UNIVERSAL
LIBRARY

OU_164544

UNIVERSAL
LIBRARY

OSMANIA UNIVERSITY LIBRARY

Call No. 541.2 C 37A Accession No 12431

Author Caven, P. M.

Title Atoms & Molecules.

This book should be returned on or before the date last marked below.

ATOMS AND MOLECULES

BLACKIE & SON LIMITED
50 Old Bailey, LONDON
17 Stanhope Street, GLASGOW

BLACKIE & SON (INDIA) LIMITED
Warwick House, Fort Street, BOMBAY

BLACKIE & SON (CANADA) LIMITED
1118 Bay Street, TORONTO

ATOMS AND MOLECULES

Being Part I and Chapter XII of
The Foundations of Chemical Theory

BY

R. M. CAVEN
D.Sc.(London), F.I.C
Professor of Inorganic and Analytical Chemistry
in the Royal Technical College, Glasgow

BLACKIE & SON LIMITED
LONDON AND GLASGOW
1927

Printed in Great Britain by
Blackie & Son, Limited, Glasgow

PREFACE

This work is a separate issue of Part I and Chapter XII of my work, *The Foundations of Chemical Theory.*

It is issued in this form in response to a request for an elementary account of the subjects with which it deals.

R. M. C.

March, 1927.

CONTENTS

CHAP | Page

I. The Older Atomic and Molecular Theories - - - - - 1

Composition of Matter—The Elements—Laws of Chemical Combination—The Atomic Theory—The Molecular Theory—Law of Volumes—Avogadro's Theory.

II. Equivalent, Atomic, and Molecular Weights - - - - - 18

Equivalent and Atomic Weights—Standard for Equivalent and Atomic Weights—Determination of Equivalent Weights—Methods of Determining Atomic Weights: (*a*) Method of Vapour Density and Avogadro's Theory—Vapour Densities by the Methods of Dumas, Hofmann, Victor Meyer; (*b*) Method of Chemical Displacement; (*c*) Method of Specific Heats (Dulong and Petit's Law); (*d*) Method of Isomorphism (Mitscherlich's Law); (*e*) Method of the Periodic Law—Illustration: The Atomic Weight of Carbon—Molecular Weights in Solution: Cryoscopic and Ebullioscopic Methods—Molecular Complexity—Molecular Compositions of Compound Gases.

III. Older Views of Valency and Chemical Constitution - - - 56

Historical—Definition of Valency—Bonds and Graphic Formulæ—Variability of Valency—Double Bond in Carbon Compounds—"Chemistry in Space"—Criterion of Valency—Nature of Valency.

IV. Classification of the Elements - - - - - - - - 69

The Periodic Law according to Mendeléeff—Law of Octaves—Development of the Periodic Law—Periodicity of Physical Properties—Periodicity of Chemical Properties—Periodicity of Valency—Uses of the Periodic Law—Correction of Atomic Weight Values—Suggestiveness of the Periodic Law—Objections to the Periodic Law.

V. The Modern View of the Atom - - - - - - - - 93

Electrolysis and the Electron—Radioactivity—The Electron and Valency—Effect of Radioactive Change—Isobares and Isotopes—Atomic Number—The Modern Statement of the Periodic Law—Positive Ray Analysis and Mass Spectra—Isotopes of Lead—Atomic Structure—Valency Theories of Lewis and Langmuir—Theory of Bohr.

CHAP Page

VI. THE MODERN VIEW OF THE MOLECULE - - - - - - - 118

Electrochemical Theory of Berzelius—Dualistic and Unitary Systems — Electrolytic Dissociation Theory of Arrhenius — Electrovalency and Covalency—The Octet Theory—Molecular Structures—Space Lattices—Crystal Units and Molecules of Solids—Formulæ, Old and New.

VII. THE COLLOIDAL STATE - - - - - - - - - - - 133

Solution and Suspension—Crystalloids and Colloids—Hydrosol and Hydrogel—Typical Colloids—The Ultra-microscope—Size of Colloidal Particles—Gradations between Suspension and Solution Coagulation of Colloids Cataphoresis—Peptization Protective Colloids Phases and Media Range of Colloidal Phenomena.

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.

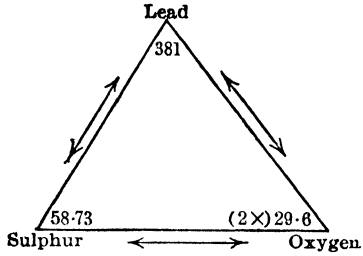
The existence of two nitrates of mercury is, however, a noteworthy fact, which appears the more striking when it is discovered that in one compound the proportion of mercury to nitrate is exactly twice what it is in the other. Further examples of this phenomenon were observed by Dalton, who showed that 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 38·1 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."

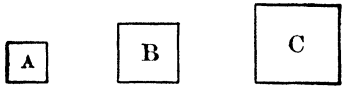
No hint is given in the context of the way in which the atomic values, which follow, were estimated, nor of the precise reason why such values were believed to exist. The idea that matter consists of discrete particles was, however, in the air. Apart from the ancient theory of atoms, a theory of particles 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."

