XXXI.—*On the Atomic Theory.*

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THERE are considerable differences, not to say discrepancies, between the statements made by different chemists on the subject of the atomic theory. In some text books of the science the replacing values of so-called equivalent weights of elements are described as being the atomic weights of those elements, while in the same and in other books, statements are made respecting the principles of the determination of atomic weights which lead to different numbers from those representing the replacing values.

It sometimes happens that chemists of high authority refer publicly to the atomic theory as something which they would be glad to dispense with, and which they are rather ashamed of using. They seem to look upon it as something distinct from the general facts of chemistry, and something which the science would gain by throwing off entirely.

Thus, in one book we find the statement:—"It appears from this that 2×8 , or 16 parts of oxygen is the smallest quantity of oxygen that can be supposed to enter into the reaction just considered, if we would avoid speaking of fractions of equivalents; and we shall find hereafter that the same is true with regard to all other well defined reactions in which oxygen takes part. Hence, this quantity of oxygen, 16 parts by weight (hydrogen being the unit), is called an indivisible weight, or atomic weight, or one atom of oxygen."

And again:—

"The question whether matter is infinitely divisible, or whether its divisibility is limited, remains, at the present day, in the same state as when it first engaged the attention of the Greek philosophers, or perhaps that of the sages of Egypt and Hindostan long before them."

Another author says:—

"The law of multiple proportions being founded on experimental facts, stands as a fixed bulwark of the science, which must ever remain true; whereas the atomic theory by which

we now explain this great law may possibly, in time, give place to one more perfectly suited to the explanation of new facts."

When we refer to the author's enunciation of this great law, in a paragraph which is referred to as containing a statement of the law, we find it stated that in the compounds of oxygen and nitrogen the oxygen is in the proportion of 1, 2, 3, 4, 5 to one and the same quantity of nitrogen, and that no compounds exist containing any intermediate quantity of oxygen.

Another distinguished chemist also lays down that the atomic weight of each element is made to agree as far as possible with the three following conditions :—

1st. The smallest proportion by weight in which the element enters into, or is expelled from a chemical compound, the weight of hydrogen so entering or leaving a chemical compound being taken as unity.

2nd. The weight of the element in the solid condition, which, at any given temperature, contains the same amount of heat as seven parts by weight of lithium at the same temperature.

3rd. The weight of the element which, in the form of gas or vapour, occupies, under like conditions of temperature and pressure, the same volume is one part by weight of hydrogen.

Now, if we endeavour to determine according to these rules the atomic weight of phosphorus, we may compare the quantity of hydric chloride containing one part by weight of hydrogen with that weight of phosphoric chloride PCl_5 , which contains the same weight of chlorine, viz., $\frac{\text{P}}{5}\text{Cl}$. In this latter com-

pound, $\frac{\text{P}}{5}$ or 6.2 parts of phosphorus, has entered into combination with 35.5 parts by weight of chlorine, instead of one part by weight of hydrogen, which unites with 35.5 of chlorine in forming hydric chloride. 6.2 is, therefore, according to this rule, taken by itself, the atomic weight of phosphorus. We should not be justified in adopting the weight of phosphorus derived from an analysis of the lower chloride, PCl_3 , because the rule directs us to take the smallest proportion, and the proportion of phosphorus in PCl_5 is smaller than in PCl_3 .

If instead of the chloride we take the acid P_2O_5 , or a phosphate such as PO_4Na_3 , and compare them respectively with $5\text{H}_2\text{O}$ and $\text{H}_5\text{Na}_3\text{O}_4$, we obtain the same atomic weight for phosphorus, 6.2. By the second rule (if we interpret it as

meaning the capacity for heat between two given temperatures), we find that seven parts of lithium, if heated from 0°C. to 1°C. , absorb 6.59 degrees of heat, while one part by weight of solid phosphorus absorbs 1885. We have, consequently, the atomic weight 34.9, which, considering the nature of the determinations, may be accepted as a reasonable approach to the atomic weight 31, now adopted by chemists.

According to the third rule, we obtain for phosphorus the atomic weight 62, inasmuch as P^6 occupy in the state of vapour under like conditions the same volume as H^2 .

