecules around the mercury. If the surface of the mercury in the flask is thought of as in a state of flux, some molecules of the oxide being continuously produced whilst others are simultaneously undergoing decomposition, it will be understood that the chances of combination are increased and of decomposition simultaneously diminished by the crowding of oxygen molecules just above the surface. Thus increase of pressure promotes combination, and diminution of pressure decomposition, altogether apart from the question of temperature. In other words, the extent and apparent direction of a chemical reaction depend on the *active masses* of the reacting substances.

These effects illustrate a general principle known as *Le Chatelier's Theorem*, which may be expressed thus: If a system in equilibrium is subjected to a constraint by which equilibrium is disturbed, a reaction tends to take place by which the effect of the constraint is destroyed. So in this case increase of oxygen pressure would be a restraint which would be counteracted by combination of oxygen with mercury until the pressure was reduced to its former value.

Thus, apart from temperature, chemical action is determined by *chemical affinity* and *active mass*. By active mass is meant concentration when a substance is a gas or in solution, and in the case of a solid the minimum amount necessary to secure equilibrium. Thus the active mass of a solid is constant under the same physical conditions; a very little solid is necessary in contact with a solution to secure saturation; and more is superfluous.

It must be understood that the proportions in which elements are in contact influence the extent of combination, but not the proportions in which this occurs.

Thermochemistry.

There is one other aspect of this simple chemical reaction between

mercury and oxygen which must be considered. The effect of temperature on the chemical reaction has been noticed; but heat is applied in quantity, and some of this heat is transformed into other kinds of energy during the progress of the reaction.

In the decomposition of the oxide, for example, oxygen leaves the solid and becomes a gas; not only is heat used up in the actual disruptive process, but also doubtless in the gasification of the oxygen, as well as in the vaporization of some of the mercury, though the latter heat is given up again if the mercury is condensed. Thus heat is absorbed in the change

$$2\,HgO \longrightarrow 2\,Hg + O_2;$$

and it has been estimated that when 2 gram-molecules (i.e. 433·2 grm.) of mercuric oxide are decomposed, producing 2 gram-atoms of liquid mercury (401·2 grm.) and 1 gram-molecule of oxygen gas (32 grm.) 44,000 calories are absorbed; and similarly, when these quantities of the separate elements unite to form mercuric oxide, the same quantity of heat is liberated.

These facts may be expressed thus:

$$2\,HgO = 2\,Hg + O_2 - 44{,}000 \text{ cals.}$$
$$\text{and } 2\,Hg + O_2 = 2\,HgO + 44{,}000 \text{ cals.}$$

So mercury and oxygen in the system [$2Hg + O_2$] contain between them an excess of energy over that in the system [2HgO] amounting in terms of heat energy to 44,000 calories. It must, however, be clearly understood that nothing is here said or known concerning the total energy in either of these systems. The rise or fall of the tide may be measured against a rock in a sea the depth of which is unplumbed. Similarly, the rise or fall of energy content in a material system may be measured although the total energy in the system cannot be estimated. The energy of a system which is transferable by chemical change is called the *free energy*, the energy which is not transferable is the *bound* or *latent energy*; these two make together the *total energy* in the system.

Now, every distribution of matter which we call a chemical change is accompanied by a corresponding distribution of energy. The branch of chemistry concerned with energy changes manifested by heat phenomena is called *thermo-chemistry*, the kind of equation which sets forth heat change accompanying changes in matter is called a *thermo-chemical equation*, and such an equation is based upon the

principle of the conservation of energy, just as an ordinary chemical equation, which is a mass equation, is based upon the principle of the conservation of mass.

It will be well to consider now some representative thermal equations chosen to illustrate the range of the subject. And first it may be remarked that thermal equations need not necessarily be thermo-chemical equations. They may express thermal phenomena accompanying physical rather than chemical change.

For example, the transformations between ice, water, and steam, may be represented thus:

$$H_2O_{(water)} = H_2O_{(ice)} + 1440 \text{ cal.}$$
$$H_2O_{(steam)} = H_2O_{(water)} + 9670 \text{ cal.}$$

These equations express, in perhaps unusual guise, the latent heats of water and steam.

Or the heat of transformation of one allotropic form of an element into another may be represented thermo-chemically thus:

$$S_{(monoclinic)} = S_{(rhombic)} + 64 \text{ cal.}$$
$$C_{(graphite)} = C_{(diamond)} + 500 \text{ cal.}$$

Thus when 32 grm. of monoclinic sulphur are converted into the same weight of rhombic sulphur, 64 calories are evolved; and similarly in the conversion of 12 grm. of graphite into diamond 500 calories would be evolved. These figures are not, however, determined directly, but are derived from the differences between the *heats of combustion* of different forms of the element. For example, the heats of combustion of graphite and diamond are:

Graphite, 94,810 cal.; diamond, 94,310 cal.;

so the difference, 500 calories, must represent the heat of transformation of graphite into diamond.

It may next be observed that in the case of a reversible change, whether physical or chemical, if the evolution of a certain quantity of heat accompanies the change in one direction, the absorption of the same quantity of heat takes place when the change is reversed.

This may be represented simply by transposing the terms of the thermal equation; thus in the case of ice and water

$$H_2O_{(water)} = H_2O_{(ice)} + 1440 \text{ cal.};$$
$$\text{but } H_2O_{(ice)} = H_2O_{(water)} - 1440 \text{ cal.}$$

Thus when 18 grm. of water are frozen, 1440 calories are removed

from the water, and to melt the ice a similar quantity of heat must again be supplied.

Changes in which heat is evolved are *exothermic* changes; those in which heat is absorbed are *endothermic* changes.

These terms are of value in considering chemical changes involving much heat energy. Thus, reverting to the original example, the formation of mercuric oxide from its elements is an exothermic change; the decomposition of the compound into its elements an endothermic change; the two changes, as regards energy, as well as matter, are equal and opposite. One, the *heat of formation*, is + 44,000 cal.; the other, the *heat of dissociation*, is − 44,000 cal.

Other kinds of thermo-chemical data of value are—heats of solution of substances in water and other solvents; heats of evaporation of solvents containing specific dissolved substances; heats of neutralization of acids and alkalis. It may be pointed out that when chemical operations are being conducted on a large scale, thermal effects, often negligible on the small scale, assume much importance. For example, how to divert or usefully to dispose of the heat evolved in a chemical action, or how most economically to conduct the evaporation of a given solution, having regard to its latent heat of evaporation, often become problems of pressing importance to the chemical engineer.

Here may be mentioned the *law of Hess*, which, briefly, states that the heat of formation of a compound is independent of its mode of formation. This law follows naturally from the principle of the conservation of energy, but it is capable of experimental proof.

Lastly, the connection between heat evolved and chemical affinity may be briefly considered.

Exothermic compounds are stable; endothermic compounds often unstable. Exothermic compounds may be compared with a boulder at the base of a mountain which has reached its position by rolling down the mountain's side, expending its potential energy the while, but having reached the lowest ground is likely to remain there. Endothermic compounds may be compared with a boulder raised and poised above the valley, and liable, after a slight disturbance, to roll down and expend energy in its fall.

High-explosives, and detonators such as fulminate of mercury, are good examples of endothermic substances, as well as ozone, acetylene, and carbon disulphide.

Ozone is formed by the absorption of energy from the electric sparks which generate it from oxygen; acetylene derives its inherent energy from the electric furnace in which calcium carbide is produced; carbon disulphide is similarly formed from its elements at high temperature.

These compounds are evidently highly artificial, and unlikely to be produced by nature in her quieter moods, though electric or volcanic action might produce them. Solar energy is, however, continuously being absorbed by growing plants, and the compounds produced by them, such as starch and sugar, may, in a wider sense, be regarded as endothermic. Similarly, wood, coal, and petroleum are in this sense endothermic, though it is unusual to extend the term to include these things.

In general, endothermic compounds are likely to be produced at high temperature, because the heat to be absorbed in their formation is thus available; whilst exothermic compounds are likely to be formed at lower temperature, because the heat evolved in their formation can more easily be dispersed.

The connection between the heat effect of a chemical change and the chemical affinities of the reacting substances may now be considered briefly.

It is generally supposed that if the reaction between two chemical elements is vigorous and accompanied by the evolution of much heat, the chemical affinity between these elements is great; and that if the reaction is sluggish and accompanied by small heat evolution, the affinity between the elements concerned is small. This is illustrated by the heats of formation of the halogen hydracids, which are:

HF	.....	38,600 calories.
HCl	.....	22,000 „
HBr	.....	8,400 „
HI	.....	− 6,000 „

Thus the heats of formation fall from HF to HI, and that of the latter is actually negative; HI is an endothermic compound. The affinities of the halogens for hydrogen undoubtedly fall from fluorine to iodine, but that of iodine cannot be regarded as actually negative, as the thermal value might suggest. So that whilst the heat effect of chemical union is some indication of the strength of attraction between the elements, it cannot be regarded as a quantitative measure of chemical affinity.

There are other considerations bearing on thermo-chemistry, and the connection between heat effect and chemical affinity, which the student may postpone to a more advanced course.

Rate and Limits of Chemical Change.

The rate of a chemical change is much influenced by the conditions under which it takes place. Thus the physical state of a reacting substance or substances determines whether or how a chemical change occurs. So it is often the case that substances which interact in solution will remain in contact with one another in the solid state without chemical change. The familiar example of a mixture of sodium bicarbonate and tartaric acid, which effervesces when water is poured upon it, may be quoted.

The modifying influence of temperature upon chemical change is noteworthy. Consider, for example, the formation of water from its elements or its dissociation into them.

If hydrogen and oxygen gases are mixed together in the proportions necessary to form water, no change is perceived at atmospheric temperature, but if the mixed gases are gradually heated, combination becomes perceptible at about 450° C., whilst at 700° C. there is a rapid and complete combination, accompanied by explosion. It is possible, however, to raise the mixed gases to such a temperature as not to promote but actually to prevent their combination. Thus above 2000° C. steam is decomposed into its elements, and hydrogen and oxygen will not combine. So there are temperature limits within which the combination of hydrogen and oxygen can take place, but outside which no combination between these gases occurs. And what is true of this particular change is true of all chemical changes. Chemical reactions, vigorous under ordinary conditions, become sluggish with reduction of temperature, and cease altogether at very low temperatures. The velocity of a reaction is frequently halved by a fall of 5° C., and if this rate of diminution proceeds regularly, the velocity will become infinitesimal, the reaction coming practically to a standstill before the temperature of liquid air is reached. On the other hand, chemical union between the elements is impossible in the hotter stars; only in the coldest stars, for example, do hydrocarbons exist.

The effect of heat in promoting change is too common to need specific illustration. The use of a Bunsen gas flame to further chemical action soon becomes instinctive to the student.

Catalysis.

Further study of the interaction of hydrogen and oxygen reveals the fact that the degree of combination between these gases is much influenced by the presence or absence of water vapour. Thus, when the pure gases have been dried perfectly by long exposure to phosphoric oxide, they do not combine at a red heat, and silver can be melted in a mixture of them at a temperature of 960° C.

Minute quantities of other foreign substances also affect the rate of combination, and this is notably the case with certain metals, especially if they are finely divided. Thus, when the mixed gases are passed through a heated capillary tube containing a thread of platinized asbestos, gradual combination takes place, whilst the thread becomes red-hot, and would eventually cause the gases kept in contact with it to explode. The platinum, however, remains quite unaltered at the end of the process.

These are examples of *catalytic action*, or *catalysis*, and the promoter of the chemical change is called a *catalyst*. Catalysis plays an important part in modern chemistry, and especially in chemical industry. A brief study of the subject may therefore be undertaken here.

The student will already be familiar with several cases of catalysis. He knows that manganese dioxide causes potassium chlorate to yield its oxygen at a lower temperature than that at which the pure salt is decomposed; also that "nitrous fumes" promote the formation of sulphuric acid from sulphur dioxide, atmospheric oxygen, and water by a cycle of reactions which may be represented thus:

$$\left.\begin{array}{l} \longrightarrow 2NO + O_2 = 2NO_2 \\ 2NO_2 + 2SO_2 + 2H_2O = 2H_2SO_4 + 2NO. \end{array}\right|$$

So nitric oxide carries oxygen from the air to sulphurous acid, being alternately oxidized and reduced. Platinized asbestos, however, causes sulphur dioxide and oxygen to combine thus: $2SO_2 + O_2 = 2SO_3$, without itself undergoing perceptible change.

Cuprous chloride, employed in the Deacon process in the oxidation of hydrogen chloride to chlorine and water, behaves similarly to nitrous fumes in the chamber sulphuric acid process, as an oxygen carrier, thus:

$$\left.\begin{array}{rl} \longrightarrow 2\,CuCl_2 &= Cu_2Cl_2 + Cl_2, \\ Cu_2Cl_2 + O &= Cu_2OCl_2, \\ Cu_2OCl_2 + 2\,HCl &= 2\,CuCl_2 + H_2O; \end{array}\right.$$

the net result being seen by adding these reactions thus.

$$2\,HCl + O = H_2O + Cl_2.$$

These well-known examples of catalysis illustrate the variety of the mechanism of the reactions which may occur. Thus in the case of the older sulphuric acid process, as well as in the Deacon process, there is no doubt that a series of reactions takes place, involving the catalysts, whilst finely divided platinum does not appear to be altered chemically when it acts as a catalyst. Manganese dioxide, however, probably undergoes a cycle of reactions when heated with potassium chlorate, being oxidized to a higher oxide which is immediately decomposed again. This view is supported by the fact that when crystallized manganese dioxide is employed to assist the evolution of oxygen from potassium chlorate, the dioxide recovered from the process is in a finely divided state.