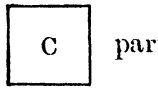
It would almost appear from such a pronouncement that Newton and not Dalton was the author of the atomic theory. Yet this statement is not a chemical theory: it is a cosmic theory intimately related to Newton's great discovery of universal gravitation. Dalton, however, was greatly indebted to Newton 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,

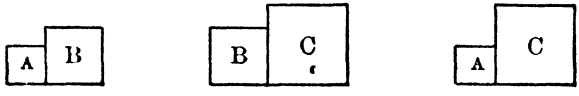
being the quantity of B which is found to combine separately with

parts of A and 

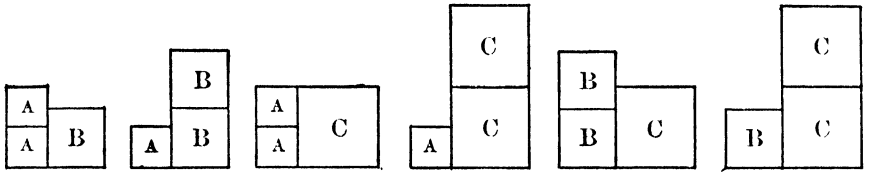
parts of C, according to the law of definite proportions; whilst

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		

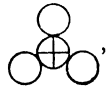
If the student compares these atomic weights with those in use at the present day, he will see that they differ widely from the modern figures. Inaccuracies in Dalton's values are to be expected, but it is not experimental error which attributes, for example, an atomic weight of 7 to oxygen, instead 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.

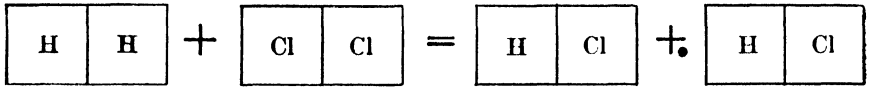
Now when two separate and different elementary atoms combine to form a compound atom, or whatever it may be called, it is one entity they form, not two. It is impossible, for instance, that 1 atom of hydrogen combining with 1 atom of chlorine can produce two compound atoms of hydrogen chloride. And yet 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?

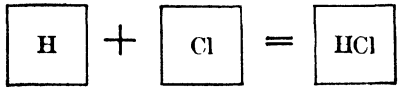
That is precisely the solution of the difficulty suggested by

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:

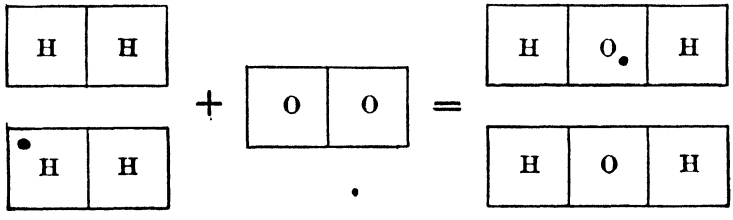


so that 1 volume of hydrogen plus 1 volume of chlorine gives 2 volumes of hydrogen chloride, instead of 1 volume, according to the scheme:

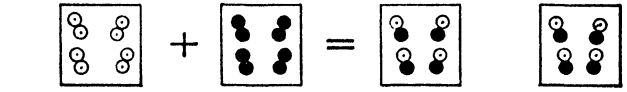


It might be objected, however, that if the molecules of hydrogen chloride are intrinsically twice the size of the atoms of hydrogen and chlorine, out of which they are formed, the volume of the compound gas might be expected in any case to be twice that of either of the simple gases. Such an objection, 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.

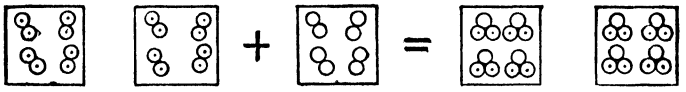
The formation of 2 molecules of steam from 2 molecules of hydrogen and 1 molecule of oxygen is thus represented:



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	$= 0{\cdot}033$ grm.
Volume of moist hydrogen measured at 12° C. and 756 mm.	$= 32{\cdot}6$ c. c.
Pressure of water vapour at 12°	$= 10{\cdot}5$ mm.
Volume of dry hydrogen at N.T.P.	$= \frac{32{\cdot}6 \times (756 - 10{\cdot}5) \times 273}{760 \times (273 + 12)}$
	$= 30{\cdot}6$ c. c.
Weight of hydrogen	$= 30{\cdot}6 \times 0{\cdot}00009 = 0{\cdot}002754$
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

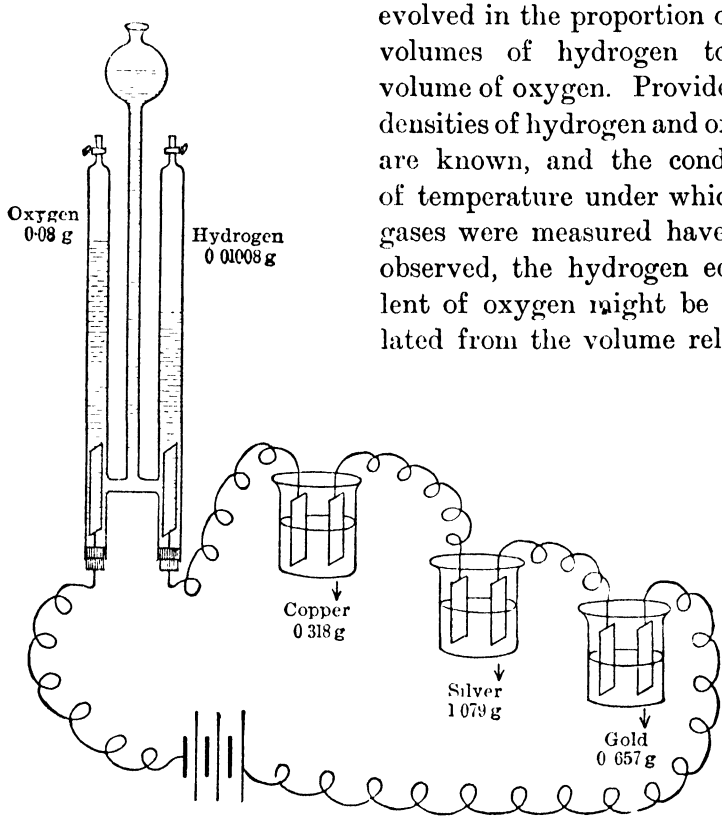


Fig. 1

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.