In the case of all elements, the first rule gives the smallest weight. Thus, calcium, in the calcic nitrate, $\text{Ca}(\text{NO}_3)_2$, replaces hydrogen in hydric nitrate in the proportion of 20 to 1. Oxygen in carbonic oxide replaces hydrogen by marsh-gas in the proportion of 4 to 1; in most of its compounds in the proportion of 8 to 1. Nitrogen in sal ammoniac replaces 5 atoms of hydrogen in the molecules 4HH and HCl , in the proportion of $2\frac{1}{2}$ to 1.

Another distinguished author describes—

“The law of definite proportions;

“The law of multiple proportions; and

“The law of equivalent proportions.”

He subsequently describes the “hypothesis of the atomic constitution of matter,” the word hypothesis being no doubt intended to indicate an opinion on his part that the atomic constitution of matter is open to more doubt than the so-called law of multiple proportions, &c. Again, in another able book we find it stated that to each element is assigned a “particular number, termed its proportionate number, which expresses the least indivisible proportion of the element that is found to enter into a combination,” hydrogen being taken as the unit,—a very intelligible description of the atomic weight of the element. In illustration of these so-called proportional numbers, the author gives Gerhardt’s table of atomic weights, which were in use at the time his work was written. He avoids the word atom in describing his indivisible proportions, although later on he occasionally falls into the use of the common words “atomic weight,” and atom. When he comes to explain molecules and equivalents, there is no more talk about proportional numbers.

It certainly does seem strange that men accustomed to con-

sult nature by experiment so constantly as chemists do, should make use of a system of ideas of which such things can be said. I think I am not overstating the fact, when I say, that, on the one hand, all chemists use the atomic theory, and that, on the other hand, a considerable number of them view it with mistrust, some with positive dislike. If the theory really is as uncertain and unnecessary as they imagine it to be, let its defects be laid bare and examined. Let them be remedied if possible, or let the theory be rejected, and some other theory used in its stead, if its defects are really as irremediable and as grave as is implied by the sneers of its detractors.

But if the theory be a general expression of the best ascertained relations of matter in its chemical changes, the only general expression which those relations have as yet found, and be hypothetical only in so far as it presupposes among unknown substances relations analogous to those discovered among those which are known, then it must be classed among the best and most precious trophies which the human mind has earned, and its development must be fostered as one of the highest aims and objects of our science.

It cannot be desirable to leave the question on its present footing; and if we have any opportunity of bringing the existing doubts and misgivings to a distinct issue, it cannot be right to delay such a consummation.

Such are the feelings which induced me to accept the invitation with which the Council has honoured me, and to bring before you an analysis of the evidence of the present atomic theory, as I conceive it to exist dispersed in the minds and among the hands of chemists at the present time.

I propose to consider the subject under three successive headings.

1st. The proportions by weight in which elements replace one another, or their so-called equivalent weights, and the multiples of those proportions.

2nd. The units of chemical action, or the so-called molecules.

3rd. Atomic values.

Equivalent Weights.

Quantitative analyses have shown that the weight of oxygen which combines with one part by weight of hydrogen to form water, is eight times as great as that of the hydrogen; that the

weight of chlorine which combines with one part by weight of hydrogen to form hydric chloride is 35.5 times as great as that of the hydrogen. Whenever we displace oxygen from water by chlorine, forming hydric chloride, we find that for every eight parts by weight of oxygen so displaced, thirty-five and a half parts by weight of chlorine are taken up; and whenever we perform the opposite substitution, viz., displace chlorine from hydric chloride by oxygen so as to form water, we find the inverse ratio, viz., eight parts by weight of oxygen, replacing 35.5 parts by weight of chlorine. These numbers, 8 and 35.5, represent the relative weights in which oxygen and chlorine combine with the unit weight of hydrogen, and they are called the equivalent weights. The decomposition of ammonia by heat yields nitrogen gas and hydrogen in the proportion of $4\frac{2}{3}$ parts by weight of nitrogen to one of hydrogen, and in like manner the decomposition of marsh-gas yields three parts by weight of carbon to every one of hydrogen. Moreover, when we displace nitrogen from ammonia by chlorine, forming hydric chloride, we find that chlorine takes the place of the nitrogen in the proportion of 35.5 parts to $4\frac{2}{3}$; and in like manner when chlorine displaces carbon from marsh-gas forming hydric chloride, it does so in the proportion of 35.5 parts to 3 of carbon. So also when oxygen replaces carbon in marsh-gas forming water, we find that eight parts of oxygen take the place of three of carbon.

