CHAPTER I

INTRODUCTION

IF marble be crushed to a fine powder, each of the particles possesses all the properties of the original substance except size and shape. This subdivision may obviously be continued so long as the particles are visible under the microscope, but it is difficult to believe that it must stop there. Is there a limit to the process of division? However small the particle may be, one can conceive of its being broken once more.

The extreme subdivisibility of matter can be shewn in a striking manner by the following experiment.

One gramme of fluorescein is dissolved in a solution of caustic soda and made up to a volume of one litre with distilled water (solution A). From this, 10 c.c. are withdrawn and diluted to one litre (solution B). The process is repeated with solution B and solution C obtained. The solution A contains 0.001 grm. of fluorescein per c.c. Solution B contains one-hundredth part of this, that is 10^{-5} grm. per c.c., and solution C, 10^{-7} grm. per c.c. If 1 c.c. of solution C be placed in a glass tube of small bore and held in a position oblique to the line of vision the fluorescence can be clearly seen. That is, there is optical evidence that 1 grm. of fluorescein is divisible into ten million parts, and there is still no evidence that the limit of divisibility has been reached.

If a piece of marble be heated strongly a gas is evolved and something remains behind which is not marble. This latter material therefore consists of at least two substances and if so, subdivision of marble must at last reach a point where the particles are *not* all alike in properties. A

chemical separation has been brought about and two substances, having different properties, obtained.

This process of splitting up substances into two or more other substances of different properties, applied to all material things with which we are acquainted, has resulted in our obtaining some ninety kinds of matter which cannot at present be further resolved. That is, no one of them can be made to yield *two* substances of different properties without the addition of something else, which in practice means without an increase in weight. These substances are the chemist's *elements**.

According to Boyle (1661) 'elements are the practical limits of chemical analysis, or are substances incapable of decomposition by any means with which we are at present acquainted.'

For a century after Boyle hardly more than a score of so-called elements were known. Soda, potash and quicklime were 'elements' until early in the nineteenth century, when Davy obtained the metals sodium, potassium and calcium from them.

The term 'element,' then, is provisional. An element of to-day may to-morrow prove to be a compound, or even a mixture. Copper is *at present* an element because nothing has been obtained from it hitherto but copper, unless by the addition of something else and a consequent increase of mass.

It must not be thought, however, that the elements of to-day are *generally* open to suspicion. In some few cases perhaps they may be, but there is evidence from many different and unconnected sources that nearly all of them are incapable of being decomposed in the sense indicated above. This point will be again referred to later. The

* Though very nearly so, this is not *absolutely* true. See radium, p. 10, and allotropy, p. 73.

usual classification of elements into metals and non-metals has a rough convenience, but it is neither rigid nor important. The element arsenic shares the properties of both classes. Metals in general have what is known as a metallic lustre, some of them in a high degree, as palladium, but the non-metal iodine also has a quasi-metallic lustre.

It will be seen later that the non-metals as a class readily unite with hydrogen, forming stable compounds with it, while the metals as a class either do not unite with hydrogen at all, or do so with difficulty, forming far less stable compounds. Every metal forms at least one basic oxide, while non-metals do not form basic oxides. The metals are all good conductors of heat and electricity, while non-metals as a class are bad conductors.

If a mixture of the elements iron and sulphur be made by using the finest iron filings and 'flowers' of sulphur, however intimate the mixture may be it is still possible, under the microscope, to detect the particles of iron and of sulphur lying side by side apparently unchanged. Further, the iron can be withdrawn from the mixture by means of a magnet, or the sulphur can be withdrawn by shaking the mixture with a solvent such as carbon bisulphide, filtering, and allowing the clear liquid to evaporate from a clock glass, when the sulphur is left behind. The mixture of iron and sulphur is stable and permanent if it be kept cool and dry. If the mixture be heated in a hard glass tube a point is soon reached at which, the external heating being stopped, heat is generated in the tube itself. A change takes place in which considerable energy is evolved in the form of heat.

If the contents of the tube be cooled and examined, a substance is found which is neither iron nor sulphur; a new body in fact, which is not attracted by a magnet, which yields nothing to carbon bisulphide and which, when

4 **INTRODUCTION**

placed in dilute sulphuric acid, gives a gas with an odour quite unlike the one obtained by similarly treating the mixture. A chemical union has been effected.

The new substance is much harder than iron and much more brittle. It is sometimes used in a modified form for cementing the joints in the iron mains conveying gas or water. The iron-sulphur mixture, together with a little ammonium chloride, is rammed tightly into the socket between the pipes when they are in position. The moisture of the earth which covers them assists the change described above, in which the metal of the pipes themselves takes part, and after a time the iron surfaces are so firmly welded that it is often easier to break the pipes than to disconnect the joint.