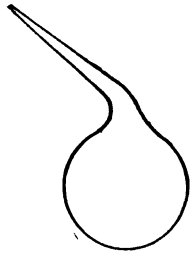


Fig 2

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

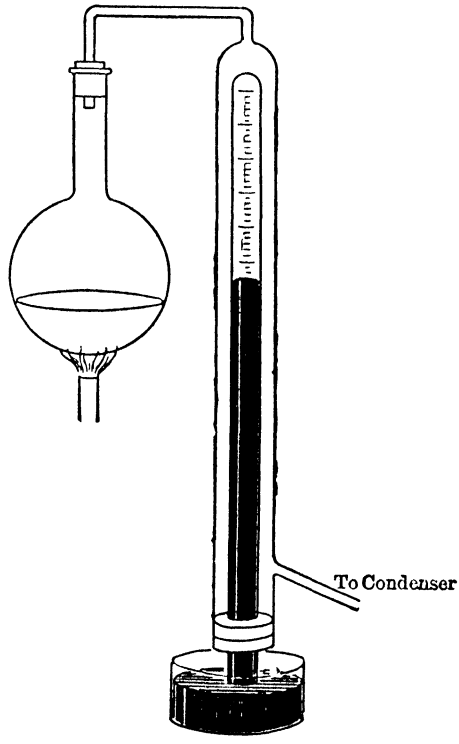


Fig. 3

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 ($SnCl_4$)	$= \frac{0 \cdot 0445}{0 \cdot 0003375} = \underline{131 \cdot 8}$.

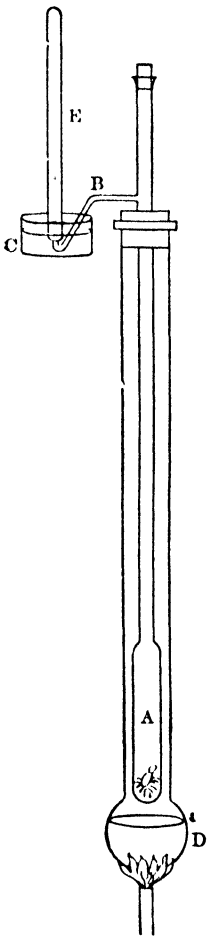


Fig. 4

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

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:

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

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):

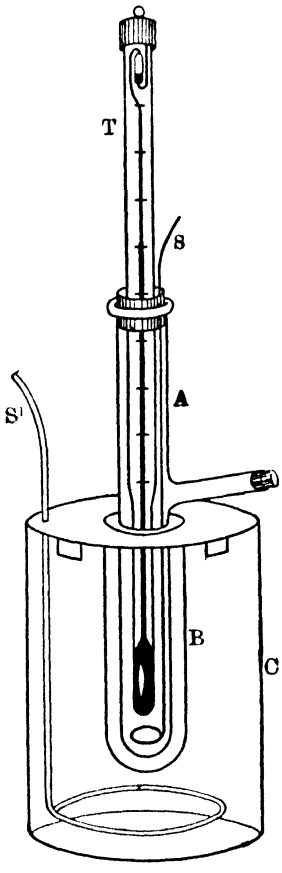


Fig. 5

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

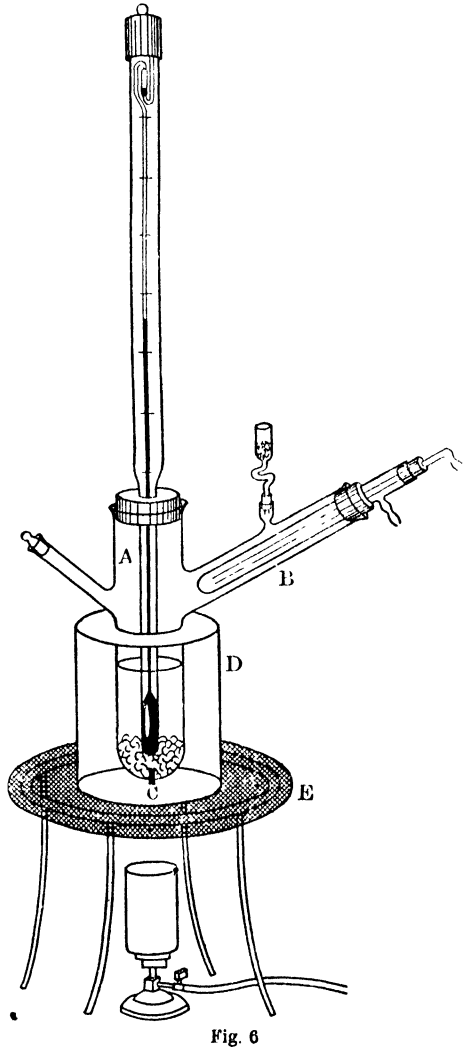


Fig. 6

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).