We have accordingly, from the comparison of these hydrogen compounds,—

35.5	as the equivalent weight of chlorine,		
8	“	“	oxygen,
$4\frac{2}{3}$	“	“	nitrogen,
3	“	“	carbon.

But chlorine can be made to replace the hydrogen in marsh-gas by successive steps, and we find that it does so in the proportion of 35.5 parts by weight to one part of hydrogen, and in the product so formed hydrogen can be made to replace chlorine, reproducing marsh-gas always in the proportion of one part by weight to 35.5 of chlorine.

Upon this and similar evidence we attribute to hydrogen, in relation to chlorine, the equivalent weight 35.5, and by so doing we extend our meaning of the word equivalent. 35.5 parts of chlorine are equivalent to 8 of oxygen, because they combine

with the unit weight of hydrogen; and 35.5 of chlorine are equivalent to one of hydrogen, because the elements replace one another in that proportion by weight in their compounds. In like manner oxygen can be made to replace hydrogen in ammonia and in marsh-gas, forming nitrous acid and carbonic acid respectively. It there reacts in the proportion of the same equivalent weight which it has in relation to chlorine. Nitrogen and carbon can, partly by such-like direct reactions, and partly by indirect reactions, be proved to replace hydrogen in the proportion of the same weights in which they combine with it. So that the equivalent weights of chlorine, oxygen, nitrogen, and carbon are the weights of those elements capable of combining (directly or indirectly) with the unit weight of hydrogen, or of replacing the unit weight of hydrogen.

Several other metals have been found to be analogous to hydrogen, viz., lithium, sodium, potassium, silver, &c., and to replace it in combination with chlorine or oxygen in the proportions corresponding to the following equivalent weights:—Lithium 7, sodium 23, potassium 39, silver 108, &c.; and in like manner bromine and iodine have been found analogous to chlorine, and to replace it in equivalent weights corresponding to 80 of bromine and 127 of iodine.

In the compounds ClH , ClK , BrH , BrK , ClAg , ICl , BrLi , OH_2 , OHK , ONa_2 , OClH , NH_3 , NH_2K , NK_3 , CH_4 , CH_3Cl , CH_2Cl_2 , CHCl_3 , CO_2 , the elements are contained in proportions corresponding to the equivalent weights above mentioned. But there are other compounds in which they occur in different proportions; thus iodine combines with chlorine in the proportion of 127 to 35.5, and also in the proportion of $42\frac{1}{2}$ to 35.5; nitrogen also combines with hydrogen and chlorine in the common compound, sal-ammoniac, and in the other compounds like it, in the proportion of $2\frac{1}{2}$ to every one of hydrogen or the equivalent weight of another element. Carbon combines with oxygen in a second proportion in carbonic oxide, viz., that of 3 to 4, and with hydrogen in many other proportions besides that which occurs in marsh-gas: viz., in methyl, four parts of carbon to one of hydrogen, in olefiant gas, six parts of carbon to one of hydrogen, and in acetylene, twelve parts of carbon to one of hydrogen, besides many others intermediate between these.

Now, Dalton knew the two oxygen-compounds of carbon, besides marsh-gas and olefiant gas. He represented the oxide

as containing one equivalent of oxygen weighing 8, with one of carbon weighing 6; the acid as containing twice 8 parts by weight of oxygen, combined with 6 of carbon.

In like manner, he considered olefiant gas as a compound of one equivalent of carbon, weighing 6, with the unit of hydrogen, marsh-gas as 6 of carbon with two units of hydrogen.

Some other compounds he found, partly by his own analyses, partly by analyses made by other chemists, to contain their elements in proportions approaching to simple multiples of certain weights peculiar to those elements respectively. He explained this coincidence by representing compounds as built up of atoms of their elements in various proportions to one another.

Many other elements are now known to combine in various proportions, which may be so represented, and it is common to refer to the fact which Dalton explained by atoms, as the law of multiple proportions.

It is desirable that we analyse the evidence which is now before chemists of these multiple proportions, and further their connection with the atomic theory.

The analyses known to Dalton have by the progress of chemistry been, for the most part, replaced by others more accurate and more trustworthy, and some of the numbers representing the combining proportions of elements, have undergone considerable modifications in consequence of our improved methods of observation; but both Dalton and we agree in one respect, viz., that taking the best numbers we can get by analyses, we calculate the composition of every compound, on the assumption that it must be built up of integral multiples of certain numbers belonging to the elements respectively; and it must be admitted as a *primâ facie* confirmation of the justice of this assumption, that the more perfect our methods of observation become, and the more carefully they are applied, the more nearly do our experimental results agree with multiple proportions of such numbers.