The following are well-known examples of catalytic agents and catalytic action.

i. Influence of Water.

It has already been seen that a trace of water-vapour greatly influences the combination of hydrogen and oxygen to form water.

In the entire absence of water the following reactions will not take place:

$$\begin{array}{ll} 2\,CO + O_2 & = 2\,CO_2. \\ 2\,NO + O_2 & = 2\,NO_2. \\ H_2 + Cl_2 & = 2\,HCl. \\ CaO + SO_3 & = CaSO_4. \\ CaO + 2\,NH_4Cl & = CaCl_2 + 2\,NH_3 + H_2O. \end{array}$$

Also, mercuric chloride and ammonium chloride do not dissociate when quite dry, and sodium and potassium can be distilled in perfectly dry oxygen without combustion. There is thus a variety of reactions which depend for their progress on the influence of water as a catalyst.

ii. Influence of Hydrogen and other Ions.

An ester, such as ethyl acetate, may be formed or hydrolyzed according to the following reversible reaction:

$$C_2H_5\cdot OH + H\cdot C_2H_3O_2 \rightleftharpoons C_2H_5\cdot C_2H_3O_2 + HOH.$$

The progress of the reaction in either direction, however, is exceedingly slow in the absence of a catalyst; but hydrogen chloride, by reason of hydrogen ions, under suitable conditions accelerates both the formation and the hydrolysis of the ester.

The hydrolysis of cane-sugar thus:

$$C_{12}H_{22}O_{11} + H_2O = \underset{\text{(dextrose)}}{C_6H_{12}O_6} + \underset{\text{(levulose)}}{C_6H_{12}O_6},$$

is also promoted by hydrogen ions, introduced as dilute acid, and the extent of hydrolysis, in this case as well as in that of an ester, is directly proportional to the concentration of the hydrogen ions; consequently, these reactions can be used to compare the strengths of acids. As regards the added acid, analysis proves that its amount remains unchanged.

Another interesting example of the catalytic influence of hydrogen and other simple ions is the coagulation of a colloid. If hydrogen sulphide gas is passed into a dilute aqueous solution of tartar-emetic—potassium antimonyl tartrate—there is no precipitate, but a deep orange, faintly-opalescent liquid results. This liquid contains antimonious sulphide in the colloidal state. If then a few drops of dilute hydrochloric acid or ammonium chloride are added, an orange precipitate is formed, the colloidal state of quasi-solution having been disturbed by the ions of the acid or salt added.

iii. Influence of Finely Divided Metals.

The catalytic influence of platinized asbestos has already been noticed. The contact process for the manufacture of sulphuric acid depends on the synthesis of sulphur trioxide in presence of platinized asbestos.

The realization of this reaction on a commercial scale was found to depend on keeping the platinum free from dust, and especially from arsenious oxide, derived from the iron pyrites used as the source of sulphur. The arsenic has been said to "poison" the catalyst; it may be regarded as a *negative catalyst*, counteracting the influence of the finely divided metal. Scrupulous cleanliness is always necessary for catalytic action at solid surfaces. Platinum black, precipitated from platinic solutions by reducing agents, is also very active in promoting gaseous synthesis. Finely divided osmium and uranium have been found valuable in promoting the synthetic formation of ammonia; platinum, as well as iron containing copper or bismuth, is employed in bringing about the

oxidation of ammonia to nitric acid; finely divided nickel at 250° C. causes hydrogen to be added to unsaturated hydrocarbons and their derivatives, a reaction employed for the hardening of fats.

Another example of the catalytic action of a finely divided metal is that of silver on hydrogen peroxide.

If aqueous hydrogen peroxide is added to silver oxide the oxide is reduced to metal with evolution of oxygen, and then if more hydrogen peroxide is poured upon the metal the evolution of gas continues. Alternate oxidation and reduction of the silver may here be postulated thus[1]:

$$2\,Ag + H_2O_2 = Ag_2O + H_2O.$$
$$Ag_2O + H_2O_2 = 2\,Ag + H_2O + O_2.$$

Colloidal metals are particularly active owing to their state of minute subdivision. Bredig has obtained platinum, silver, &c., in colloidal suspension in water by striking an electric arc between poles of the metal beneath the surface of the water. In this way the metal becomes diffused through the water in a colloidal state, and is very active catalytically.

iv. Influence of Oxides and Salts.

Various oxides and salts may act as catalysts; and the use of oxides of nitrogen in sulphuric acid manufacture, of manganese dioxide in the preparation of oxygen, as well as of cuprous chloride in the Deacon chloride process, have already been noticed.

The use of cobalt oxide in the preparation of oxygen from bleaching powder is a well-known lecture experiment; and the rôle of copper oxide in the combustion and ultimate analysis of organic compounds may be regarded as catalytic because of alternate reduction and oxidation by the compound and atmospheric oxygen respectively. Ferric oxide is employed in the manufacture of hydrogen by the reaction:

$$CO + H_2O \rightarrow CO_2 + H_2;$$

in the removal of sulphur compounds from coal gas, the "spent oxide" being revivified by the combustion of its sulphur in sulphuric acid manufacture; and also in the promotion of the reaction:

$$2\,H_2S + O_2 \rightarrow 2\,H_2O + 2\,S,$$

[1] Hydrogen peroxide, moreover, is very sensitive to catalytic action; precipitated manganese dioxide will decompose it, as well as finely divided platinum, and even powdered glass. Indeed, sharp points and edges promote its decomposition. If a concentrated solution of hydrogen peroxide is poured into a glass vessel the surface of which has been scratched, the evolution of gas bubbles along the line of the scratch may be observed.

by which sulphur has been recovered from alkali-makers' waste by the Claus process.

Vanadic oxide is used as a catalyst to promote oxidation in some processes of organic chemistry; cerium oxide in the Welsbach gas mantle is believed to act as a catalyst in promoting combustion, whilst magnesia and other oxides are employed as catalysts to promote the surface combustion of furnace gases.

As regards salts, manganous sulphate is known to act as a catalyst in promoting the oxidation of oxalic acid by permanganate in volumetric analysis, and ferrous sulphate likewise hastens the liberation of iodine from potassium iodide by hydrogen peroxide, whilst silver nitrate is well known to promote the oxidation of small quantities of manganese in solution to permanganate by persulphate.

v. Influence of Enzymes.

Enzymes are unorganized ferments produced by living organisms, and they are very powerful catalysts.

For example, *diastase*, produced in germinating seeds, converts starch into sugar, thus:

$$2\,C_6H_{10}O_5 + H_2O = C_{12}H_{22}O_{11},$$

and so renders stored up food available for the growing plant; *zymase*, in yeast, also converts sugars of the type $C_6H_{12}O_6$ into alcohol and carbon dioxide, thus:

$$C_6H_{12}O_6 = 2\,C_2H_6O + 2\,CO_2.$$

Similarly, there are unorganized ferments in the human alimentary canal, which aid the digestion of food. All these actions are catalytic.

Theory of Catalysis.

The foregoing examples of catalysis are sufficient to show the wide influence of this phenomenon; indeed, according to Ostwald, "there is probably no kind of chemical reaction which cannot be influenced catalytically, and there is no substance, element or compound, which cannot act as a catalyser".

When various examples of catalysis are reviewed with the purpose of forming a general theory of their action, it becomes evident that some catalysts, such as the oxides of nitrogen, are definitely chemical in their action, forming part of a cycle of reactions, whilst others, such as finely divided platinum, are of

such a nature that it is difficult to postulate for them chemical participation in the reactions which they promote.

Nevertheless platinum, like manganese dioxide, is found to undergo change when it is employed as a catalyst. Thus photomicrographic study of platinum gauze before and after use shows that the metal becomes coated with minute craters which are tinged with grey or black platinum. Some chemists, indeed, believe that an oxide of platinum is formed and reduced during the catalytic activity of the metal.

An alternative view of the action of platinum is that the finely divided metal presents a very large surface on which the reacting gases are condensed and brought into an intimate contact which promotes their chemical combination. Even in this case, however, the action must probably be regarded as chemical, for surface action is now known to be brought about on the external molecular layer of a solid by forces which are chemical rather than physical in nature.

According to Lowry, the modern view of the action of catalysts may be summarized thus: "A catalyst is a reagent which is reproduced as one of the products of the reaction."

A catalyst is generally present in relatively small amount, and its amount may be minute. Thus it serves over and over again, and may remain active for an indefinite length of time. The velocity of the reaction, however, is often proportional to the amount of catalyst present.

Further, a catalyst is believed by some chemists not to initiate, but only to hasten, or sometimes to retard, a chemical change. It is true that in the absence of the catalyst the change often appears not to occur, but this may be due, as in the synthesis of water, to the reaction being exceedingly slow.

A catalyst has been compared with the oil which facilitates the running of a machine; and just as the friction between the parts of a machine may be too great to allow movement to begin until oil is added, so there may be chemical reactions which, under certain conditions, cannot begin until the necessary catalyst is present. This appears to be the case regarding the influence of water on certain reactions.

Moreover, a catalyst does not effect the final state of equilibrium of the reacting substances; it only alters the time in which this equilibrium is reached. This must be the case, since it contributes

no energy to the reaction, but only provides a stimulus; otherwise a kind of perpetual motion would have been discovered. Lastly, where intermediate reactions are known to occur, they must, when taken together, necessarily proceed faster than the original reaction in order to hasten it; there must be "a saving of time in the longer way round".

SUMMARY

THERMAL DISSOCIATION.—Thermal dissociation is a reversible chemical change caused by heat.

EXO- AND ENDO-THERMIC COMPOUNDS.—An exothermic compound is a compound produced from its elements with the evolution of heat.

An endothermic compound is a compound produced from its elements with absorption of heat.

The *heat of formation* of a compound is the heat evolved in its formation from its elements.

CATALYST.—A catalyst is a substance which alters the velocity of a reaction, and is reproduced as one of its products.

CHAPTER XV

CHEMICAL CHANGES CLASSIFIED

It is customary to classify chemical reactions in the following manner:

I. Combination of elements or compounds, e.g.:

$$2\,Hg + O_2 = 2\,HgO.$$
$$SO_3 + H_2O = H_2SO_4.$$

II. Decomposition of compounds into simpler compounds or elements, e.g.:

$$CaCO_3 = CaO + CO_2.$$
$$Ag_2O = 2\,Ag + O_2.$$

III. Re-arrangement of the atoms within a molecule, e.g. the formation of urea from ammonium cyanate, thus:

$$NH_4CNO = CO(NH_2)_2.$$

IV. Condensation of two or more molecules into one molecule (polymerization), e.g.:

$$3\,C_2H_2 = C_6H_6.$$

V. Single displacement, e.g.:

$$CuSO_4 + Zn = ZnSO_4 + Cu.$$

VI. Double decomposition, e.g.:

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2\,HCl.$$

Such a classification is, however, rather formal, and not very illuminating, because it overlooks cause and effect in chemical change; and reactions which are similar in form may differ essentially in nature.

Compare, for example, the above reaction of double decomposition with the following:

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl.$$

The two reactions are similar in form, but quite different in cause and effect.

More chemistry may be learned by studying reactions according to the conditions under which they take place than according to a few set types accepted *a priori*.

Thus, the study of changes effected by the action of heat on solid substances, either singly or mixed, or by bringing together solids and liquids such as non-metals and metals and their compounds on the one hand, and water, acids, and alkalis on the other, or of changes occurring in aqueous solution, will be found to cover a very wide field of chemistry, and yield much insight into the nature of chemical change. Or, again, the phenomena of oxidation and reduction well repay classification and thoughtful study.

Chemical Action of Heat on Compounds.

It has already been seen that the change in a substance produced by heat may be reversible or irreversible, and that in the former case the change is one of dissociation, in the latter one of decomposition. A change which is really dissociation may, however, be described as decomposition if one or more products are gaseous and escape. Thus, limestone may be said to be decomposed by heat because the carbon dioxide is allowed to escape; similarly the action of heat on lead nitrate will generally be regarded as one of decomposition unless the reversibility of the reaction is recognized.

Thermal Dissociation.

The general principles of thermal dissociation have been studied in the previous chapter by reference to the case of mercuric oxide; the subject will now be further illustrated by a few chosen examples.

Nitrogen Peroxide. — Nitrogen peroxide exists at ordinary atmospheric temperature as a brown gas which becomes deeper in colour when heated, but paler when cooled, yielding at 10° C. a yellow liquid which at −10° C. forms colourless crystals. The alteration in colour of the gas is due to the following reversible change:

$$N_2O_4 \rightleftharpoons 2NO_2$$

NO_2 being deep brown, while N_2O_4 is pale. Thus one molecule of N_2O_4 is dissociated by heat into two similar molecules of NO_2. The

progress of dissociation is indicated by an increase of pressure of the gas at constant volume, or by a reciprocal decrease in density at constant pressure after a correction has been made in either case for change of temperature. Thus the density of nitrogen peroxide gas at 4·2° C. is 2·588 (air = 1) to which a molecular weight of 74·8 corresponds, whilst its density at 97·5° C. is 1·783, with a corresponding molecular weight of 51·5. These calculated molecular weights show that 62·6 and 11·9 per cent respectively of the mixed gases is N_2O_4.