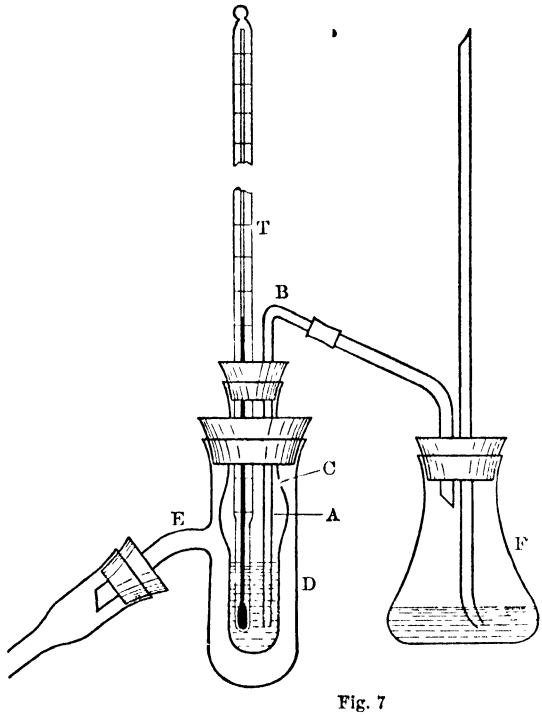


Fig. 7

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.

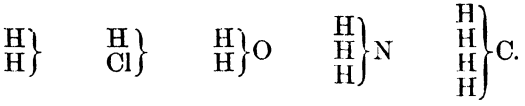
Consequently this chapter on "Older Views of Valency and Chemical Constitution" is historical; touching lightly the great subjects with which it deals, it brings chemical knowledge up to the boundary of the new domain, and leaves for a further chapter the task of exploration. It will be enough for the 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	

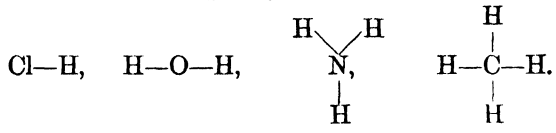
These oxides are in a different category from that of the foregoing hydrides and halides. In those the molecular formulæ have in all cases been established by vapour density or other measurements, and the valency of the element concerned is directly indicated by the number of attached hydrogen or halogen 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.

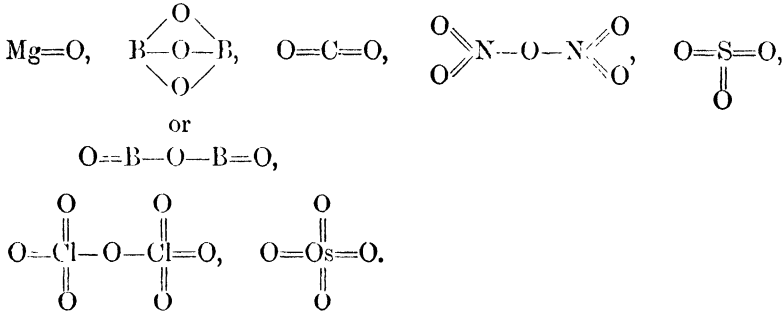
The establishment of the idea of valency was soon followed by a device by which the facts of atomic union were represented graphically.

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:

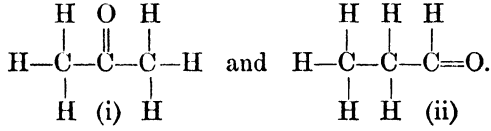


Formulæ such as these are chiefly of historic interest, for they have to be reconsidered carefully in the light of modern knowledge and theory concerning the atom. It will appear later that Couper's bonds ought not to be used indiscriminately or similarly for all these compounds; e.g. while they are 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.

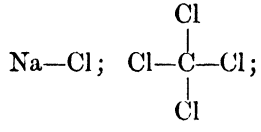
Is, then, the writing of graphic formulæ merely an interesting geometrical exercise based on the facts of valency alone? Consider, for example, a substance with the formula C_3H_6O. Since carbon is quadrivalent, oxygen bivalent, and hydrogen univalent, two graphic formulæ are possible for this substance:



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.

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.

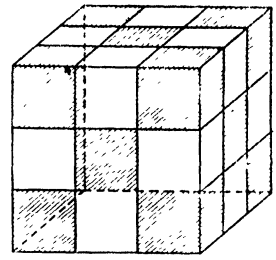
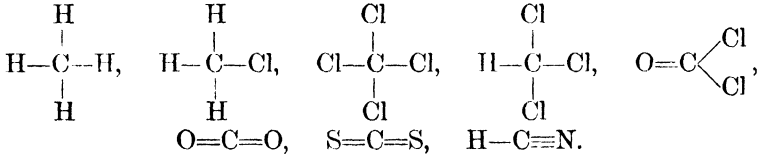


Fig. 8

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:

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

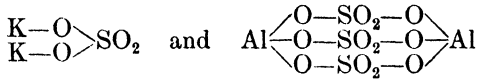
Presumably this dissociation involves a reduction in operative valency, since such valency is necessary to hold together the two parts of the double molecule, but becomes inoperative on dissociation.

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.

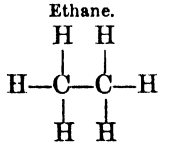
as a rule halides are not so stable as the corresponding oxides. For example, NCl_3 is so unstable as to be highly explosive, whilst N_2O_3 does not split off oxygen; PCl_5 dissociates into PCl_3 and Cl_2, whilst P_2O_5 is stable; SO_2 may be united with oxygen to form SO_3, whilst SCl_4, formed below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

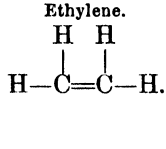
The Double Bond in Carbon Compounds.

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

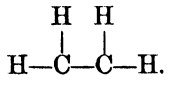
Ethane.



and Ethylene.