In the case of compounds of very simple constitution, the agreement between our experimental results and the theory of multiple proportions is so close, that it would be unreasonable to attribute the coincidences to chance. But, on the other hand, the progress of research leads frequently to the discovery of compounds of which the constituents are present in less simple

proportions, and others again in which the proportion can be represented only by high numbers. And in many cases the difference between the numbers corresponding to the formula which is admitted, and the numbers corresponding to some other formula, is not greater than the unavoidable errors of experiment. So that analysis does not decide which of the formulæ is the true one, nor does it furnish an argument in favour of any formula. Thus a high term of the marsh-gas series, such as $C_{27}H_{56}$, cannot be analysed with certainty. The numbers found by combustion were—

C 85·5

H 14·9.

The formula $C_{27}H_{56}$ requires C 85·27 H 14·73,	the formula $C_{26}H_{54}$ requires C 85·25 H 14·75,	and requires $C_{27}H_{54}$ C 85·71 H 14·29
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The actual result of observation agrees with none of these formulæ, yet, in examining it, chemists assume that it ought to agree with some such formula. They select the most probable, and attribute to errors of observation the divergence from it.

The most important evidence brought to bear on the composition of this body was of two kinds: first, an examination of a silver-salt, formed from the product of its cautious oxidation, and containing the following percentages, viz. :—

C 62·36

H 10·31

Ag 20·92,

which approach more nearly to the numbers—

C 62·66

H 10·25

Ag 20·9,

required by the formula $C_{27}H_{53}AgO_2$, than to any other probable formula; and, secondly, a study of the action of bromine upon it proving that it was a marsh-gas and not an olefant gas, like that last mentioned.

The hydrocarbon itself approached nearer in composition to the formula $C_{27}H_{56}$ than to any other, and the study of two of its reactions thus agrees in indicating that formula for the original hydrocarbon as more probable than any other atomic formula.

It would be quite correct to say that *some* elements are found capable of uniting with one another in the proportion of simple multiples of certain weights, and not in intermediate proportions. Thus carbon unites with oxygen in the proportion of 12 parts of carbon to 16 of oxygen, and also in the proportion of 12 of carbon to 2×16 of oxygen. If we take less oxygen than 16 parts to every 12 of carbon, some of the carbon remains as such uncombined, and no compound of the two elements has ever been got with less oxygen than 16 parts to every 12 of carbon. But if we take more and more oxygen in proportion, we find that carbon can unite with it till it has got 2×16 parts. Yet we do not admit that it unites in all proportions intermediate between 16 and 2×16 , for by examining these products, formed by adding more and more oxygen to the compounds of 16 grammes with 12 carbon, we find that they are mixtures of carbonic acid and carbonic oxide; the former being rapidly soluble in aqueous potash, whereas the latter remains undissolved.

But the theory of multiple proportions is not limited in so modest a manner. It is applied to all elements and to all compounds of them, in spite of the fact that the usual results of observation require straining to agree with any multiple formula, and the immense majority of substances have not as yet been reduced by the process to any definite formulæ whatever. The very great majority of mineral and of organic substances which we meet with on the surface of the earth, have not been proved to have a composition agreeing with any formula.

When multiple proportions are spoken of, it is not usually explained whether multiples of equivalent weights are meant, or multiples of the atomic weights of the elements. It is sometimes asserted that we have a law of multiple proportions, which is a direct representation of experimental facts, whereas the atomic theory is a hypothesis, and independent of such law. Those who make this statement must be understood to refer to multiples of equivalent weights, and not to multiples of atomic weights; for if, as they assert, atomic weights are hypothetical, then any relation between the multiples of atomic weights are only multiples of hypothetical numbers, and cannot have greater certainty than the atomic weights themselves.

If we knew the empirical proportions of elements, and did

not believe in atoms, we should describe carbonic oxide as the compound of three parts of carbon with four of oxygen, and carbonic acid as the compound of three parts, by weight, of carbon with eight of oxygen. The hydrocarbons mentioned would be described as follows, viz.: marsh-gas, as a compound of three parts of carbon with one of hydrogen; olefiant gas, a compound of six parts of carbon with one of hydrogen; methyl, a compound of four parts of carbon with one of hydrogen; ethyl, a compound of twenty-four parts of carbon with five of hydrogen; and so on. We should probably use the simplest entire numbers corresponding to the actual proportion between the elements; but we should not use the higher numbers standing to one another in the same proportions which are introduced by the atomic theory.