This is the simplest example of dissociation that can be given, for the whole system is gaseous, and there is only one kind of dissociation product. The formation of N_2O_4 from two molecules of NO_2 may be regarded as a case of polymerization.

Phosphorus Pentachloride.—The vapour of phosphorus pentachloride readily dissociates thus:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2,$$

the dissociation at various temperatures being indicated by the following densities, reduced to normal temperature and pressure:

Temperature C	182°	200°	250°	300°	336°
Density	73·3	70·0	57·6	52·4	52·5

The normal density of PCl_5 is 104·2; thus dissociation, considerable at 182° C. is complete at 300° C.

Now, suppose that instead of vaporizing into empty space, PCl_5 is made to vaporize into a space containing much vapour of PCl_3. Every Cl_2 molecule derived from PCl_5 by incipient dissociation would then encounter many molecules of PCl_3, and its chance of remaining uncombined with one of these surrounding molecules would be very small. Thus PCl_3 molecules would hinder the dissociation of PCl_5. This has been found to be the case. Würtz vaporized PCl_5 into PCl_3 vapour and found the PCl_5 vapour density at 160° to 175° C. to be nearly 104·2, that of the undissociated compound.

This is a notable case of the influence of mass on chemical change. Vaporization of PCl_5 into chlorine gas would produce a similar result.

Ammonium Chloride.

This salt, when vaporized, dissociates into NH_3 and HCl, thus:

$$NH_4Cl \rightleftharpoons NH_3 + HCl.$$

The dissociation may be proved by the separation of ammonia from hydrogen chloride by the more rapid diffusion of the lighter ammonia through a porous pipe stem.

Mercurous Chloride.—The vapour density of mercurous chloride ordinarily corresponds to the molecular weight of HgCl, but it may be shown that the vapour is a mixture of Hg and $HgCl_2$, since the mercury will diffuse through a porous tube and condense in globules outside. Consequently the formula for mercurous chloride is Hg_2Cl_2, and the vapour dissociates thus:

$$Hg_2Cl_2 \rightleftharpoons Hg + HgCl_2.$$

It has been shown, however, by Baker that when water is very carefully excluded the vaporized salt does not dissociate, but shows a density corresponding to the formula Hg_2Cl_2.

Calcium Carbonate.

This compound dissociates thus:

$$CaCO_3 \rightleftharpoons CaO + CO_2,$$

and the dissociation pressures of this salt at various temperatures are these:

$t°$ C.		Pressures.
547°	.....	27 mm. Hg.
610°	.....	46 „
740°	.....	255 „
810°	.....	678 „
865°	.....	1333 „

Dissociation ceases at any given temperature when the pressure reaches the corresponding value; consequently the accumulation of the gaseous product of dissociation hinders dissociation. This is a principle of mass action which is true in general. Its application in the case under consideration may be seen in this way. If precipitated chalk is to be converted into quicklime by ignition in a crucible, whilst it is desirable to have as high a temperature as possible, the lid must not be allowed to cover the crucible too tightly or carbon dioxide will accumulate within it and hinder dissociation. This example of dissociation differs from the foregoing, because one of the dissociation products is permanently solid.

Barium Peroxide.

Barium peroxide furnishes an important example of dissociation. When heated to a dull red heat it yields oxygen, thus:

$$2\,BaO_2 \rightleftharpoons BaO + O_2,$$

and the resulting BaO will reabsorb oxygen at a lower temperature than that at which the peroxide dissociates. If, however, the material is kept at a constant temperature of 700° C., the direction of the reaction may be reversed by altering the pressure. In contact with air at 2 atmospheres pressure BaO at 700° C. absorbs oxygen forming BaO_2; but when the air is pumped away the reaction is reversed, and oxygen is evolved from the BaO_2. This is the principle of Brin's process for obtaining oxygen from the air, and as the direction of the reaction depends upon the concentration of the reacting substances, it is a good example of the action of mass.

Crystallo-hydrates.—The numerous salts and other substances containing water of crystallization afford material for illustrating the phenomena of dissociation. Water of crystallization is often but loosely retained by a salt, and it may sometimes be lost even at atmospheric temperature.

The student will now appreciate the fact that the condition of a salt with reference to water of crystallization depends not only on temperature, but also on the concentration of water vapour in the vicinity of the salt. There is a certain range of temperature and external pressure of water vapour within which a given salt or its hydrate can exist permanently. Outside this range the compound will give rise to a product containing a different proportion of combined water. Lowering of temperature and increase of external water-vapour pressure will promote the formation of a higher hydrate; raising of temperature and diminution of external vapour pressure will cause the salt to lose water, so as to form a lower hydrate or become anhydrous.

Thus some hydrated salts are permanent in air because of favourable temperature and water-vapour pressure, while others tend to lose water or absorb it from the air.

Crystals of blue vitriol, $CuSO_4 \cdot 5H_2O$, for example, neither lose nor gain water under ordinary atmospheric conditions, but crystals of washing-soda lose water according to the scheme:

$$Na_2CO_3 \cdot 10\,H_2O \rightleftharpoons Na_2CO_3 \cdot H_2O + 9\,H_2O,$$

because the vapour pressure of the system consisting of the deca- and mono-hydrate is greater than the pressure of water vapour in the air at ordinary temperature. So the salt *effloresces*, becoming opaque on the surface, owing to the formation of the powdery monohydrate, *efflorescence* being the phenomenon in which hydrated crystals lose water vapour to the air.

Hydrated salts having small vapour pressures are frequently very soluble in water, and their saturated solutions may have vapour pressures less than the vapour pressure of water vapour in the air. Atmospheric water vapour will be absorbed by a salt of this kind until a liquid solution is produced of such a strength as to have a water-vapour pressure equal to that in the superincumbent atmosphere. Then the salt is said to *deliquesce*. Crystallized calcium chloride, $CaCl_2 \cdot 6H_2O$, is a good example of a deliquescent salt.

Thermal Decomposition.

It has been seen in the previous chapter that whilst some reactions caused by heat are reversible, being cases of dissociation, others, such as the decomposition of complex organic substances, are undoubtedly irreversible. The question now arises as to the extent and boundaries of reversible and irreversible thermal change, and whether many changes which at present appear irreversible are really so. The investigation of this question leads to some interesting results, but not to a definite conclusion in every case.

The thermal decomposition of oxides, hydroxides, and oxysalts furnishes a sufficiently wide field for investigation.

Thermal Decomposition of Oxides.

The student has already learned that the thermal decomposition of mercuric oxide is reversible; the action is one of dissociation, thus:

$$2HgO \rightleftharpoons 2Hg + O_2.$$

Silver and auric oxides are similarly decomposed by heat:

$$2Ag_2O = 4Ag + O_2,$$
$$2Au_2O_3 = 4Au + 3O_2;$$

but these reactions are not reversible; gold and silver are not susceptible of atmospheric oxidation; they are too electro-negative, too inert chemically, for that. Silver, however, is oxidized by ozone.

Cupric oxide is an interesting case; when heated to a white heat it loses half its oxygen, the following reaction being reversible:

$$4\,CuO \rightleftharpoons 2\,Cu_2O + O_2.$$

No oxides of metals more electro-positive than mercury lose all their oxygen when heated,

The loss of some of their oxygen by higher oxides under the influence of heat furnishes an instructive series of phenomena. Consider, for example, the oxides N_2O_5, P_2O_5, As_2O_5, Sb_2O_5, Bi_2O_5, which are decomposed by heat, thus:

$$\begin{array}{rcl} 2\,N_2O_5 & \longrightarrow & 4\,NO_2 + O_2. \\ \left\{\begin{array}{l} P_2O_5 \\ 2\,P_2O_5 \end{array}\right. & & \text{stable.} \\ & \longleftarrow & P_4O_6 + O_2. \\ 2\,As_2O_5 & \longrightarrow & As_4O_6 + 2\,O_2. \\ 2\,Sb_2O_5 & \longrightarrow & 2\,Sb_2O_4 + O_2. \\ Bi_2O_5 & \longrightarrow & Bi_2O_3 + O_2. \end{array}$$

None of these reactions appears to be reversible. The behaviour of N_2O_5 is unique, like that of the element nitrogen itself. P_2O_5 is easily produced by the atmospheric oxidation of the element or the lower oxide; but arsenic is less oxidizable than phosphorus, and the higher oxide must be formed by the chemical oxidation of the lower oxide, which alone is produced when the element burns. The oxide Bi_2O_5 is a peroxide, formed only in the wet way; it has feebly acidic properties, but easily loses oxygen. Thus the oxides P_2O_5, As_2O_5, Sb_2O_5, Bi_2O_5, with the possible exception of Sb_2O_5, stand in the order of decreasing stability.

The dioxides of the fourth group—CO_2, SiO_2, GeO_2, SnO_2, PbO_2, are similarly related as regards stability; PbO_2 alone is decomposed by heat. Or consider the superoxides—Na_2O_2, BaO_2, SrO_2, CaO_2, MgO_2, &c. Sodium peroxide does not lose oxygen when heated short of very high temperatures; BaO_2, and the oxides which follow it, are decomposed with increasing readiness as electro-positiveness diminishes. Only the more electro-positive metals form superoxides, i.e. derivatives of hydrogen peroxide, at all.

The reversible reaction,

$$6\,PbO + O_2 \rightleftharpoons 2\,Pb_3O_4,$$

is instructive, and it is noteworthy that PbO_2 is not formed by the atmospheric oxidation of PbO; Pb_3O_4 is a compound of 2 PbO and PbO_2, that is, it is a salt, and the two oxides being mutually

satisfied, the PbO in Pb_3O_4 is not free to combine with more oxygen.

If, however, another base is present with which PbO_2 can combine, PbO may be completely oxidized to PbO_2 by atmospheric oxygen. Thus the following reaction is reversible:

$$2\,PbO + O_2 + 2\,Na_2CO_3 \rightleftharpoons 2\,Na_2PbO_3 + 2\,CO_2.$$

This is also a good example of mass action, since preponderance of oxygen or carbon dioxide determines the direction of the reaction.

The case presented by the following reaction is similar:

$$4\,CrO_3 \rightarrow 2\,Cr_2O_3 + 3\,O_2.$$

The reverse reaction takes place only in the presence of alkali, when atmospheric oxygen may be absorbed at high temperature to form chromate, thus:

$$2\,Cr_2O_3 + 3\,O_2 + 4\,Na_2CO_3 \rightarrow 4\,Na_2CrO_4 + 4\,CO_2.$$

Amongst non-metallic oxides the case of sulphur trioxide is important. It is well known that the reaction

$$2\,SO_2 + O_2 \rightarrow 2\,SO_3$$

takes place to any considerable extent only in presence of a catalyst, whilst the reverse reaction,

$$2\,SO_3 \rightarrow 2\,SO_2 + O_2,$$

occurs when the vapour of the trioxide is passed through a tube heated to 1000° C. Nevertheless, when the dioxide is heated to 1200° C., or is submitted to the action of electric sparks, it undergoes the following reversible change:

$$3\,SO_2 \rightleftharpoons 2\,SO_3 + S.$$

Thermal Decomposition of Hydroxides.

Hydroxides may be basic or acidic, and their stability depends on the basic or acidic intensity of the corresponding oxides.

Consider, for example, the *basic hydroxides*:

$NaOH$, $Ba(OH)_2$, $Ca(OH)_2$, $Mg(OH)_2$, $Al(OH)_3$, $Cu(OH)_2$, $AgOH$, NH_4OH.

NaOH and $Ba(OH)_2$, producible from the corresponding oxides by violent reactions with water, cannot be dehydrated by heat alone; $Ca(OH)_2$, produced also from the oxide by slaking, is easily dehydrated by heating above 150° C.; $Mg(OH)_2$ is formed by very

slow combination of MgO with water, but more readily by precipitation, and is stable at 100° C.; $Al(OH)_3$, formed by precipitation in the cold, loses water, forming $Al_2O(OH)_4$ or AlOOH, when heated at 100° C. or dried over sulphuric acid; $Cu(OH)_2$ is formed as a blue precipitate in the cold, which turns dark brown when warmed with water, forming $Cu_4O_3(OH)_2$; AgOH exists only in very dilute aqueous solution, for the precipitate formed by adding alkali to a silver salt is Ag_2O, which dissolves very slightly in water, producing a faintly alkaline solution containing AgOH.

Ammonium hydroxide. — NH_4OH, is unique. A hydrate, $NH_3 \cdot H_2O$ exists in crystals, melting at −78° C., but it cannot be asserted that this is ammonium hydroxide. A solution of ammonia in water contains much NH_3 as well as ionized NH_4OH, formed thus:

$$NH_3 + H^{\cdot} + OH \rightleftharpoons NH_4^{\cdot} + OH',$$

there being no need to assume the formation and subsequent ionization of NH_4OH molecules. The presence of both NH_3 and hydroxide ions is proved by the use of ammonia solution to form an ammine, such as $CuSO_4 \cdot 4NH_3 \cdot H_2O$, as well as to precipitate a base such as $Fe(OH)_3$. When an aqueous solution of ammonia is boiled, the above reactions are reversed, and all the ammonia escapes as gas.

The following *acidic hydroxides* (oxy-acids) may be considered:

$$SO_2(OH)_2,\ PO(OH)_3,\ SO(OH)_2,\ CO(OH)_2.$$

Sulphuric acid, $SO_2(OH)_2$, is fairly stable towards heat and may be distilled, for SO_3 is a powerfully acidic oxide, and as such holds its combined water tenaciously. At 440° C., however, dissociation according to the scheme

$$H_2SO_4 \rightarrow SO_3 + H_2O$$

is complete.