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

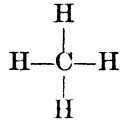
[1] Ruff and Tschirch, *Ber.*, 1913, *46*, 929.

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.

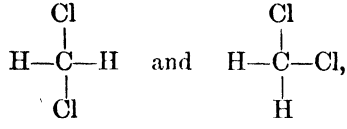
There is still a third characteristic of the double bond, which, however, can only be made clear by the study of the stereochemistry of carbon compounds.

"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:

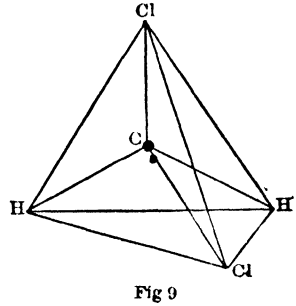


Fig 9

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:

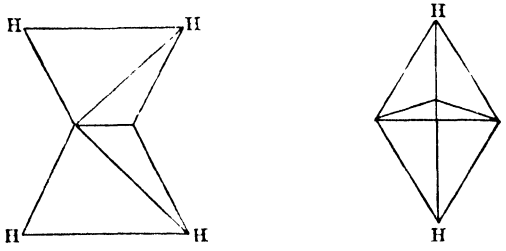


Fig. 10

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.

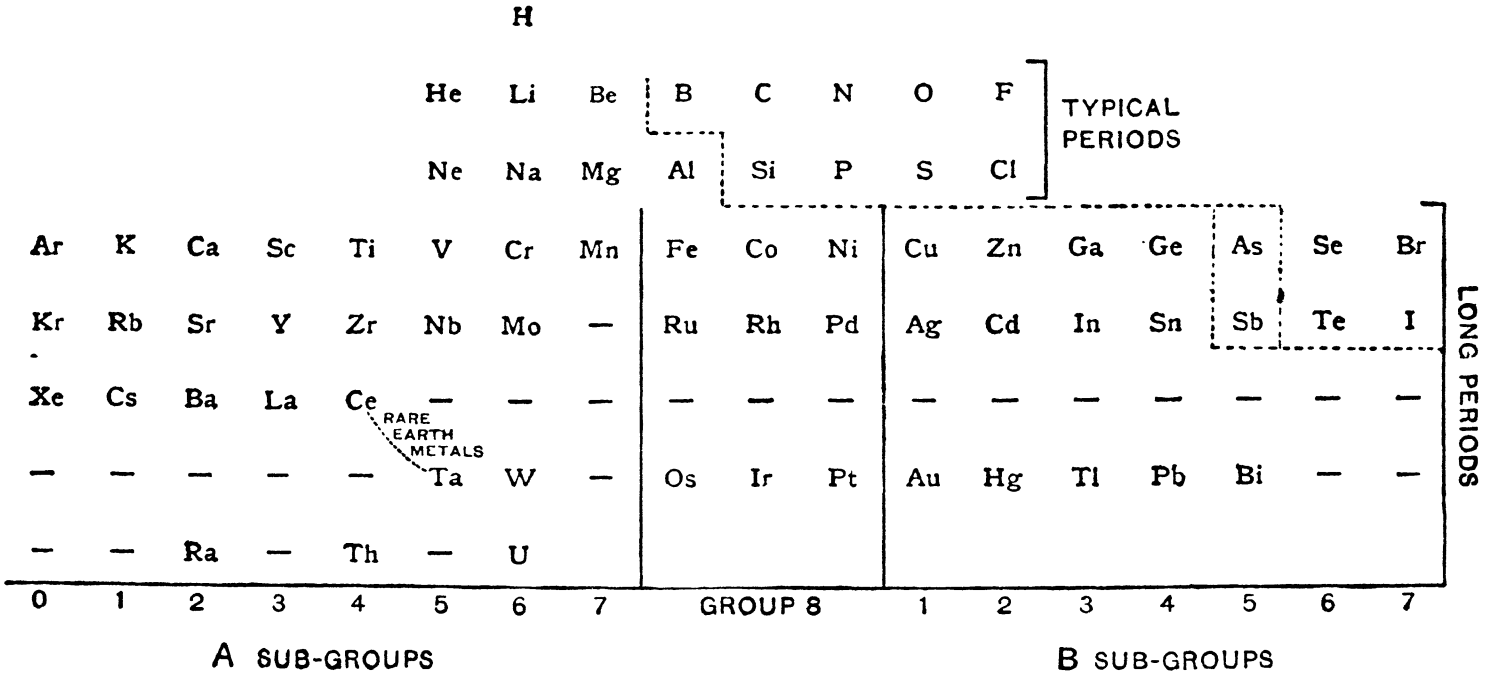
Hydrogen, the element of lowest atomic weight, became the sole member of Series 1 in Mendeléeff's system. Series (2) and (3) were the same as in the octaves of Newlands, thus:

(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 — — — — — — — — — — — — —
RARE EARTH METALS
— — — — — Ta W — Os Ir Pt Au Hg Tl Pb Bi — —
— — Ra — Th — U
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	Kr	Rb Ag	Sr Cd	Y In	Zr Sn	Cb Sb	Mo Te	— I	Ru Rh Pd
6	Xe	Cs	Ba	La	Ce		—	—	— — —
7		—	—	—	Rare Earth Metals	—	—	—	
8	—	—	—	—		Ta	W	—	Os Ir Pt
9		Au	Hg	Tl	Pb	Bi	—	—	
10	—	—	Ra	—	Th	—	U		
11									
12	—	—	—	—	—	—	—	—	—
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:

	Li	
(A)	Na	(B)
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.