A marked feature of this change is that the new substance on examination proves to consist always of 63·7 per cent. of iron and 36·3 per cent. of sulphur. If the original mixture did not contain the elements in these proportions, then the new body *either* contains unchanged iron and will still be attracted by a magnet, *or* some sulphur will be boiled off and will condense in the cold part of the tube.

This constancy of composition is more conveniently shewn in the case of common salt, since here the whole of the experimental work can easily be carried out by the student himself.

If a small piece of the element sodium be placed in a crucible in a large jar of the elementary gas chlorine, the sodium combines with the chlorine with the formation of salt. This can be collected, washed with a little concentrated hydrochloric acid and dried (specimen 1).

If sea-water be evaporated down to about one-tenth of its original volume, filtered to remove suspended impurities and then made strongly acid with pure concentrated hydrochloric acid, common salt is deposited from the

solution. This can be filtered, washed with a few drops of water and dried (specimen 2).

If a solution of washing soda be slowly acidified with hydrochloric acid and evaporated to small volume, common salt is deposited and can be treated as above (specimen 3).

The percentage of chlorine (and therefore by difference the percentage of sodium) can be determined by analysis, when the same values will be obtained from all three specimens.

It may thus be shewn experimentally that (pure) common salt however obtained (and the examples given do not of course exhaust the possible methods of obtaining it) always consists of 60·7 per cent. of chlorine and 39·3 per cent. of sodium.

Another set of experiments shewing this constancy of composition may be made with black copper oxide.

1. If a little thin foil of pure copper be carefully weighed into a crucible and heated to redness with free access of air until the weight no longer increases, the masses of copper and oxygen which unite can be calculated.

2. If copper oxide be prepared by heating copper carbonate to a red heat; a known weight of this oxide taken and heated in a current of hydrogen until no further loss of weight occurs; the mass of copper remaining can be weighed and this, by subtraction, gives the mass of oxygen united with it in the specimen taken.

3. If a few grammes of copper nitrate be heated in a crucible, gently at first but finally to a red heat, a third specimen of copper oxide will be obtained which can be examined as in 2.

In the three cases the percentage of copper in the copper oxide proves to be the same, viz. copper, 79·9 per cent.; oxygen, 20·1 per cent. As in the case of common salt, the three specimens have been prepared by methods

independent of each other, yet they are identical in com-
position.

The results of these and other experiments are sum-
marized in the Law of Constant Composition (or Law of
Constant Proportions) first clearly formulated as the result
of a controversy between Berthollet and Proust (1803–
1806). The former maintained that the composition of
compounds might be dependent on the conditions of their
preparation, but the careful experimental work of the
latter shewed that compounds are of constant composition.
The law is usually stated thus:

*The same compound always consists of the same elements
united in the same proportions.*

This law therefore is to be regarded as nothing more than
a summary of experience. Innumerable experiments con-
firm it, and hitherto no exception to it has been estab-
lished.

Conservation of Mass and Energy. If a piece of dry
phosphorus be placed in a dry flask which is then closed
with a tightly fitting rubber stopper, the whole carefully
weighed and then dipped for a moment into hot water, an
obvious chemical change begins. The flask should be gently
rotated while the phosphorus is burning to avoid danger of
breakage. When the action is over and the flask has re-
turned to room temperature it is dried and again weighed.
No change of weight is observed. If the flask be opened
under water a quantity of water enters, approximating to
one-fifth of the volume of the flask if sufficient phosphorus
has been used. The water which previously was without
action on litmus, now turns it red. If too much phosphorus
is used a portion of it remains unburnt.

The experiment shews that this chemical change takes
place without loss or gain of weight in the system as a
whole. Is it true of all chemical changes?

The principle of Conservation of Mass was first clearly
stated by Lavoisier in the year 1789, as the result of ex-
periments which he carried out on the transformation of
sugar into alcohol and carbonic acid gas under the in-
fluence of yeast. His experiments on the calcination of
metals in closed vessels in 1774 had previously indicated
its truth. These experiments were essentially similar to
that on the combustion of phosphorus just described. All
subsequent quantitative experimental work has led to con-
clusions which are in agreement with the principle, but it
is important to note that there is no *a priori* reason why
it should be true.

The fundamental importance of the principle of con-
servation of mass led to very careful work in recent years
to test its degree of accuracy. The most searching experi-
ments are those of Landolt, who examined some fifteen
different reactions. In his final experiments, published in
1908, the total reacting mass employed was about 400 grm.
and the maximum error was 0·03 mg. Landolt concluded
that the law of the conservation of mass can be considered
as proved within the limit of error of one part in ten
million. It is sometimes called the law of the indestructi-
bility of matter, the meaning of which is, simply, that in any
chemical change the total mass of the substances which
interact is (within the limits mentioned) equal to the total
mass of the products of the reaction*.