Phosphoric acid, $PO(OH)_3$, loses water when heated, thus:

$$\underset{\text{Ortho-}}{2\,PO(OH)_3} \rightarrow \underset{\text{Pyro-}}{P_2O_3(OH)_4} \rightarrow \underset{\text{Meta-phosphoric acid;}}{P_2O_4(OH)_2}$$

but it is noteworthy that the meta-acid is the final dehydration product, from which water cannot be removed. The meta- and the pyro-acid both revert to the ortho-acid in contact with water, and there is evidence that the meta-acid passes through the pyro form on the way back to the ortho-acid.

Sulphurous acid, $SO(OH)_2$ or $SO_2 : H(OH)$, shares with carbonic

and nitrous acids, which also have gaseous anhydrides, the property of existing only in aqueous solution; several crystallo-hydrates of this acid exist however. The following reaction is reversible:

$$SO_2 + H_2O \rightleftharpoons SO(OH)_2,$$

though, like ammonia, some sulphur dioxide exists in aqueous solution without being hydroxylated. It may be that sulphurous acid in aqueous solution passes into the unsymmetrical form, thus:

$$SO(OH)_2 \rightleftharpoons SO_2{<}^{H}_{OH};$$

though modern theory seems to make this view superfluous.

Carbonic acid, $CO(OH)_2$, is formed when carbon dioxide dissolves in water, thus:

$$CO_2 + H_2O \rightleftharpoons CO(OH)_2;$$

the carbonic acid so formed being ionized to a considerable extent, thus:

$$H_2CO_3 \rightleftharpoons H^{\cdot} + HCO_3'.$$

When a solution of carbonic acid is boiled, both these reactions are reversed, and all the carbon dioxide escapes from the liquid.

Thermal Decomposition of Oxy-Salts.

The usual mode of thermal decomposition of oxy-salts is into basic and acidic oxides or their decomposition products; e.g.:

$$CaCO_3 \rightarrow CaO + CO_2.$$
$$2\,Cu(NO_3)_2 \rightarrow 2\,CuO + 4\,NO_2 + O_2.$$

Whether such a reaction occurs depends upon the relative basic and acidic strengths of the respective oxides, and upon the volatility of the acidic oxide.

Thus, when both basic and acidic oxides are powerful, as, for example, in the case of sodium sulphate, thermal decomposition does not take place, and even when the acidic oxide is feeble an alkali oxide is sufficiently powerful to retain it, as in the case of sodium carbonate, which is not decomposed at 1000° C. The sulphates of the feebler basic oxides lose sulphur trioxide when heated; for example, copper sulphate forms a basic salt at a dull red heat, and ferrous sulphate loses all its SO_3, leaving a residue of ferric oxide.

The behaviour of nitrates and chlorates when heated is instruc-

tive. Those of the alkali metals do not lose their nuclear nitrogen or chlorine; thus potassium nitrate forms nitrite, and chlorate chloride. Nitrates and chlorates of feebler metals, however, leave a residue of oxide; e.g. the lead salts decompose thus:

$$2\,Pb(NO_3)_2 \rightarrow 2\,PbO + 4\,NO_2 + O_2.$$
$$2\,Pb(ClO_3)_2 \rightarrow 2\,PbO + 2\,Cl_2 + 5\,O_2.$$

An interesting question arises here as to reversibility. The reaction:

$$2\,KClO_3 \rightarrow 2\,KCl + 3\,O_2$$

appears not to be reversible. Why is this? Hypochlorite easily undergoes self-oxidation and reduction thus:

$$3\,KOCl \rightarrow 2\,KCl + KClO_3;$$

yet chloride seems incapable of oxidation to chlorate. The explanation is to be found in the fact that the chloride ion is more stable than the ion of any oxyacid of chlorine, and that the ions of the oxyacids stand in the following order of increasing stability: hypochlorite, chlorate, perchlorate. These facts are illustrated by the formulæ attributed to these ions according to the electronic theory of valency (q.v.).

Besides relative basic and acidic strengths of oxides in an oxy-salt, the volatility of the acidic oxide determines the stability of the salt. Silica, for example, is not volatile like carbon dioxide, and so calcium silicate, unlike calcium carbonate, is not decomposed by heat. For the same reason silica at high temperature displaces carbon dioxide from chalk, thus:

$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2,$$

a reaction common in metallurgy.

Phosphates, moreover, are not decomposed by heat; for example, bone ash, $Ca_3(PO_4)_2$, is unchanged at a white heat; for, although phosphoric oxide itself is volatile, it cannot be separated from a combined basic oxide any more than it can be separated from water combined with it in metaphosphoric acid, $H_2P_2O_6$.

In general, the mode of decomposition of an oxy-compound when heated reveals the relative stabilities at high temperatures of the possible decomposition products.

Thus the isomorphous salts $KClO_4$ and $KMnO_4$ behave very differently when heated, because in spite of the superficial resemblance between them and the similarity of their constitution, the elements concerned, namely chlorine and manganese, are widely

different in chemical nature. The following reactions represent the manner of decomposition of these salts:

$$KClO_4 = KCl + 2O_2.$$
$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

The chief ammonium oxy-salts are decomposed by heat thus:

$$\left.\begin{matrix}(NH_4)_2SO_4 \\ NH_4HSO_4\end{matrix}\right\} = NH_4HSO_4 + NH_3. \quad = H_2O + SO_3 + NH_3.$$
$$NH_4NO_3 = 2H_2O + N_2O.$$
$$NH_4NO_2 = H_2O + N_2.$$
$$(NH_4)_2HPO_4 = HPO_3 + H_2O + 2NH_3.$$
$$\left.\begin{matrix}(NH_4)_2CO_3 \\ NH_4HCO_3\end{matrix}\right\} = NH_4HCO_3 + NH_3. \quad = H_2O + CO_2 + NH_3.$$

Chemical Interaction of Water with Elements and Compounds.

The interaction of elements and pure water is limited almost completely to the behaviour of a few electro-positive metals.

The metals of the alkalis and alkaline earths decompose water at atmospheric temperature, displacing hydrogen with formation of the hydroxide of the metal. The vigour of the reaction with water increases with the electro-positiveness of the metal from lithium to cæsium, and from calcium to barium. The reaction is attributable firstly to the ionization of water, although this is so small, and secondly, to the solution pressure of the metal which is superior to that of hydrogen.

The student has met with this latter idea before, under the subject of electrolysis (q.v.). Thus metallic sodium, striving to assume the ionic state when brought into contact with water, displaces the hydrogen ions of the latter, causing them to lose their electric charges and escape as gas.

Besides the metals of the alkalis and alkaline earths, amalgamated aluminium reacts with water at atmospheric temperature evolving hydrogen, and powdered aluminium as well as magnesium decomposes steam. The rusting of iron is believed to be due, first of all, to the action on water of the metal containing impurities which set up slight electro-potential differences throughout the mass; and it is well known that steam is decomposed by red-hot iron, whilst hydrogen can reduce heated iron oxide to metal. Copper, however, has no action on water or steam, for it is less electro-positive than hydrogen and does not displace this element from water or dilute acids.

So the following reactions are instructive:

i. $Mg + H_2O \rightarrow MgO + H_2$.
ii. $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$.
iii. $Cu + H_2O \leftarrow CuO + H_2$.

Reactions (i) and (iii) proceed in single and opposite directions; reaction (ii) is reversible because of the intermediate character of iron.

Of the non-metals the halogens alone react with water. Fluorine decomposes water in the dark, and chlorine in the daylight, both with evolution of oxygen. It is probable that the following is the first reaction between chlorine and water:

$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl;$$

for chalk and chlorine water yield calcium chloride and hypochlorous acid, the latter not reacting with chalk.

Hydrolysis.

The chemical decomposition of compounds by water is hydrolysis. This, again, is to be attributed to the hydrogen and hydroxide ions existing in water.

Ideal salts, consisting of powerfully basic and acidic ions, are not hydrolyzed by water; their aqueous solutions are ionized but remain neutral.

Normal salts are not necessarily neutral. Sodium chloride and trisodium phosphate, Na_3PO_4, are both normal salts, but whilst NaCl is also a neutral salt in the sense of giving a neutral solution with water, this is not the case with Na_3PO_4, the solution of which is alkaline on account of hydrolysis with production of free alkali, i.e. OH′ ions in solution, thus:

$$Na_3PO_4 + HOH \rightleftharpoons Na_2HPO_4 + NaOH.$$
$$NaOH \rightleftharpoons Na^{\cdot} + OH'.$$

Even the hydrogen salt Na_2HPO_4 yields an alkaline solution owing to hydrolysis, thus:

$$Na_2HPO_4 + HOH \rightleftharpoons NaH_2PO_4 + NaOH;$$

for although the salt NaH_2PO_4 is itself acid, it does not produce such a concentration of $H^{\cdot}$ ions as the equivalent of NaOH produces of OH′ ions.

The reactions of the three sodium phosphates are:

Na_3PO_4, strongly alkaline;
Na_2HPO_4, alkaline;
NaH_2PO_4, acid;

the point of neutrality thus lying between Na_2HPO_4 and NaH_2PO_4.

An alternative way of explaining the alkalinity of Na_3PO_4, applicable to the effect of mixing equivalents of NaOH and H_3PO_4, is that NaOH being stronger as a base than H_3PO_4 is as an acid, the alkali provides a larger proportion of OH' ions than the acid of $H^{\cdot}$ ions, and so an excess of OH' ions remains over after all the $H^{\cdot}$ ions from the acid have been neutralized.

These considerations have an important bearing on the volumetric estimation of acids and alkalis. Only acids and alkalis which produce salts not appreciably hydrolyzed in aqueous solution can be titrated in the ordinary way; obviously phosphoric acid cannot be directly titrated with an equivalent standard alkali.

As regards salt hydrolysis in general, whilst the salts of strong bases with weak acids are alkaline in reaction, those of weak bases with strong acids are acid. An example of the latter is furnished by ferric chloride which is hydrolyzed in aqueous solution with formation of a basic salt and free acid, somewhat as follows:

$$FeCl_3 + HOH \rightleftharpoons FeOHCl_2 + H^{\cdot} + Cl'.$$

The formation of the basic salt is shown by the darkening of the solution. The same thing is especially noticeable when ferric alum is dissolved in water. The pale-violet crystals yield a brown solution which becomes colourless when a little sulphuric acid is added to convert the basic salt into the normal salt. If a solution of ferric alum is poured into much boiling water a precipitate of ferric hydroxide separates owing to complete hydrolysis. Ferric acetate is similarly hydrolyzed by boiling water with the precipitation of a basic acetate.

That salt hydrolysis is a frequent phenomenon is shown by the following facts:

Soluble salts of the following acidic radicles have alkaline reactions in solution:

Borate, carbonate, chromate, cyanide, hypochlorite, nitrite, phosphate, silicate, sulphide, sulphite.

Soluble salts of the following metallic radicles possess an acid reaction:

Mercurous, mercuric, cupric, aluminium, chromic, ferrous, ferric, stannous, stannic, antimonious, bismuthous.

Salts of weak bases with weak acids are generally insoluble in water, and on that account less amenable to hydrolysis.

A fat may be hydrolyzed by superheated steam with the production of glycerol and fatty acid, thus:

$$C_3H_5X_3 + 3\,HOH = C_3H_5(OH)_3 + 3HX.$$

$(C_3H_5)^{\cdots}$ = glyceryl.

X = $C_{15}H_{31}COO\cdot$(palmitate), or $C_{17}H_{35}COO\cdot$(stearate).

The catalytic effect of $H^{\cdot}$ ions in promoting the hydrolysis of an ester or of cane sugar has already been noticed (p. 267).

Sometimes the basic salt produced by hydrolysis is insoluble and is precipitated. Thus, bismuthous and antimonious chlorides are not only hydrolyzed by water but yield precipitates of the basic chlorides:

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2\,HCl.$$
$$SbCl_3 + H_2O \rightleftharpoons SbOCl + 2\,HCl.$$

On this account hydrolysis is accentuated, for the reversal of the reaction is greatly hindered by the separation of the hydrolytic product in the solid state.

Incidentally it may be observed that whilst BiOCl is stable towards water, SbOCl, on account of the feebler basic properties of antimonious oxide, loses all its chlorine when boiled with water.

So far the hydrolysis of salts has been considered; but the process is not confined to salts.

Consider the series of chlorides:

$$NaCl,\ MgCl_2,\ AlCl_3,\ SiCl_4,\ PCl_5.$$

The series begins with a powerfully metallic chloride, and ends with a non-metallic chloride. The chloride of a powerful metal, being a true salt, is not hydrolyzed by water, whilst the chloride of a non-metal is at once and completely hydrolyzed. Between these two extremes there is a gradation of hydrolysis.

$MgCl_2$ gives a neutral solution with water, but when this solution is evaporated nearly to dryness hydrogen chloride gas escapes with the steam, and the resulting pasty mass, containing the basic salt Mg(OH)Cl, reacts alkaline. By ignition the oxide MgO is eventually formed.

$AlCl_3$ dissolves in water, reacting vigorously with it if anhydrous,

and produces an acid solution by incipient hydrolysis; when this solution is evaporated to dryness and ignited, the oxide Al_2O_3 remains.