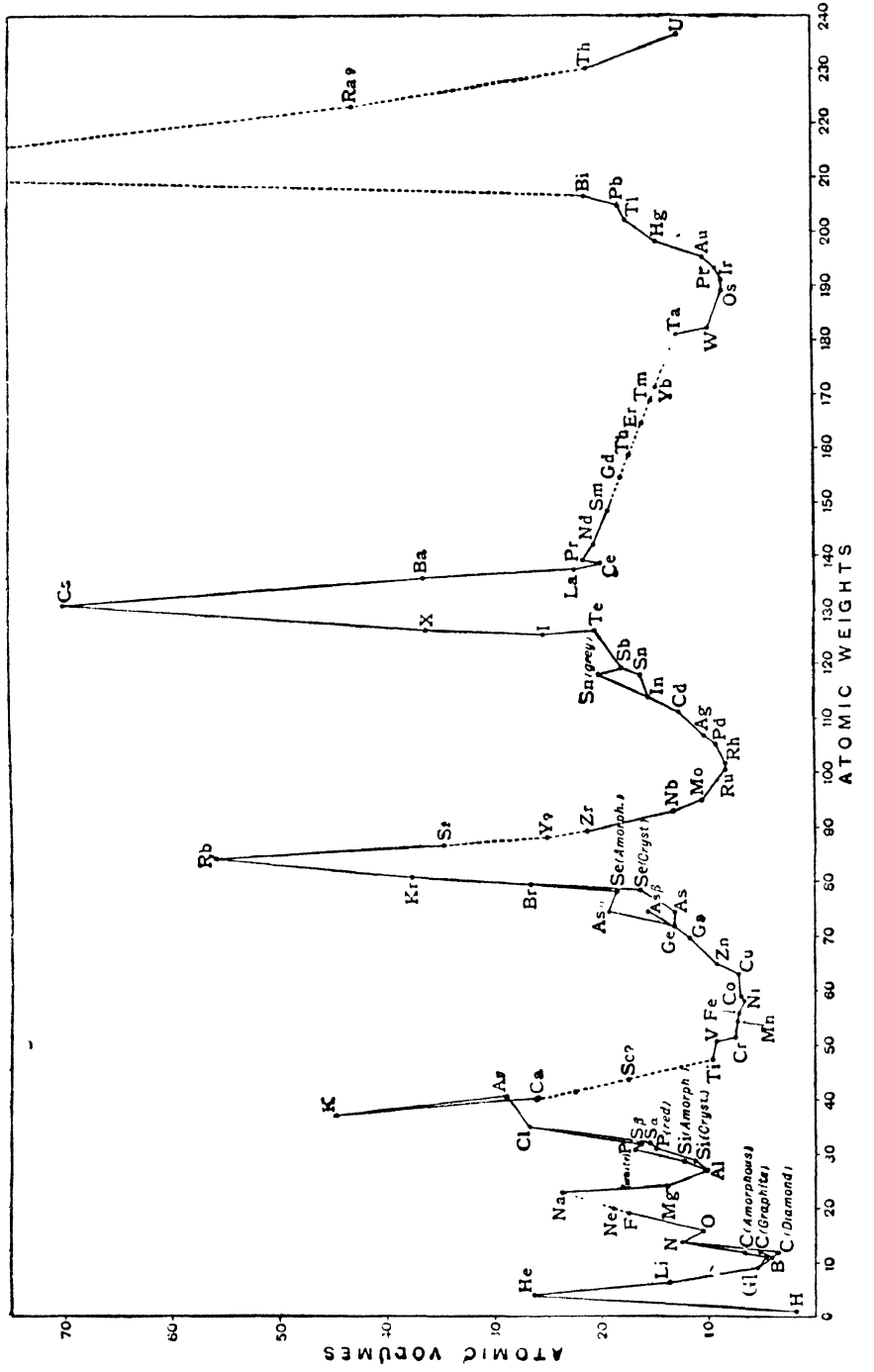
The periodic law, according to Mendeléeff, states that the physical and chemical properties of the elements and their compounds are periodic functions of their atomic weights. This statement must now be illustrated.

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
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
H
He
Li
(Li)
B
C (Diamond)
C (Graphite)
C (Amorphous)
O
N
F
Ne?
Mg
Na
Al
Si (Cryst.)
Si Amorph
P (red)
P
S
Cl
K
Ar
Ca
Sc?
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
As β
As α
Se (Cryst.)
Se (Amorph.)
Br
Kr
Rb
Sr
Y?
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
Ra?
Th
U

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:

$$Na{-}O{-}O{-}Na, \quad Ba\begin{smallmatrix} O \\ \diagup\diagdown \\ O \end{smallmatrix}, \quad \text{or} \quad \begin{smallmatrix} Na \\ \diagdown \\ Na \end{smallmatrix}\!\!>O{:}O, \quad Ba{=}O{:}O;$$

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.	Atomic weight, 69·9.
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.	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 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.	Oxide, Ga_2O_3; density not known; dissolves in acids, forming salts GaX_3. The hydroxide dissolves 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.	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.
The element will probably be discovered by spectrum analysis.	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.: $NH_3 + H^{\bullet} = NH_4^{\bullet}$.[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.
[2] Both basic and acidic, ἀμφότερος = both.