It is quite true that the elements of some simple, well-known compounds are shown by analysis to be present in proportions corresponding to simple multiples of a particular weight belonging to each of them respectively; but in compounds of less simple constitution, no such relation is obvious. The analysis of most organic bodies does not suggest any simple proportion between the numbers of those weights of their constituents, and it sometimes suggests a relation which is not the true one. Thus, the only simple representation of the results of analyses of the high term of the marsh-gas series above mentioned, would be to describe it as containing six parts, by weight, of carbon to one of hydrogen. The actual process by which we establish the composition of such complex bodies is by *assuming* that the composition of each of them must correspond to entire multiples of the atomic weights of their elements, and by treating as errors of observation any divergence between the proportions discovered by analysis and such atomic proportions.

It is not easy to judge of the evidence of one part of a system by itself. The doctrines of equivalence, of molecular weights, and of atoms mutually support one another, and are habitually used by chemists in connection with one another. Our present task is to examine the doctrine of multiple proportions of equivalents; first, in respect of the evidence upon which it rests; secondly, in respect of the proof which it affords, if any, of the existence of atoms.

The second question may be best investigated in the form of a comparison between the atomic method of multiples, and

what I may be permitted to call the tomic method of sub-multiples; carbonic acid is represented in the atomic plan as containing twice as much oxygen as is contained in carbonic oxide; whereas, on the other plan, it may be represented as differing from carbonic oxide by containing half as much carbon as is contained in the oxide. It is true that by combining oxygen with carbonic oxide we get carbonic acid; but it is equally true that by combining carbon with carbonic acid we obtain carbonic oxide. As far as the proportion of the elements is concerned, we have no better right to suppose that the carbon is indivisible, and that the acid contains twice as much oxygen as the oxide, than we have to suppose that the carbon is divisible, and that half of the carbon is taken out of carbonic oxide in forming carbonic acid.

We cannot be too careful in considering this fact, for many important consequences follow from it. Our proposition relates to an undefined quantity of carbonic oxide. It is known that by combining four parts, by weight, of oxygen with seven parts by weight of carbonic oxide, we get exactly eleven parts of carbonic acid; or, what is the same thing from another point of view, that if we take away four parts of oxygen from eleven of carbonic acid, we get seven of carbonic oxide. It is also known that if we take away 1.5 parts of carbon from 7 of carbonic oxide, we get 5.5 parts of carbonic acid; and, reciprocally, that if we add 1.5 parts of carbon to 5.5 of carbonic acid, we get 7 of carbonic oxide. These parts by weight may be tons, or pounds; or ounces, or grains, or any other actual experimental weight. A philosopher disbelieving in the existence of atoms, would point out that whereas the divisibility of matter is infinite, we find that by the chemical processes available for the removal of carbon from carbonic oxide, the carbon divides into equal portions, one remaining with the oxygen, the other leaving it; and his statement that this half of the carbon is added on again when the process is reversed, is as consistent with the evidence as that of the believer in atoms, who asserts that in forming carbonic acid, oxygen is added in quantity equal to the oxygen in the carbonic oxide, while the formation of carbonic oxide from the acid consists in taking away half the oxygen. What has been here said of the proportions between the elements in carbonic oxide and carbonic acid may be said with equal force

of the proportions between the elements contained in other compounds, such as the following:—

FeCl_2 , FeCl_3 , CH_4 , CH_3 , CH_2 , C_2H_3 , CH , NH_3 , NH_4Cl , SH_2 , SCL , OH_2 , OH , PI_2 , PCl_3 , PCl_5 , ICl , ICl_3 , SiCl_4 , SiF_6K_2 , PtCl_2 , PtCl_4 , PtCl_6K_2 , BF_3 , BF_4K , AuCl , AuCl_3 , AuCl_4Na , CrCl_2 , CrCl_3 , CrF_6 , SnCl_2 , SnCl_4 , HgCl , HgCl_2 , CuI , CuCl_2 .

If we examine consistently with the principles above adopted, the equivalent weight of each element contained in these compounds, we find that we must describe it as the weight which in any compound is combined with the unit of hydrogen, or might be replaced by it. This is easily obtained by dividing the number represented by the atomic symbol by the number of equivalents of the hydrogen or chlorine families with which it is combined.