When the chemical change takes place spontaneously
there is always a liberation of energy of some kind. Since
heat is the lowest form of energy, the chemical energy

* More recently (Rutherford, 1922) the validity of this law, on which
all the quantitative work of the chemist depends, has assumed a new
aspect. 'We now know with certainty that four neutral hydrogen atoms
weigh appreciably more than one helium atom, though they contain the
same units, four protons and four electrons.' Aston, 1924.

8 INTRODUCTION

liberated by the reaction is usually manifested (and measured) as heat. This is a particular case of the general principle of the conservation of energy, which was clearly established by Joule in 1850 as the result of his work on the mechanical equivalent of heat. The law of the conservation of energy may be stated in the following terms. In an isolated system the sum of the various kinds of energy is constant. If a quantity of one form of energy disappears, an equal quantity of some other form of energy makes its appearance. The statement amounts to this: if A unites with B to form C with the evolution of n units of energy, then n units of energy will be required to reverse the change and reproduce A and B from C.

Atoms and Molecules. We have seen above that the divisibility of matter is not infinite. A point is at length reached when further subdivision must result in producing substances with different properties. The smallest particle of marble which shews all the properties of marble is the *molecule,* a term which is defined as the smallest particle of matter which is capable of an independent existence. Subdivision of the molecule of marble produces smaller molecules of substances which are not marble.

An indication of the order of magnitude of these ultimate particles has been obtained in the following way.

A fragment of camphor placed on the surface of water appears to be in rapid motion, doubtless due to local alterations of surface tension, but a thin film of oil on the water prevents this movement. In a series of experiments Lord Rayleigh (1890) determined the minimal thickness of the layer necessary to stop the motion, which he found to be 1.6×10^{-7} cm. Now it cannot be assumed that the oil layer was only one molecule thick, but it cannot have been *less* than one, therefore this value represents the superior limit of molecular dimension, which is to say that

the diameter of a molecule of the oil cannot be greater than sixteen millionths of a millimetre.

Lord Kelvin's estimate (1870) places the superior limit of molecular dimension at 10^{-8} cm. and the inferior at 5×10^{-10} cm. His illustration is given in the following terms. 'Imagine a raindrop, or a globe of glass as large as a pea, to be magnified up to the size of the earth, each constituent molecule being magnified in the same proportion. The magnified structure would be coarser grained than a heap of small shot, but probably less coarse grained than a heap of cricket balls.' More recent estimates assign somewhat greater values than these.

It has been shewn that common salt is a compound of the elements sodium and chlorine. The smallest particle of common salt which can have an independent existence, the molecule of common salt, is therefore capable of further subdivision; but this subdivision results in the realization of a second and smaller type of ultimate particle, namely, the smallest particle of an element that can take part in a chemical change. This latter kind of ultimate particle is termed the *atom.*

The conception of an atomic structure of matter dates back to very early times. It was revived by Dalton in his *New System of Chemical Philosophy* published in 1808. Dalton however did not draw a clear distinction between the ultimate particle of an element and the ultimate particle of a compound, which latter he spoke of as a 'compound atom.' In other words, Dalton's ideas did not extend to the modern conception of the fundamental difference between the molecule and the atom. The necessity of drawing such a distinction was first recognized by Avogadro who in 1811, introduced and defined the idea of the molecule in order to explain certain experimental results observed by Gay-Lussac on the combination of gases

by volume. (See Chap. II.) We cannot therefore speak of
an atom of a compound such as marble. The term would
be meaningless, since the smallest particle of marble which
is capable of a separate existence consists of three different
kinds of atoms.

The molecule and the atom are identical in some few
cases. Argon and helium, for example, have mon-atomic
molecules, but as is shewn later, the molecules of nitrogen,
chlorine, hydrogen, etc., consist each of two atoms firmly
united in some way which we do not as yet clearly under-
stand.

Up to the end of the nineteenth century the atom was
considered to be indivisible and unalterable, and even at
the present time it can still be considered as such, so far as
chemical reactions are concerned. The existence of sub-
atomic particles known as electrons was however placed
beyond doubt by Sir J. J. Thomson (1897). Electrons, which
can be considered as 'atoms' of negative electricity, are
universal constituents of all atoms. Further, elements which
are radio-active have unstable atoms, the most notable of
which is the element radium. Ramsay and Soddy (1904)
shewed that the atom of the element radium undergoes
spontaneous disintegration, giving rise to atoms of helium
and other elements. Atomic disintegration is a process
which is independent of experimental conditions, and takes
place at a definite rate which is fixed for each unstable
element; that is, the rate of breaking down can be neither
hastened nor retarded by any method known to us. Still
more recently Sir E. Rutherford (1922) has been successful
in artificially disintegrating in a minute degree the atoms
of certain elements, notably those of nitrogen, into atoms
of helium and hydrogen.

A characteristic property of atoms as formerly under-
stood was the absolute identity of all those of the same