$SiCl_4$ is instantly decomposed by water with separation of gelatinous silica H_2SiO_3:

$$SiCl_4 + 3H_2O \rightarrow H_2SiO_3 + 4HCl.$$

To a certain extent the reaction is reversible, for H_2SiO_3 is more soluble in hydrochloric acid than in water.

PCl_5 is similarly decomposed, liquid $POCl_3$ being first formed, and then H_3PO_4 thus:

$$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl.$$
$$POCl_3 + 3H_2O \rightarrow PO(OH)_3 + 3HCl.$$

This is an extreme case of hydrolysis, for the reaction is not reversible.

Chemical Interaction of Acids and Metals.

It has been seen that there is an interaction between water and some metals, and that this is believed to be due to the slight ionization of water without which this substance would be inert. Now acids owe their essential nature to the presence of hydrogen ions, the strength of an acid in aqueous solution being measured by the concentration of these ions. Consequently, acids containing a much higher concentration of hydrogen ions behave much more vigorously toward metals than water.

Consider the following metals arranged in order of decreasing electro-positiveness:

Cs, Rb, K, Na, Ba, Sr, Ca, Mg, Al, Mn, Zn, Cd, Tl, Fe, Co, Ni, Sn, Pb, H,
Sb, Bi, As, Cu, Hg, Ag, Pd, Pt, Au.

Metals preceding hydrogen can displace it as a gas from dilute hydrochloric or sulphuric acid; those that follow H do not generate this gas in contact with dilute acid. Or, using an idea the student is already familiar with: metals preceding hydrogen have a greater, metals following it a less, solution pressure than this element. It has already been seen that metals as far as calcium, and under some circumstances aluminium, displace hydrogen from cold water, and that if steam is used and the metal is heated reactivity extends as far as iron.

The extent to which a metal displaces hydrogen from a dilute acid depends upon:

i. The nature and purity of the metal.
ii. The nature and state of dilution of the acid.

i. *The nature and purity of the metal.*—If dilute hydrochloric acid is poured upon fragments of magnesium, zinc, iron, and tin, in separate test-tubes, the reaction will be very vigorous with magnesium, less so with zinc, still less so with iron, and very slight with tin; indeed, it is necessary to heat tin with moderately concentrated hydrochloric acid to dissolve the metal with evolution of hydrogen. All this is quite in accord with the order of electro-potential of the metals.

The purity of a metal has a marked effect on its interaction with acid. If a stick of pure zinc is placed in dilute hydrochloric acid, very slow action takes place; but if a length of fine copper wire is coiled round the zinc, action becomes vigorous and the hydrogen is seen to be coming off from the surface of the copper, although this metal is found unchanged when the zinc has been dissolved. These different effects are due to the fact that in the first case the displaced hydrogen forms a protective film on the surface of the zinc, thus polarizing it, whilst in the second case electrical action is set up, hydrogen flows with the electric current from the zinc to the copper, and is evolved from the surface of the latter metal, whilst the zinc is left continuously exposed to the action of the acid. A similar effect is produced by adding a few drops of copper sulphate or platinic chloride to the acid in which the zinc is immersed. Copper or platinum is deposited on the zinc, and causes the production of electric circuits with the consequent promotion of chemical action. If the zinc is impure, and contains a small proportion of a less electro-positive metal, solution is hastened by this impurity without the help of an added metal. Such action may be regarded as catalytic.

ii. *The nature and state of dilution of the acid.*—The strength of an acid, i.e. its degree of ionization, determines the rate at which a metal displaces hydrogen from it. Thus, if parallel experiments are done with zinc in (*a*) dilute hydrochloric acid, (*b*) dilute acetic acid of equivalent strength, the rate of evolution of hydrogen from the acetic acid will be exceedingly slow, whilst that from the hydrochloric acid may be vigorous. The explanation is simple. Hydrochloric acid is a strong acid, almost completely ionized in dilute

solution, whilst acetic acid is a weak acid which is but slightly ionized, and therefore approaches water in its behaviour towards metals.

The state of dilution of a particular acid also determines the rate of evolution of hydrogen. If an acid is much diluted the concentration of hydrogen ions is correspondingly reduced, together with the vigour of the reaction. If, however, too little water is present there may not be room enough in the solvent for extensive ionization, and consequently displacement of hydrogen by a metal will not be effected.

This is not the case with concentrated hydrochloric acid, which contains only about 32 per cent of hydrogen chloride; but it is the case with concentrated sulphuric acid, which consists of about 98 per cent of the absolute acid and 2 per cent of water. Thus zinc does not displace hydrogen from concentrated sulphuric acid; a reaction commences when this acid is heated with the metal; the gas evolved, however, is not hydrogen but sulphur dioxide, thus:

$$Zn + 2\,H_2SO_4 = ZnSO_4 + 2\,H_2O + SO_2.$$

Since a similar reaction takes place with copper, it is not necessary to assume that free hydrogen has anything to do with it.

Interaction of Nitric Acid and Metals.

Since nitric acid contains much oxygen, and is easily reducible the question arises whether hydrogen can escape from the acid when displaced from its molecules by a metal, or whether it will necessarily reduce the acid instead. If the acid is reduced, since there are various reduction products of nitric acid, the possible reactions of the acid with metals are various.

Hydrogen is among the gases evolved from dilute nitric acid by magnesium, the most electro-positive of the metals which do not react with cold water; but with this exception hydrogen is not obtained.

The possible reduction products of nitric acid may be shown by separating water from the acid, and breaking up the resulting anhydride thus:

$$\begin{aligned} 2\,HNO_3 &= H_2O + N_2O_5, \\ &= H_2O + 2\,NO_2 + O, \\ &= H_2O + N_2O_3 + 2\,O, \\ &= H_2O + 2\,NO + 3\,O, \\ &= H_2O + N_2O + 4\,O, \\ &= H_2O + N_2 + 5\,O. \end{aligned}$$

Besides the five reduction products, NO_2, N_2O_3, NO, N_2O, N_2, hydroxylamine, NH_2OH, and ammonia, NH_3, are sometimes produced.

The question now arises whether displaced hydrogen or the metal itself reduces the acid. Hydrogen cannot reduce nitric acid in the case of a metal which does not displace this element from an acid. It can scarcely be assumed that nascent hydrogen is responsible for the reduction of nitric acid by copper, since this metal does not displace hydrogen from any acid. As a matter of fact, metals may be divided into two categories as regards their behaviour towards nitric acid. The metals zinc, cadmium, iron, tin, and others more electro-positive than hydrogen may reduce nitric acid as far as ammonia; the metals bismuth, copper, mercury, silver, which are less electro-positive than hydrogen, do not reduce the acid beyond the stage of nitric oxide.

Presumably the reduction to nitric oxide does not necessitate the intervention of hydrogen; reduction beyond this stage may. Displaced hydrogen must evidently play a part in the formation of NH_2OH and NH_3; it may be indirectly the cause of the evolution of nitrogen, which may be derived from ammonium nitrite thus:

$$NH_4NO_2 = N_2 + 2H_2O,$$

whilst N_2O may come from hyponitrous acid thus:

$$HON : NOH = N_2O + H_2O.$$

With regard to the reduction of nitric acid by metals of the copper series there is evidence that the pure, diluted acid, free from nitrous acid, does not react with these metals, but that nitrous acid is necessary to start the reaction, which proceeds thus:

i. $Cu + 4HNO_2 = Cu(NO_2)_2 + 2H_2O + 2NO;$
ii. $Cu(NO_2)_2 + 2HNO_3 = Cu(NO_3)_2 + 2HNO_2;$
iii. $HNO_3 + 2NO + H_2O = 3HNO_2;$

and adding

iv. $Cu + 3HNO_3 = Cu(NO_3)_2 + HNO_2 + H_2O.$

So, by the aid of a little HNO_2 more is produced, which, instead of accumulating, decomposes thus:

v. $3HNO_2 = HNO_3 + H_2O + 2NO.$

Thus nitric oxide gas is evolved, and the nitrate of the metal is formed in solution.

This theory of the activity of nitrous acid does not invalidate the usual equation:

$$3\,Cu + 8\,HNO_3 = 3\,Cu(NO_3)_2 + 4\,H_2O + 2\,NO,$$

which may be obtained by multiplying equation (iv) by three, and adding the product to equation (v).

The concentration of the nitric acid employed affects the nature of the reduction products. This may be seen by pouring very dilute nitric acid on zinc in a test-tube, and then gradually increasing the strength of the acid. At first no gas is evolved, then a colourless gas, and afterwards a brown gas.

With the most dilute acid ammonia is produced, and combines with the acid, forming ammonium nitrate; then, with increasing strength of acid, nitrogen and nitrous oxide appear, and afterwards nitric oxide, and possibly still higher oxides of nitrogen with the strongest acid. In general, the more dilute the acid the more perfectly it is reduced.

The following equations represent the formation of nitrous acid and ammonia respectively when zinc and nitric acid interact.

$$4\,Zn + 10\,HNO_3 = 4\,Zn(NO_3)_2 + 5\,H_2O + N_2O.$$
$$4\,Zn + 10\,HNO_3 = 4\,Zn(NO_3)_2 + 3\,H_2O + NH_4NO_3.$$

That the quantities on the left side of the equation are the same in both cases is interesting. To argue that the same products should therefore result would be fallacious, for chemical equations do not represent the concentrations in which reacting substances are brought together.

Effect of Solubility and Volatility on Chemical Change.

There are two laws associated with the name of Berthollet which state (i) that if two substances by reacting in solution can yield a product less soluble than themselves, that product will be formed; and (ii) that if two substances when heated together can yield a product more volatile than themselves, that product will result. The facts thus expressed find ready explanation according to the principles of mass action.

The direction of the reaction,

$$AX + BY \rightleftharpoons AY + BX,$$

will depend on the effective concentration of each component; if one component, from any cause, is placed partly or wholly outside

the sphere of action, its power of directing the course of the reaction will be so far diminished. Consider, for example, the following two reactions placed at the beginning of this chapter:

$$BaCl_2 + H_2SO_4 \longrightarrow BaSO_4 + 2\,HCl.$$
$$2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl.$$

Superficially these reactions appear to be alike; actually they differ very much. The first is supposed to take place in dilute solution, $BaSO_4$ being precipitated and HCl remaining in solution; the second takes place when solid NaCl and concentrated H_2SO_4 are heated together, solid Na_2SO_4 resulting, while HCl escapes.

If the conditions are reversed, the results are not so effective. Thus if solid $BaCl_2$ is heated with concentrated sulphuric acid the reaction will be only partial, because the $BaCl_2$ will be protected from the acid by a crust of $BaSO_4$; and if NaCl and H_2SO_4 are mixed in dilute aqueous solution no HCl gas escapes.

The first reaction ordinarily proceeds to finality because of the insolubility of $BaSO_4$. When $BaCl_2$ and H_2SO_4 interact in aqueous solution, $BaSO_4$ and HCl are first formed in solution, and if both remained in this state they would be effective in establishing an equilibrium with the original substance, and no change would be apparent.

But $BaSO_4$ is at once precipitated because it is so very slightly soluble in water, and only the very minute quantity of this salt remaining in solution can have any effect in reversing the change. This effect is quite negligible, and, practically speaking, the reaction proceeds to completion from left to right.

The second reaction proceeds to finality because of the volatility of hydrogen chloride. When NaCl is heated with concentrated H_2SO_4, torrents of HCl gas are evolved, and the reversal of the reaction by means of this gaseous product which has escaped is out of the question.

The principles here illustrated are very far-reaching, and the student should make sure he grasps them.

Consider another example: The preparation of nitre by interaction of sodium nitrate and potassium chloride in aqueous solution, thus:

$$NaNO_3 + KCl \rightleftharpoons NaCl + KNO_3.$$

All the four possible salts are soluble in water, but sodium chloride is the least soluble of the four. When, therefore, sodium nitrate

and potassium chloride are mixed in equivalent proportions in solution and the latter is evaporated, sodium chloride is the first salt to crystallize; and thus potassium nitrate remains in solution, and may be crystallized after the sodium chloride has been removed.

A salt such as sodium chloride may be eliminated more effectually if it is formed in contact with a non-aqueous solvent in which it is not soluble. An interesting example of this is furnished by the preparation of free hydroxylamine, NH_2OH, from the hydrochloride by causing the following reaction to take place in methyl alcoholic solution:

$$NH_2OH \cdot HCl + NaOCH_3 = NaCl + HOCH_3 + NH_2OH.$$

Sodium methoxide, $NaOCH_3$, reacts effectively with hydrogen chloride because of the insolubility of sodium chloride in methyl alcohol, CH_3OH, and the methyl alcohol produced at the same time becomes part of the solvent, so that after the precipitated sodium chloride has been removed nothing remains in solution but free hydroxylamine.

The reaction,

$$Na_2CO_3 + SiO_2 \rightleftharpoons Na_2SiO_3 + CO_2,$$

which is of wide, terrestrial significance, serves further to illustrate the principle of volatility. If silica is heated with sodium carbonate, the reaction proceeds from left to right, because carbon dioxide is volatile and silica is not; but if carbon dioxide acts on sodium silicate in aqueous solution, the reaction is reversed, because carbonic acid is soluble in water, whilst hydrated silica is not so soluble, and largely separates from solution. Thus, in the early ages of the earth's history much silica was probably combined with bases in the earth's crust, and much free carbon dioxide existed in the atmosphere: but "weathering" of siliceous rocks has now been going on for ages in presence of water and at moderate temperature, with the fixation of carbon dioxide and consequent separation of silica.