We thus obtain the values :

$\frac{\text{Fe}}{2}$, $\frac{\text{Fe}}{3}$, $\frac{\text{C}}{4}$, $\frac{\text{C}}{3}$, $\frac{\text{C}}{2}$, $\frac{2\text{C}}{3}$, $\frac{\text{C}}{3}$, $\frac{\text{N}}{3}$, $\frac{\text{N}}{5}$, $\frac{\text{S}}{2}$, $\frac{\text{S}}{2}$, $\frac{\text{O}}{2}$, $\frac{\text{O}}{2}$, $\frac{\text{P}}{2}$, $\frac{\text{P}}{3}$, $\frac{\text{P}}{5}$, $\frac{\text{I}}{3}$, $\frac{\text{I}}{4}$, $\frac{\text{Si}}{4}$,
 $\frac{\text{Si}}{8}$, $\frac{\text{Pt}}{2}$, $\frac{\text{Pt}}{4}$, $\frac{\text{Pt}}{8}$, $\frac{\text{B}}{3}$, $\frac{\text{B}}{5}$, Au , $\frac{\text{Au}}{3}$, $\frac{\text{Au}}{5}$, $\frac{\text{Cr}}{2}$, $\frac{\text{Cr}}{3}$, $\frac{\text{Cr}}{6}$, $\frac{\text{Sn}}{2}$, $\frac{\text{Sn}}{4}$, Hg ,
 $\frac{\text{Hg}}{2}$, $\frac{\text{Cu}}{2}$.

I have taken only a few of the well known compounds, yet among them there are ten elements, each of which has two distinct equivalent weights, four of the elements have got three equivalent weights each, and another (carbon) is shown to have five different equivalent weights. It might easily be shown to have many more.

Now it is interesting to observe that whenever examples are given of the supposed law of multiple proportions, Chemists take not these fractional expressions representing equivalents, but usually the atomic symbols themselves. They describe, in fact, *atoms* as occurring thus combined with one another in the proportions of entire multiples of their weight; in fact, the so-called law of multiple proportions has no existence apart from the atomic theory; those who adopt it seem not to be aware that they are using the notion of atoms, or else they are shy of mentioning it.

The fact that two elements, such as carbon and oxygen, are

capable of combining in more than one proportion is in reality (when we consider it by itself) quite as much an argument against the atomic theory as an argument in favour of it. That the carbon in carbonic oxide can be divided in the proportion of $\frac{1}{2}$, or the oxygen can be multiplied in the proportion of 2 to 1, are equally true statements of the proportion. If oxygen could neither take more nor less carbon than in the proportion of three parts by weight to every four of oxygen, we could say with certainty that that proportional weight of carbon cannot be divided, or in other words that it is an atomic proportion; but the existence of the two compounds, although not inconsistent with the atomic theory, points as much to proportional divisibility of carbon as to proportional multiplicability of oxygen.

When one of those who profess to disbelieve in the atomic theory has ascertained by analysis the percentage composition of a compound, and wants to find its formula, he divides the percentage weight of each element by its atomic weight. He seeks for the smallest integral numbers which represent the proportion of atoms, and he attributes to impurity of his sample or to errors of analysis any deviation from the atomic formula thus obtained. He looks to the reactions of the body for aid in constructing his atomic formula, and controls his analyses by considerations derived from well established reactions, but whenever he is led by any of these considerations to a formula which contains a fraction of any atomic weight, he takes a multiple of the formula sufficiently high to be entirely free from such fractions. In no case does he reason on a basis independent of the atomic theory.

Existence of Molecules.

The atomic theory led to the discovery of molecules. Chemists saw in the phenomena of combination in multiple proportions, processes which were in accordance with their pre-conceived belief in atoms, and they studied combining proportions from the point of view of atoms. They acted on the assumption that each element consists of small indivisible particles of like nature; that the atoms of each element are different in many chemical properties, and usually in weight, from those of every other element; that the unlike atoms combine

together in various relative numbers to form clusters, or so-called molecules, every pure compound consisting of such molecules, each one like the rest, but differing from the molecules of every other compound. Thus a given quantity of carbonic oxide was supposed to consist of an aggregate of molecules, each one composed of an atom of carbon united with an atom of oxygen; carbonic acid, to consist of molecules, each one built up of three atoms, viz., one of carbon, and two of oxygen. In calculating the molecular weight of any compound from the ascertained proportion of its elements, they assumed that each molecule must contain at least such a number of atoms of each of its elements as would, when multiplied by the atomic weight of the respective elements, represent the actual proportion by weight in which the elements had combined. Thus 44 parts by weight of carbonic acid have been found to contain 32 of oxygen, and twelve of carbon. Two atoms of oxygen, each weighing 16, with one atom of carbon weighing 12, must be contained in the smallest existing particle of carbonic acid.