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:

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

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:

$$\overset{+}{K}\overset{-}{O}\overset{+}{S}\overset{-}{O_3} \qquad \overset{+}{Al_2}\overset{-}{O_3}\,3\overset{+}{S}\overset{-}{O_3}$$

$$\overset{+}{K}\overset{-}{O}\;\overset{+}{S}\overset{-}{O_3} \qquad \overset{+}{Al_2}\overset{-}{O_3}\;3\overset{+}{S}\overset{-}{O_3}$$

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

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

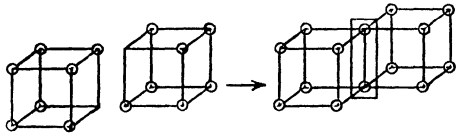
possible for electropositive hydrogen to be replaced by electronegative chlorine, so as to produce CCl_3COOH?

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.

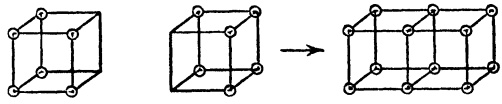
This difficulty is met by a conception due to G. N. Lewis and developed by Langmuir: the conception of covalency, as distinct from electrovalency, which is the kind of valency hitherto considered. Now an atom of chlorine has 7 electrons in its sheath, and requires 1 to complete the *octet* characteristic 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.

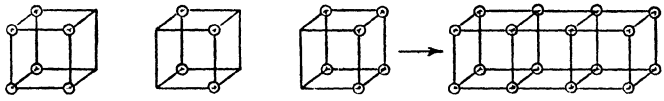
Thus, by this view, there are two kinds of valency: *electrovalency* and *covalency.* The theory of electrovalency is the modern equivalent of the dualistic theory of Berzelius; that of covalency corresponds with the unitary theory of Dumas.

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:

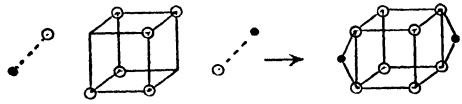


Similarly, carbon dioxide, O = C = O, can be represented by

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

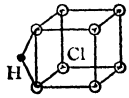


The combination of hydrogen with oxygen, and with chlorine, to form water and hydrogen chloride respectively, may now be considered. Since water is a non-electrolyte, the two hydrogen atoms in each molecule are supposed to unite with the oxygen atom by covalency, in a manner which may be represented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



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

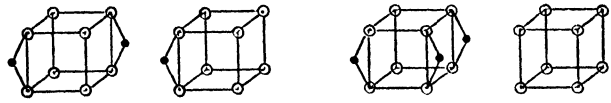
As regards hydrogen chloride, since in the anhydrous state this compound is a non-electrolyte, its molecule may be represented thus, the atoms of hydrogen and chlorine being united by covalency:



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:



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.

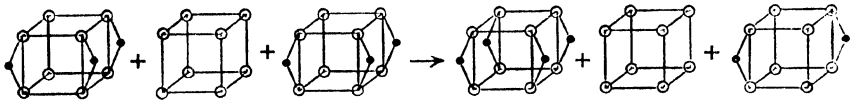
[1] *Vide* Lowry, *Chemistry and Industry*, 1923, 46.

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:

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

or

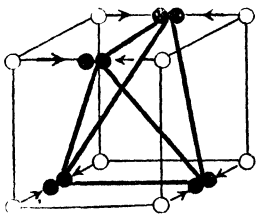


the neutralization being due to the fact that the ammonia molecule appropriates another hydrogen nucleus to form the highly symmetrical ammonium ion with greater force than the water molecule retains it. Nevertheless, just as $[OH_3]^{\cdot}$ is unstable, easily losing a hydrogen nucleus in presence 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.

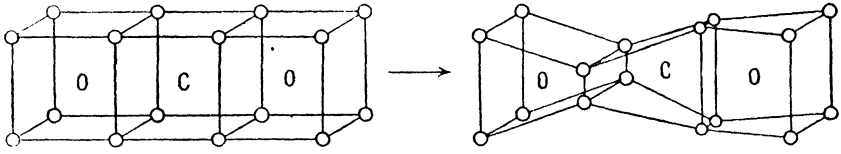
The student of organic chemistry is conversant with the theory that the four valencies of the carbon atom are directed towards the angular points of a regular tetrahedron; and he knows that this theory has been most fruitful in elucidating the structure and stereochemistry of carbon compounds. It is 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.

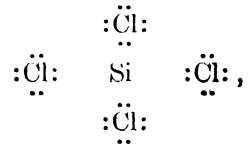
So it appears that a pair of electrons, acting as a unit of covalency, is equivalent to a single chemical bond. It is to be noted, moreover, that with the exception of H, which has two electrons, and Na, which is an ion with eight electrons in a lower layer, every atom is represented as having or sharing 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 accompanying photograph is of a chart which was exhibited in the British Empire Exhibition (Wembley, 1924), and is included here by courtesy of the Royal Society and the National Physical Laboratory.

Where the crystalline structure of an element has been determined by the X-ray method, a model of the space lattice is shown in the appropriate place in the periodic table. It will be noted that the majority of these lattices are cubic. The atomic weight and the atomic number are given for each element, the latter being in brackets.