The phenomena of precipitation, so important in analysis, may now be seen in a clearer light. Some precipitates are amorphous, some crystalline. Suddenly-formed precipitates are frequently amorphous, because they have not had time to crystallize, and occasionally they become crystalline when kept in contact with the liquid from which they have been separated.

Thus magnesium ammonium phosphate, $MgNH_4PO_4 \cdot 6H_2O$, when it is precipitated from concentrated solutions, appears amorphous, though when it separates gradually from dilute solutions it is distinctly crystalline.

Similarly barium sulphate, precipitated from cold, dilute solutions, is so finely divided as to run through the pores of ordinary filter-paper, but when the precipitate is heated with water it slowly becomes granular, that is, micro-crystalline, and can then be easily filtered. The same condition is more quickly assumed if the precipitation is carried out by mixing boiling solutions.

Calcium carbonate is another example of an amorphous precipitate which may become crystalline; for when heated in the liquid from which it has been precipitated it gradually assumes the crystalline form of aragonite.

Sulphide precipitates are, however, colloidal,[1] and do not crystallize. They are exceedingly insoluble in water, though some of them may assume the state of colloidal suspension. A curious case is presented by the sulphides of nickel and cobalt. These precipitates do not dissolve readily in dilute hydrochloric acid, though this acid prevents their formation. The explanation of this paradox is that on precipitation these sulphides polymerize, i.e. simple molecules combine to form more complex and therefore less soluble molecules. Thus dilute acid prevents the formation of the simple and more soluble molecules of the sulphides, but is unable to dissolve readily the more complex molecules formed by precipitation from alkaline solution.

The student should now understand that crystallization and precipitation are linked phenomena. Indeed, crystallization from solution is slow precipitation; the slower the precipitation the larger and more perfect are the crystals; the more rapid the precipitation the smaller and less perfect are the crystals, until precipitation becomes too rapid, and the separated solid is amorphous.

He will also understand that chemical affinity has little if anything to do with precipitation. For example, the reaction,

$$NaCl + AgNO_3 = AgCl + NaNO_3,$$

takes place in aqueous solution, not because silver has a greater affinity for chlorine than sodium, for that is not the case, or because sodium has a greater affinity for nitrate than for chloride, but

[1] *Vide* Chapter XII, on the colloidal state.

because silver chloride happens to be practically insoluble in water, and a reaction which might be reversible fails to be so because the effective mass of the silver chloride is so small. Thus silver nitrate is a reagent for all chlorides, or, more properly, silver ions are a reagent for chloride ions from whatever source they are derived.

Oxidation and Reduction.

Berzelius called oxygen the pole of chemistry; and it is true that no other element occupies so significant a position among the rest. It has already been seen that the kinds of oxides an element forms go far to reveal the chemical nature of the element.

Again, Lavoisier invented the name *oxygen*, thinking that this element was a constituent of all acids; and although this idea was false the name was not badly chosen after all, for the addition of oxygen to a substance generally enhances its acidic character.

Consider, for example, the oxides of manganese:

$$MnO,\ Mn_3O_4,\ Mn_2O_3,\ MnO_2,\ MnO_3,\ Mn_2O_7.$$

The first oxide, MnO, is wholly basic, but with successive additions of oxygen the oxides lose their basic power, becoming more and more acidic, until Mn_2O_7, a strongly acidic anhydride, is reached.

Oxidation *is the addition of oxygen to an element or compound*; **reduction** *is its removal.*

The removal of hydrogen is also regarded as oxidation, and sometimes also the addition of chlorine or an equivalent electronegative atom or radicle.

Thus, alcohol is oxidized to aldehyde by the removal of hydrogen in effect:

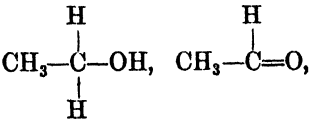
$$C_2H_6O + O = C_2H_4O + H_2O;$$

and the conversion of a ferrous into a ferric compound is oxidation, however effected; e.g.

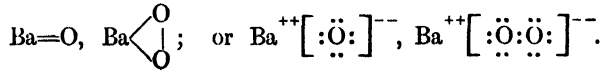
$$\begin{aligned} & 2\,FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O, \\ \text{or}\ & 2\,FeCl_2 + Cl_2 = 2\,FeCl_3. \end{aligned}$$

Oxidation generally involves an increase in the valency of the nuclear element of the compound oxidized; for example iron is bivalent in ferrous compounds and tervalent in ferric. This is not

always the case, however, for carbon is quadrivalent in both alcohol and aldehyde:



and barium is bivalent in both BaO and BaO_2:



Similarly, the addition of hydrogen to a molecule may be regarded as reduction, as for example in the formation of leuco-compounds from organic dyes through addition of hydrogen by means of sulphurous acid, thus:

$$H_2SO_3 + OH_2 = H_2SO_4 + 2H.$$

Oxidation and reduction are reciprocal processes; the oxidation of one substance often involves the reduction of another; as for instance the oxidation of ferrous sulphate by nitric acid:

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO.$$

This reciprocal relationship necessarily exists when the reducing and oxidizing substances are both compounds; indeed the process is essentially the transference of oxygen from one compound to another.

Common Oxidizing and Reducing Agents.

The following are the principal oxidizing and reducing agents met with in inorganic chemistry.

Oxidizing Agents	Reducing Agents
Free oxygen and ozone.	Hydrogen, gaseous and "nascent".
Hydrogen peroxide and other peroxides.	Unstable hydrides, e.g. H_2S, HI.
Reducible basic oxides, e.g. Ag_2O.	Oxidizable elements, e.g. carbon, the alkali metals, and magnesium.
The halogens, oxyacids and their salts, e.g. nitric and chloric acids and their salts.	Lower oxides, e.g. CO.
Higher oxides and oxyacids of metals, e.g. chromic and permanganic acids and their salts.	Lower oxyacids and their salts, e.g. sulphites, nitrites.
	Lower salts, e.g. ferrous, stannous.
	Cyanides, formates.

Conditions of Action.

Oxidation and reduction may take place either in presence or absence of water. These two conditions are well illustrated by the reactions of qualitative analysis carried out in the dry way and in solution respectively.

A familiar example of *oxidation in the dry way* is the formation of a chromate by oxidizing fusion, thus:

$$Cr_2O_3 + 2\,Na_2CO_3 + 3\,NaNO_3 = 2\,Na_2CrO_4 + 3\,NaNO_2 + 2\,CO_2,$$
or $$Cr_2O_3 + 3\,Na_2O_2 = 2\,Na_2CrO_4 + Na_2O;$$

and of *reduction in the dry way* the liberation of a metal from its oxide by heating it with charcoal in a reducing flame, e.g.:

$$SnO_2 + 2\,C = Sn + 2\,CO.$$

The dry reactions of qualitative analysis, which are frequently neglected, are at any rate of value because they illustrate in miniature important manufacturing processes.

The oxidation of chromic oxide, for example, in presence of alkali, is employed to obtain chromium compounds from the natural source of chromium, chrome ironstone or ferrous chromite: $FeO \cdot Cr_2O_3$. It is interesting to observe, moreover, that although Cr_2O_3 is not oxidized when heated alone in the air, and that on the contrary CrO_3 loses oxygen under these conditions, nevertheless, in presence of a base with which CrO_3 can combine chromate is formed, thus:

$$4\,FeO \cdot Cr_2O_3 + 7\,O_2 + 8\,CaCO_3 = 8\,CaCrO_4 + 2\,Fe_2O_3 + 8\,CO_2.$$

From this it may be inferred that the following is a reversible reaction:

$$2\,Cr_2O_3 + 3\,O_2 \rightleftharpoons 4\,CrO_3,$$

the presence of a base with which it can combine promoting the formation of the acidic oxide CrO_3, whilst the absence of a base, being the absence of the condition of stability of this oxide, permits its decomposition by heat.

Further, it is easy to understand why CrO_3 oxidizes hydrochloric acid according to the reaction

$$2\,CrO_3 + 12\,HCl = 2\,CrCl_3 + 6\,H_2O + 3\,Cl_2,$$

for the acid is oxidizable, and at the same time promotes the formation of the salt of the lower and basic oxide Cr_2O_3.

Similar considerations apply to the oxides of manganese. The

oxide MnO_2 loses oxygen when heated alone, but manganates corresponding to it are formed when any other manganese oxide is heated in air with alkali; e.g.:

$$2\,MnO_2 + O_2 + 2\,Na_2CO_3 = 2\,Na_2MnO_4 + 2\,CO_2.$$

Thus a deep-green mass of sodium manganate is produced when a trace of a manganese compound is heated strongly with fusion mixture. Without alkali, however, no manganate appears; so when manganese is tested for by means of a borax bead, the bead is not green, but amethyst in the oxidizing and colourless in the reducing flame, these colours being due to manganic and manganous borates, derived from Mn_2O_3 and MnO respectively.

The processes of metallurgy, i.e. the winning of metals from their ores, afford numerous examples of reduction in the dry way; and these are often imitated on a small scale by blowpipe and other laboratory reactions.

The following reactions are typical of reduction in the dry way:

$$\begin{aligned}
K_2CO_3 + 2\,C &= 2\,K + 3\,CO.\\
Fe_2O_3 + 3\,C &= 2\,Fe + 3\,CO.\\
4\,KOH + 3\,Fe &= 4\,K + Fe_3O_4 + 2\,H_2.\\
Sb_2S_3 + 3\,Fe &= 2\,Sb + 3\,FeS.\\
Na_2SiF_6 + 4\,Na &= Si + 6\,NaF.\\
CoO + H_2 &= Co + H_2O.\\
2\,AgCl + 2\,Hg &= 2\,Ag + Hg_2Cl_2.\\
Cr_2O_3 + 2\,Al &= 2\,Cr + Al_2O_3.\\
2\,PbS + 3\,O_2 &= 2\,PbO + 2\,SO_2.\\
2\,PbO + PbS &= 3\,Pb + SO_2.\\
PbSO_4 + PbS &= 2\,Pb + 2\,SO_2.
\end{aligned}$$

The last three reactions are remarkable. They concern the metallurgy of lead by what is paradoxically called the "air-reduction process". A similar reaction occurs in the metallurgy of copper, between cuprous oxide and sulphide, thus:

$$2\,Cu_2O + Cu_2S = 6\,Cu + SO_2.$$

Oxidation and reduction in solution are frequent laboratory operations.

The reactions of nitric acid have already been studied.

Sodium peroxide, or hydrogen peroxide in presence of alkali, is frequently employed, e.g. to oxidize precipitated chromic hydroxide to chromate:

$$2\,Cr(OH)_3 + 3\,Na_2O_2 = 2\,Na_2CrO_4 + 2\,NaOH + 2\,H_2O.$$

Similarly sulphide is oxidized to sulphate:

$$Na_2S + 4\,Na_2O_2 + 4\,H_2O = Na_2SO_4 + 8\,NaOH.$$

The oxidation of sodium sulphide, or rather hydrogen sulphide, by nitric acid, produces, however, not sulphuric acid in the first instance, but free sulphur, thus:

$$H_2S + 2\,HNO_3 = S + 2\,H_2O + 2\,NO_2,$$

although by the action of hot, concentrated nitric acid sulphur is gradually converted into sulphuric acid. This difference between the manner of oxidation of a sulphide in acid and alkaline solution is a further illustration of the influence of conditions on the course of a reaction.

Chloric acid, derived from a mixture of potassium chlorate and hydrochloric acid, is sometimes employed in qualitative analysis to oxidize finely-divided sulphur to sulphuric acid. When a chlorate is heated with hydrochloric acid a mixture of chlorine and chlorine dioxide, Davy's "euchlorine", is evolved, the reaction being most simply represented, thus:

$$2\,KClO_3 + 4\,HCl = 2\,KCl + \overline{2\,ClO_2 + Cl_2} + 2\,H_2O.$$

It does not follow, however, that this proportion between chlorine dioxide and chlorine is maintained, for the former may in turn oxidize hydrochloric acid, thus:

$$2\,ClO_2 + 8\,HCl = 4\,H_2O + 5\,Cl_2,$$

so that the proportion of chlorine is increased; but that is immaterial, for the mixture of gases evolved represents quantitatively the oxygen content of the chlorate, so that an equivalent amount of iodine would always be liberated from hydriodic acid, thus:

$$2\,KClO_3 + 12\,HI = 2\,KCl + 6\,H_2O + 6\,I_2.$$

A very sensitive reaction is that between iodate and iodide in presence of dilute acid, thus:

$$KIO_3 + 5\,KI + 3\,H_2SO_4 = 3\,K_2SO_4 + 3\,H_2O + 3\,I_2;$$

indeed the acidity of a solution may be estimated by the iodine liberated when it is mixed with excess of iodate and iodide, which do not interact in neutral solution.

Among the most important oxidizing reactions in solution are

those of permanganate and dichromate, so commonly employed in volumetric analysis.

The reactions of permanganate afford a most interesting example of the principle already noticed from time to time—that differing conditions determine which of several possible reactions shall take place.

The following scheme represents in terms of oxides the reduction of permanganate in stages, with corresponding colours of the reduction products:

Mn_2O_7	$\longrightarrow$	$2MnO_3 + O$	$\longrightarrow$	$2MnO_2 + 3O$	$\longrightarrow$	$2MnO + 5O$
Crimson Permanganate.		Green. Manganate.		Brown. Hydrated manganese dioxide, or manganous acid.		Pale Pink Manganous salt.