Ammonia contains hydrogen and nitrogen in the proportion of 3 parts of the former to 14 of the latter. 3 atoms of hydrogen, each weighing 1, with one atom of nitrogen weighing 14, represent the simplest molecular constitution corresponding to that proportion of the elements. The molecule of olefiant gas, in like manner, must contain at least one atom of carbon with two atoms of hydrogen, while that of marsh gas contains at least one of carbon with four of hydrogen.

An acid hydric salt, the tartrate, was found by analysis to contain carbon, hydrogen, and oxygen, in proportions corresponding to the minimum formula $C_2H_3O_3$. When neutralised by potash, its solution yielded a potash salt corresponding to the minimum formula $KC_2H_2O_3$, and it is known that the weight of hydric sulphate indicated by the formula $\frac{SO_4H}{2}$ or $\frac{S}{2}O_2H$ would react on the same weight of potash forming a neutral salt. This relation between the tartrate and sulphate may be expressed by saying that 75 parts by weight of the tartrate are equivalent to 49 parts by weight of the sulphate.

In like manner a compound of basic properties, called quinia, was found to contain carbon, hydrogen, nitrogen, and oxygen, in proportions which can be represented by the minimum formula $C_{10}H_{12}NO$. It was found that the base unites with hydric

chloride, and forms a platinum-salt, analogous to the salt formed by ammonia, and known to have the composition $\text{PtCl}_6\text{H}_2(\text{NH}_3)_2$. The weights of these bases denoted by the formulæ NH_3 and $\text{C}_{10}\text{H}_{12}\text{NO}$, are accordingly equivalent to one another in the sense in which we have hitherto used that word. It is well known that, in the actual development of our knowledge of these relations, the notion of equivalence sprang up among acids and bases, and was extended from them to elementary bodies.

It is interesting and instructive to observe that, for a considerable time, the proportions in which compounds react on one another were represented by formulæ according to the atomic theory as it then prevailed, which recorded the empirical proportions of the constituents, but were not correct or consistent representations of the molecular weights. These labours served to collect an immense amount of evidence for the establishment of molecular weights, but the end was not distinctly in view, and the only rational guide was the imperfect atomic theory then existing.

Thus the great Berzelius, the master spirit of that period, used formulæ which in our system of atomic weights may be thus rendered:

Water	H_2O
Potash	K_2O
Potassic hydrate	$\text{H}_2\text{OK}_2\text{O}$
Nitric acid.....	N_2O_5
Potassic nitrate	$\text{K}_2\text{ON}_2\text{O}_5$
Hydro-potassic sulphate	$\text{H}_2\text{OSO}_3\text{K}_2\text{OSO}_3$
Ether.....	$\text{C}_4\text{H}_{10}\text{O}$
Alcohol	$\text{C}_4\text{H}_{10}\text{OH}_2\text{O}$
Carbonic acid	CO_2
Carbonic chloride.....	CCl_4
Phosgene	CO_2CCl_4
Chloro-sulphuric acid	$2\text{SO}_3 + \text{SCl}_6$
Chloro-chromic acid.....	$2\text{CrO}_3 + \text{CrCl}_6$
Bismuthic oxychloride.....	$\text{Br}_2\text{O}_3\text{BrCl}_3$
Hydric chlor-acetate ($\text{C}_2\text{Cl}_3\text{HO}_2$)..	$\text{C}_2\text{O}_3\text{C}_2\text{Cl}_6\text{H}_2\text{O}$
Hydric oxamate ($\text{C}_2\text{NH}_3\text{O}_3$)	$\text{C}_2\text{O}_3\text{H}_2\text{OC}_2\text{O}_2\text{N}_2\text{H}_4$
Bichlorinated ether ($\text{C}_2\text{H}_3\text{Cl}_2$) ₂ O..	$2\text{C}_4\text{H}_6\text{Cl}_6\text{C}_4\text{H}_6\text{O}_3$.