The stability of CCl_4, as well as of CH_4, as compared with SiCl 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:

$$H:\ddot{\underset{\cdot\cdot}{Cl}}: \rightarrow H\ :\ddot{\underset{\cdot\cdot}{Cl}}: \rightarrow [H]^+ + \left[:\ddot{\underset{\cdot\cdot}{Cl}}:\right]^-.$$

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^+, and the anions SiO_4'''', PO_4''', SO_4'', MnO_4'', MnO_4', ClO_4', which are formulated thus:

$$\left[\begin{matrix} & :\ddot{O}: & \\ :\ddot{O}:&\ddot{Si}&:\ddot{O}: \\ & :\ddot{O}: & \end{matrix}\right]\equiv \left[\begin{matrix} & :\ddot{O}: & \\ :\ddot{O}:&\ddot{P}&:\ddot{O}: \\ & :\ddot{O}: & \end{matrix}\right]\equiv \left[\begin{matrix} & :\ddot{O}: & \\ :\ddot{O}:&\ddot{S}&:\ddot{O}: \\ & :\ddot{O}: & \end{matrix}\right] \left[\begin{matrix} & :\ddot{O}: & \\ :\ddot{O}:&Mn&:\ddot{O}: \\ & :\ddot{O}: & \end{matrix}\right] \left[\begin{matrix} & :\ddot{O}: & \\ :\ddot{O}:&Mn&:\ddot{O}: \\ & :\ddot{O}: & \end{matrix}\right] \left[\begin{matrix} & :\ddot{O}: & \\ :\ddot{O}:&\ddot{Cl}&:\ddot{O}: \\ & :\ddot{O}: & \end{matrix}\right]$$

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
4 O = −8	4 O = −8	4 O = −8	4 O = −8	4 O = −8	4 O = −8
$SiO_4 = -4$	$PO_4 = -3$	$SO_4 = -2$	$MnO_4 = -2$	$MnO_4 = -1$	$ClO_4 = -1$

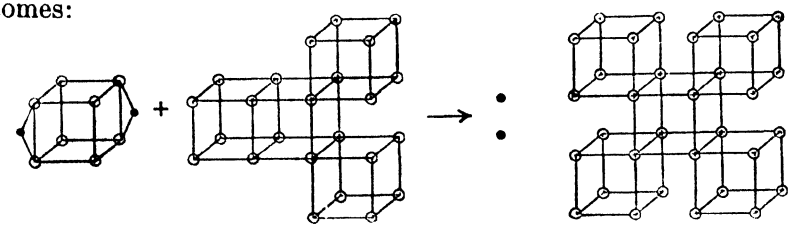
It is noteworthy that the covalent bond, i.e. the duplet, is the same whether the uniting element is univalent like H or bivalent like O. Consequently the practice of representing O as united with other elements by means of double bonds, unless these are double covalent bonds, disappears.

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.

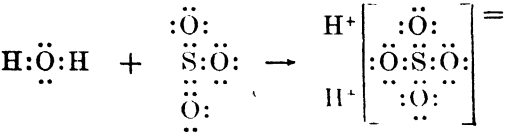
Actually, of course, H_2SO_4 is produced by the union of H_2O and SO_3, both of which are neutral molecules because their component atoms mutually satisfy each other in covalent union. In order that the sulphur octet in SO_3 may be completed, however, one oxygen atom is represented as united with the 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:

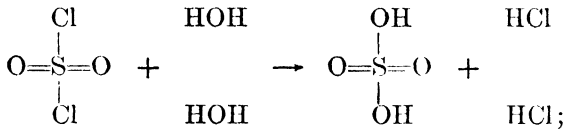


or

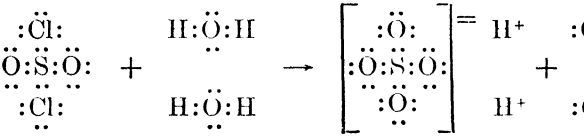


It is thus plainly seen that the two extra electrons provided by the hydrogen are necessary because, owing to the opening out of the double bond, an oxygen atom fully furnished with an octet of electrons must be available to convert the molecule SO_3 into the ion SO_4.

It has been usual to show the constitution of sulphuric acid by its derivation from sulphuryl chloride thus:



this reaction now becomes:

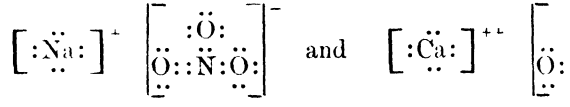


Thus the connection between the old and the new way in chemistry is perceived. In this new way, or something like it, chemical compounds will be formulated in the textbooks of the future.

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.

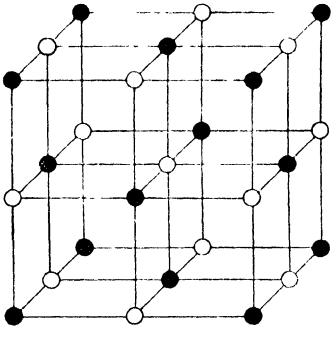
In connection with the arrangement of the atoms within the crystal, the idea of a space-lattice has been introduced. Consider a piece of wooden trellis-work, which can be opened to show a pattern of diamond-shaped spaces. Such a pattern, indefinite in extent, but with units which are similar parallelograms, 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-

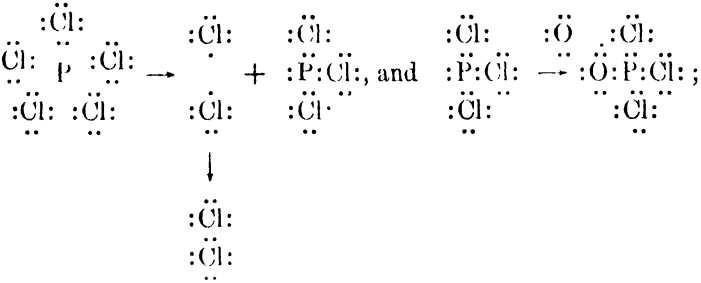
[1] "The Significance of Crystal Structure", *Trans. Chem. Soc.*, 1922, *121*, 2766.

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.

CHAPTER VII

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 $0\cdot4\times10^{-6}$ to $0\cdot8\times10^{-6}$ mm., and of hydrogen $0\cdot1\times10^{-6}$ 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.