These stages may be readily observed by the use of sulphite as reducing agent. Thus, if a little neutral or alkaline sulphite solution is added to a dilute solution of permanganate, made somewhat alkaline, the colour becomes deep green, owing to the formation of manganate. If more sulphite is added, and especially if the solution is not too alkaline, and is warmed, the green solution gives place to a brown and turbid liquid containing hydrated manganese dioxide. Finally, if sulphite is added to an acidified permanganate solution, the colour is instantly discharged, manganous salt being produced. Thus an alkaline solution with little reducing agent promotes the formation of manganate; a nearly neutral solution with more reducing agent causes the manganese dioxide stage to be reached, whilst the presence of acid is the best condition for complete reduction to manganous salt.

All this is what might be expected; MnO_3 is an acidic oxide, most likely to be permanent as a salt in presence of alkali; MnO is a basic oxide, and its salts are likely to be formed in presence of acid; whilst MnO_2 is neither strongly basic nor acidic, and is therefore likely to result when the solution is nearly neutral.

It must not, however, be assumed that reduction cannot proceed beyond the stage of MnO_2 in absence of acid, for this is not true.

It is possible to create conditions of stability for compounds corresponding to MnO in presence of alkali. Thus, if a few drops of permanganate solution are added to a solution of alkali sulphide containing free alkali, the brown precipitate of hydrated MnO_2 first observed quickly becomes paler as it mixes with the solution, being converted by excess of reducing agent into the less-soluble MnS.

Or, if the same permanganate solution is added to excess of alkali sulphite containing much ammonium chloride, the brown precipitate, when heated with the liquid, completely dissolves, yielding a colourless solution, because, as the student should know, manganous solution can remain unprecipitated by alkali in presence of much ammonium chloride.

Occasionally a compound intermediate in oxygen content between two other compounds may behave either as an oxidizing or a reducing agent, according to circumstances. Instances of such compounds are nitrous acid and the aldehydes. This double function of nitrous acid may be expressed in terms of oxides, thus:

$$2\,NO \xleftarrow{-O} N_2O_3 \xrightarrow{+2O} N_2O_5;$$

that is to say, nitrous acid may be oxidized to nitric acid or reduced to nitric oxide.

If a solution of nitrite is carefully added to an acidified solution of permanganate the latter is decolourized, whilst the nitrite is oxidized to nitrate without evolution of gas, thus:

$$2\,KMnO_4 + 5\,HNO_2 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,HNO_3.$$

If, however, nitrite solution is mixed with hydriodic acid or acidified potassium iodide, the following reaction occurs:

$$2\,HNO_2 + 2\,HI = 2\,H_2O + 2\,NO + I_2;$$

the hydriodic acid being oxidized with liberation of iodine, whilst nitric oxide gas escapes as the reduction product of nitrous acid. Nitrous acid can also oxidize ammonia, nitrogen resulting, both as the reduction product of the former and the oxidation product of the latter; so ammonium nitrite decomposes, thus:

$$NH_4NO_2 = N_2 + 2\,H_2O.$$

Aldehydes are intermediate as regards oxygen content between alcohols and carboxylic acids, e.g.:

$CH_3 \cdot CH_2OH$	CH_3COH	$CH_3 \cdot COOH$
Ethyl alcohol.	Acetaldehyde.	Acetic acid.

So an aldehyde may be reduced to an alcohol, thus behaving as an oxidizing agent, or oxidized to an acid, thus behaving as a reducing agent.

Nascent hydrogen reduces an aldehyde thus:

$$CH_3 \cdot COH + 2\,H = CH_3 \cdot CH_2OH;$$

but silver oxide oxidizes an aldehyde thus:

$$CH_3 \cdot COH + Ag_2O = CH_3COOH + 2\,Ag.$$

Hydrogen peroxide may perform both oxidizing and reducing functions, though in both cases it is reduced to water, so that when it reduces a compound, oxygen gas is evolved. The following equations will make this plain:

$$H_2O_2 + X = XO + H_2O, \text{ oxidizing function.}$$
$$H_2O_2 + XO = X + H_2O + O_2, \text{ reducing function.}$$

The behaviour of hydrogen peroxide towards manganese compounds furnishes an admirable example of the influence of acidity or alkalinity on the course of a reaction. If H_2O_2 is added to manganese hydroxide in presence of alkali, oxidation occurs, thus:

$$Mn(OH)_2 + H_2O_2 = MnO_2 + 2\,H_2O;$$

but if the liquid containing the precipitated MnO_2 is now acidified, reduction to manganous salt is brought about by H_2O_2, thus:

$$MnO_2 + H_2SO_4 + H_2O_2 = MnSO_4 + 2\,H_2O + O_2.$$

Permanganate is similarly reduced in acid solution, thus:

$$2\,KMnO_4 + 3\,H_2SO_4 + 5\,H_2O_2 = K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2;$$

reduction of a compound by H_2O_2 does not, however, necessarily take place in presence of acid, for chromic acid is oxidized in acid solution to the deep blue perchromic acid. But in general, since the lower oxides of a metal are basic, they are likely to be produced by reduction in presence of acids, whilst the higher oxides, if acidic, are more likely to result by oxidation in presence of alkali.

The above reaction between permanganate and hydrogen peroxide is a case of the mutual reduction of two oxidizing agents, each of which contributes one atom of oxygen towards a molecule of this gas. Similar examples are furnished by the reactions between H_2O_2 and silver oxide and ozone respectively:

$$H_2O_2 + Ag_2O = 2\,Ag + H_2O + O_2.$$
$$H_2O_2 + O_3 = H_2O + O_2 + O_2.$$

A reaction which may be regarded as the converse of the above is the partition of molecular oxygen between water and an oxidizable substance, as in the following reaction, which is believed to be part

of what takes place in the process of solution of gold by potassium cyanide in presence of air:

$$2\,Au + H_2O + O_2 = Au_2O + H_2O_2.$$

There are a few compounds, intermediate in oxygen content, which, under suitable conditions, undergo self-oxidation and reduction, producing compounds poorer or richer in oxygen respectively than themselves. Thus a hypochlorite solution, when boiled, passes into chloride and chlorate, thus:

$$3\,KOCl = 2\,KCl + KClO_3;$$

whilst chlorate, when heated suitably, yields chloride and perchlorate, thus:

$$4\,KClO_3 = KCl + 3\,KClO_4.$$

Phosphite and hypophosphite pass by heating into phosphate and phosphine, thus:

$$4\,Na_2HPO_3 = 2\,Na_3PO_4 + Na_2HPO_4 + PH_3.$$
$$2\,NaH_2PO_2 = Na_2HPO_4 + PH_3;$$

and sulphite and thiosulphate behave thus when heated:

$$4\,Na_2SO_3 = 3\,Na_2SO_4 + Na_2S.$$
$$4\,Na_2S_2O_3 = 3\,Na_2SO_4 + Na_2S_5.$$
$$\downarrow$$
$$Na_2S + 4\,S.$$

In all these cases the compounds pass into others more stable under the given conditions.

SUMMARY

HYDROLYSIS.—Hydrolysis is the chemical decomposition of a compound by water.

OXIDATION AND REDUCTION. — Oxidation is the addition of oxygen to an element or compound; reduction is its removal.

CHAPTER XVI

EQUATION-BUILDING

The student of chemistry becomes familiar early with chemical equations. It may be that before he mastered the rudiments of the atomic and molecular theories he was taught to employ the equation as a brief and pointed way of stating what happens in chemistry; and that without fully understanding their significance he has committed to memory a number of equations representing the reactions that occur in the varied preparations of his elementary course. Consequently he has been in danger of magnifying the equation unduly and regarding it as a kind of talisman by means of which natural processes may be foretold or brought to pass. He may have supposed that by manipulating the formulæ of certain reacting substances, and of other substances that might result from their interaction, a chemical change may be successfully expressed without any practical experience of that change. This, in fact, is how beginners often behave in answering questions. Their chief concern is to make the equation balance, in faithfulness to the principle of the indestructibility of matter, supposing that the exigencies of chemical science are completely satisfied if nothing is lost by the way.

The student must learn that chemistry is not a branch of mathematics, that chemical equations are not to be solved like algebraic equations. To employ a chemical equation for a reaction until that reaction is understood qualitatively and quantitatively, so far as the distribution of matter it expresses is concerned, is unscientific and vain.

What is the use of a chemical equation? it may be asked.

Such a question is best answered by considering what chemistry would be without equations. The science might still exist, but it would be an exceedingly clumsy science, and would probably be in a much more rudimentary state than it is at present. Nature

has not ordained the chemical equation; it is a human invention; and man might still be mixing or heating things together and watching for results if he had never invented a means of expressing briefly the results of his discoveries. What language is to thought, so roughly the equation is to chemistry; and just as the educated man chooses language to express his thoughts, and avoids the danger of allowing his language to outstrip his thoughts, so the chemist uses equations to express discovered chemical facts, and avoids allowing his equations to outstrip his facts.

Chemical equations, then, are chemical notation, that is, a means of noting chemical facts in a convenient form. Facts first; equation afterwards. Let the student remember this, and he will at least be in the way of learning chemistry properly.

Nevertheless, to express chemical reactions by equations, not learned by rote, but developed intelligently from well-understood principles, is an art which should be learned by every student of chemistry. It is the present purpose to show how even the most complex equations met with in inorganic chemistry may be built up when the underlying principles of the reactions they express are understood.

Consider the simplest possible reaction; the preparation of hydrogen by the interaction of zinc and dilute sulphuric acid.

If the student knows the symbol Zn and the formula H_2SO_4, and knows also that zinc displaces the hydrogen from the sulphuric acid, he may still go wrong with his equation.

For how shall he decide whether:

$$2\,Zn + H_2SO_4 = Zn_2SO_4 + 2H,$$
$$\text{or} \quad Zn + H_2SO_4 = ZnSO_4 + 2H,$$
$$\text{or} \quad Zn + 2\,H_2SO_4 = Zn(SO_4)_2 + 4\,H,$$

or some other relation between the zinc and the displaced hydrogen is the right one? He may be told what the right relation is, and therefore what the proper equation should be, but he should also be told why.

Now, whilst the equivalent weight of zinc is 32·65, the atomic weight of this metal, as shown by the method of specific heats and other methods is 65·3. Therefore, an atom of zinc displaces 2 atoms of hydrogen, and the equation becomes:

$$Zn + H_2SO_4 = ZnSO_4 + 2\,H.$$

There remains another question, however; that is, whether it is

quite proper to represent the atom of zinc or hydrogen as remaining single in the elementary state. The answer is that zinc is known so to exist, but that hydrogen gas consists of molecules H_2. Therefore, amended, the equation finally becomes:

$$Zn + H_2SO_4 = ZnSO_4 + H_2.$$

When a student has his equation he is inclined to ask whether it explains everything. Then he has to be told that it explains nothing. A chemical equation does not explain a chemical reaction; it expresses it, with certain limitations. It is plain that the equation gives but a limited expression to the reaction between zinc and sulphuric acid; for it does not express the fact that the acid must be considerably diluted with water before any hydrogen can be obtained.

The student will be aware that there are other circumstances of this reaction of which this simple equation gives no account. Nevertheless, it does express, qualitatively and quantitatively, a reaction between the metal and the acid.

If concentrated instead of dilute acid is added to zinc, there is little if any evolution of hydrogen; but when the mixture is heated a vigorous reaction takes place, and much sulphur dioxide gas is evolved.

If this quite different reaction is to be expressed by an equation, it must first be understood. Sulphur dioxide necessarily comes from the sulphuric acid, whence it is derived by reduction, which may be represented thus:

$$H_2SO_4 - O = H_2O + SO_2,$$
$$\text{or} \qquad H_2SO_4 = H_2O + SO_2 + O.$$

It is pertinent to ask how this reduction is effected. Now, since hydrogen is a reducing agent, a facile theory of the process is the following:

$$Zn + H_2SO_4 = ZnSO_4 + 2H.$$
$$2H + H_2SO_4 = 2H_2O + SO_2.$$

The student may now add these two equations together, in this case treating them as if they were algebra; then, since hydrogen is eliminated, the final equation becomes:

$$Zn + 2H_2SO_4 = ZnSO_4 + 2H_2O + SO_2.$$

Now this is the equation for the reaction in question whether

hydrogen is liberated, and in the nascent state acts as a reducing agent, or not.

But it is certainly open to question whether hydrogen is liberated at all in this reaction; and there is no need to assume that it is. Zinc itself is a reducing agent, so why should it not react directly? Now, whilst zinc oxide cannot appear in presence of excess of acid, it is symbolic of the state of oxidation assumed by the zinc; so that if the reaction is to be represented without assuming the agency of liberated hydrogen, the following device may be adopted:

$$\begin{aligned} Zn + H_2SO_4 &= ZnO + H_2O + SO_2 \\ ZnO + H_2SO_4 &= ZnSO_4 + H_2O \\ \text{and adding} \quad Zn + 2H_2SO_4 &= ZnSO_4 + 2H_2O + SO_2. \end{aligned}$$

The same result is shown as above, and if it is not assumed that ZnO is actually separated, this method of arriving at the result is freer from assumption than the former one.

Equations which often puzzle beginners are those representing the interaction of hydrogen sulphide with metallic salt solutions. The reaction

$$CuSO_4 + H_2S = CuS + H_2SO_4$$

is simple enough, because the molecules are matched; but how is $SbCl_3$ to be represented as reacting with H_2S? The answer is simple if it is remembered that the reaction is one of double decomposition; antimony chloride + hydrogen sulphide give antimony sulphide + hydrogen chloride. That is, hydrogen and chlorine atoms must be in equal numbers on the left-hand side of the equation to produce hydrogen chloride molecules on the right. This can result only if the equation is written:

$$2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl;$$

thus not only showing six complete molecules of hydrogen chloride, but also satisfying the tervalency of antimony.

The reaction

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$$

may now be considered.

Since copper does not displace hydrogen from dilute acid, the nascent hydrogen theory will not be assumed to account for the reduction of the nitric acid. The copper will be represented as being directly oxidized by the nitric acid, but as appearing as nitrate instead of oxide, because of the excess of acid present. It is

important, however, to realize how the nitric acid is reduced to the state of nitric oxide, and this reduction may be represented thus:

$$2\,HNO_3 = H_2O + N_2O_5 = H_2O + 2\,NO + 3\,O.$$

To remove these 3 atoms of oxygen from 2 molecules of nitric acid 3 atoms of copper are needed, thus:

$$3\,Cu + 3\,O = CuO;$$

but nitrate is formed rather than oxide, thus:

$$3\,CuO + 6\,HNO_3 = 3\,Cu(NO_3)_2 + 3\,H_2O.$$

And now, adding together these three equations, the following equation is obtained as representing the actual reaction that takes place:

$$3\,Cu + 8\,HNO_3 = 3\,Cu(NO_3)_2 + 4\,H_2O + 2\,NO.$$

Thus, by this method of construction it becomes apparent why 3 atoms of copper and 8 molecules of nitric acid are required; and the student should now recognize that the equation has been built by a sound method based on an understanding of the scientific principles involved. He may ask himself how otherwise he would produce the equation if he did not remember it. Only by haphazard and guesswork could he make the attempt.

In the chapter on the Classification of Chemical Changes the following equations are found:

$$\text{i. } 4\,Zn + 10\,HNO_3 = 4\,Zn(NO_3)_2 + 5\,H_2O + N_2O,$$
$$\text{and ii. } 4\,Zn + 10\,HNO_3 = 4\,Zn(NO_3)_2 + 3\,H_2O + NH_4NO_3.$$

They may be built as follows:

$$\begin{aligned} \text{i. } 2\,HNO_3 &= H_2O + N_2O + 4O \\ 4\,Zn + 4\,O &= 4\,ZnO \\ 4\,ZnO + 8\,HNO_3 &= 4\,Zn(NO_3)_2 + 4\,H_2O \\ \text{adding } 4\,Zn + 10\,HNO_3 &= 4\,Zn(NO_3)_2 + 5\,H_2O + N_2O; \end{aligned}$$

or, using the nascent hydrogen theory, which is perhaps preferable here:

$$\begin{aligned} 2\,HNO_3 &= H_2O + N_2O + 4O \\ 4\,Zn + 8\,HNO_3 &= 4\,Zn(NO_3)_2 + 8\,H \\ 8\,H + 4\,O &= 4\,H_2O \\ \text{adding } 4\,Zn + 10\,HNO_3 &= 4\,Zn(NO_3)_2 + 5\,H_2O + N_2O \end{aligned}$$

$$\begin{aligned} \text{ii. } HNO_3 + 8\,H &= 3\,H_2O + NH_3 \\ 4\,Zn + 8\,HNO_3 &= 4\,Zn(NO_3)_2 + 8\,H \\ NH_3 + HNO_3 &= NH_4NO_3 \\ \text{Adding } 4\,Zn + 10\,HNO_3 &= 4\,Zn(NO_3)_2 + 3\,H_2O + NH_4NO_3 \end{aligned}$$

The student will see that the method of procedure is to fix on the essential reduction product, and consider how it can be formed. Now, in the above example, a molecule of ammonia is formed from one of nitric acid by the action of 8 atoms of hydrogen. These are therefore produced from 8 other molecules of the acid. So the final equation is easily and surely obtained.

Allied to these reactions are those concerned in the use of permanganate and dichromate in volumetric analysis. Consider the following equations representing the oxidation of ferrous iron:

$$2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 5\,Fe_2(SO_4)_3 + 8\,H_2O;$$
$$K_2Cr_2O_7 + 6\,FeSO_4 + 7\,H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3\,Fe_2(SO_4)_3 + 7\,H_2O.$$

It may be observed in passing that the numbers of molecules of sulphuric acid required and of water formed correspond with the number of oxygen atoms in the oxidizing agent. But this circumstance does not really furnish a key to the reactions. This is supplied by considering the available oxygen of the oxidizing agent and the oxygen essential for oxidizing the iron.

Expressed in terms of oxides, these are shown thus in the case of permanganate:

$$2\,KMnO_4 = K_2O + Mn_2O_7 = K_2O + 2\,MnO + 5\,O.$$
$$2\,FeO + O = Fe_2O_3.$$

Thus, since 2 molecules of permanganate in presence of acid yield 5 atoms of oxygen for oxidizing purposes, together with potassium and manganous salts, to which the above oxides correspond; and 2 atoms of iron require 1 atom of oxygen to oxidize them from the ferrous to the ferric state, it appears that 10 molecules of ferrous sulphate are oxidized by 2 molecules of permanganate in presence of sufficient acid, the quantity of which participating in the reaction is easily arrived at by adding together the following equations:

$$2\,KMnO_4 = K_2O + 2\,MnO + 5\,O$$
$$10\,FeSO_4 + 5\,O + 5\,H_2SO_4 = 5\,Fe_2(SO_4)_3 + 5\,H_2O$$
$$K_2O + H_2SO_4 = K_2SO_4 + H_2O$$
$$2\,MnO + 2\,H_2SO_4 = 2\,MnSO_4 + 2\,H_2O$$

Adding $2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$

The equation for the dichromate reaction is similarly obtained, the chromium being reduced from the state of CrO_3 to Cr_2O_3, thus:

$$2\,CrO_3 = Cr_2O_3 + 3\,O;$$

and the iron oxidized by the available oxygen as before:

$$\begin{aligned} K_2Cr_2O_7 &= K_2O + Cr_2O_3 + 3\,O \\ 6\,FeSO_4 + 3\,O + 3\,H_2SO_4 &= 3\,Fe_2(SO_4)_3 + 3\,H_2O \\ K_2O + H_2SO_4 &= K_2SO_4 + H_2O \\ Cr_2O_3 + 3\,H_2SO_4 &= Cr_2(SO_4)_3 + 3\,H_2O \end{aligned}$$

Adding $K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O.$

Other equations for other reactions of permanganate and dichromate are built up similarly, e.g. the following:

$$2\,KMnO_4 + 5\,H_2C_2O_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 10\,CO_2$$
$$2\,KMnO_4 + 5\,H_2O_2 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2.$$

$$K_2Cr_2O_7 + 3\,H_2S + 4\,H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 7\,H_2O + 3\,S.$$
$$K_2Cr_2O_7 + 6\,HI + 4\,H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 7\,H_2O + 3\,I_2.$$

The reactions of potassium chlorate with sulphuric and hydrochloric acids are interesting, and the building of equations to represent them is instructive.

When sulphuric acid is added to potassium chlorate chloric acid is liberated thus:

$$2\,KClO_3 + H_2SO_4 = K_2SO_4 + 2\,HClO_3;$$

but this acid is dehydrated when it is heated with sulphuric acid.

The anhydride Cl_2O_5, however, does not exist; and in place of it $2ClO_2 + O$ are produced. The oxygen, which would otherwise accompany the chlorine dioxide, does not appear as gas, but oxidizes some of chloric to perchloric acid, which is stable in presence of sulphuric acid; or, otherwise expressed, chloric acid undergoes self-oxidation and reduction thus:

$$3\,HClO_3 = 2\,ClO_2 + H_2O + HClO_4.$$

Consequently, the equation representing the reaction between potassium chlorate and sulphuric acid may be built up thus:

$$\begin{aligned} 2\,KClO_3 + H_2SO_4 &= K_2SO_4 + 2\,HClO_3 \\ 2\,HClO_3 &= H_2O + 2\,ClO_2 + O \\ KClO_3 + O &= KClO_4 \end{aligned}$$

Adding $3\,KClO_3 + H_2SO_4 = K_2SO_4 + KClO_4 + H_2O + 2\,ClO_2.$

If potassium chlorate is heated with hydrochloric instead of

sulphuric acid, chlorine accompanies the chlorine dioxide, since hydrochloric acid is oxidized in preference to chloric acid:

$$\begin{aligned} 2\,KClO_3 + 2\,HCl &= 2\,KCl + 2\,HClO_3 \\ 2\,HClO_3 &= H_2O + 2\,ClO_2 + O \\ 2\,HCl + O &= H_2O + Cl_2 \\ \text{Adding } 2\,KClO_3 + 4\,HCl &= 2\,KCl + 2\,H_2O + 2\,ClO_2 + Cl_2. \end{aligned}$$

The interaction of sodium hydrogen sulphite and sodium iodate in aqueous solution, by which iodine is liberated quantitatively from the iodate, is a reaction the equation for which may be built up from first principles, thus:

$$\begin{aligned} 2\,NaIO_3 &= Na_2O + I_2O_5 \\ I_2O_5 + 5\,NaHSO_3 &= 5\,NaHSO_4 + I_2 \\ 2\,NaHSO_4 + Na_2O &= 2\,Na_2SO_4 + H_2O \\ \text{Adding } 2\,NaIO_3 + 5\,NaHSO_3 &= 2\,Na_2SO_4 + 3\,NaHSO_4 + H_2O + I_2. \end{aligned}$$

The equation for the cyanide process for gold extraction may be built up as follows:

$$\begin{aligned} 2\,Au + O_2 + H_2O &= Au_2O + H_2O_2 \\ 2\,Au + H_2O_2 &= Au_2O + H_2O \\ 2\,Au_2O + 8\,KCN + 2\,H_2O &= 4\,KAu(CN)_2 + 4\,KOH \\ \text{Adding } 4\,Au + 8\,KCN + 2\,H_2O + O_2 &= 4\,KAu(CN)_2 + 4\,KOH. \end{aligned}$$

The parts of this reaction are remarkable; for whilst the first two equations represent what cannot possibly take place alone, since gold is not susceptible of atmospheric oxidation, they likewise show the fact of the intermediate formation of hydrogen peroxide through the partition of the oxygen molecule between gold and water, which is not shown in the final equation.

The preparation of phosphine by heating white phosphorus with sodium hydroxide solution is a reaction which is represented by the following equation:

$$P_4 + 3\,NaOH + 3\,H_2O = 3\,NaH_2PO_2 + PH_3,$$

the product in solution being sodium hypophosphite.

In endeavouring to build this equation the first question that occurs is: Where does the hydrogen come from to produce the phosphine? The answer is that it comes from the sodium hydroxide, and the simplest representation of this fact is:

$$NaOH + P = NaOP + H$$

NaOP is not sodium hypophosphite, however; but if the elements of water are added the formula for this salt, NaH_2PO_2, is obtained. A further stage, therefore, is:

$$NaOH + H_2O + P = NaH_2PO_2 + H.$$

If now this equation is multiplied by three, and an atom of phosphorus is added to give PH_3, the above equation results thus:

$$3\,NaOH + 3\,H_2O + P_4 = 3\,NaH_2PO_2 + PH_3.$$

Phosphonium iodide, PH_4I, is prepared by dropping water on to an intimate mixture of finely-divided phosphorus and iodine in an inert atmosphere; and the following equation, representing the reaction, is one of the most difficult in inorganic chemistry:

$$9\,P + 5\,I + 16\,H_2O = 5\,PH_4I + 4\,H_3PO_4.$$

It presents two problems: First, to understand why these products result; and second, to discover the reason for the remarkable molecular proportions exhibited by the equation.

There is apparently some connection between this reaction and the foregoing, though water alone seems to perform the function of the sodium hydroxide solution above. Then if hypophosphorous acid itself is formed instead of its sodium salt, it is unstable, and yields phosphoric acid and phosphine. Hydriodic acid is required, however, to combine with the phosphine, and this may be produced by the interaction of iodine and phosphorus to produce the iodide which is subsequently hydrolyzed, yielding hydriodic and phosphoric acids In this way the reaction may be accounted for, and the equation built as follows:

$$\begin{aligned}
8\,P + 12\,H_2O &= 6\,H_3PO_2 + 2\,PH_3 \\
6\,H_3PO_2 &= 3\,H_3PO_4 + 3\,PH_3 \\
P + 5\,I &= PI_5 \\
PI_5 + 4\,H_2O &= H_3PO_4 + 5\,HI \\
5\,PH_3 + 5\,HI &= 5\,PH_4I \\
\text{Adding } \quad 9\,P + 5\,I + 16\,H_2O &= 4\,H_3PO_4 + 5\,PH_4I.
\end{aligned}$$

This is a rather complicated theory to account for the formation of phosphonium iodide, but it may stand in default of a better; it has the merit of accounting for a complicated equation.

These examples are sufficient to illustrate the art of equation-building. Many other examples will occur to the student; and he will discover by practice that any reaction of which he has an intelligent knowledge can be expressed by an equation constructed by the application of the corresponding chemical principles.

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