Some of his atomic weights were inconsistent with our mole-

cular formulæ. Thus hydrogen, chlorine, nitrogen, and some other elements, he really treated as having atomic weights twice as great in relation to oxygen as we now consider them to have. For his couple of volumes of hydrogen, denoted by the symbol H , were not allowed to separate from one another, so that his formula HO for water was in its uses similar to the formula HO , and analogous to his formula for potash, which was written KO .

The theory of radicals did much towards classifying compounds. The names ammonium and cyanogen were given to groups of elements which exhibited analogies with single elements. Ethyl was another radical which did admirable service; and benzoyl afforded an instance of a radical of another kind.

The theory of organic radicals is in reality an extension of the atomic theory, and it was needed as a step towards the proof of that theory.

The equivalent proportions of elements, and the multiples of those proportions in which they combine, afforded no proof of the existence of atoms, but they led to the discovery of compound atoms analogous to undecomposed atoms. At the same time, many of these organic radicals, although exhibiting the closest analogy with elements, are known to be only capable of existing under certain conditions, and are easily burnt or decomposed.

It was a great step to extend the use of the word atom to groups of elements known to hold together only under certain limited conditions. For by including in one common term, atom, the smallest particles of the elements, and the smallest particles of these compounds which behave like elements, we deprive the word atom of the only objectionable peculiarity of which it might have been accused. It is no longer an absolute term; and in its application to the elements it denotes the fact that they do not undergo decomposition under any conditions known to us. If anybody use the word in its absolute sense in its present applications, he is guilty of a manifest inconsistency.

It must not, however, be supposed that the existence of groups of elements, which perform functions analogous to those of single elements, is any proof of the existence of atoms, for compounds like $\text{C}_2\text{H}_5\text{Cl}$, $\text{C}_{16}\text{H}_{33}\text{Cl}$, NH_4Cl , $\text{C}_6\text{H}_7\text{Cl}$, &c., may be

represented as containing submultiples of the less numerous atoms, just as NH_3 can be represented as $\frac{\text{N}}{3}\text{H}$, or CO_2 as $\frac{\text{C}}{2}\text{O}$.

One of the most fruitful ideas in the work of establishing the molecular constitution of compounds, was the idea of types—and the correlative idea of substitution. If we maintain unity of type, the knowledge of a few molecular formulæ serves as a guide to many others. Thus, if we take water as H_2O , alcohol can be proved by normal substitutions to be $\text{C}_2\text{H}_6\text{O}$. We find that phosgene reacts upon alcohol according to the equation $\text{C}_2\text{H}_5\text{OH} + \text{COCl}_2 = \text{C}_2\text{H}_5\text{OCOCl} + \text{HCl}$, whereas, if the molecular formula of Berzelius for phosgene were true, the first action would be $\text{C}_2\text{H}_6\text{O} + \text{C}_2\text{O}_2\text{Cl}_4 = \text{C}_2\text{H}_5\text{OC}_2\text{O}_2\text{Cl}_3 + \text{HCl}$; the second action would be the formation of the compound $\text{C}_2\text{O}_2\text{Cl}_2\text{O}_2(\text{C}_2\text{H}_5)_2$.

The process is a mere replacement of chlorine by $\text{C}_2\text{H}_5\text{O}$, forming a compound of the molecular formula $\text{C}_3\text{H}_5\text{ClO}_2$, instead of one of double that formula. Now, having found that as small a weight as COCl_2 can take part in one distinct reaction, we know that the molecular weight is not greater than that. Again, the molecular formula of water being known, we have the reaction $\text{SO}_2\text{Cl}_2 + \text{H}_2\text{O} = \text{SO}_3\text{HCl} + \text{HCl}$, and $\text{SO}_3\text{HCl} + \text{H}_2\text{O} = \text{SO}_4\text{H}_2 + \text{HCl}$, which establish for chlorosulphuric acid the maximum formula SO_2Cl_2 , and for hydric sulphate the formula SO_4H_2 . So also the hydric chloracetate reacts on a molecule of potassic hydrate thus, $\text{C}_2\text{HCl}_3\text{O}_2 + \text{HOK} = \text{C}_2\text{KCl}_3\text{O}_2 + \text{H}_2\text{O}$. In these reactions there are alternative explanations: thus, if phosgene is $\text{C}_2\text{O}_2\text{Cl}_4$, then the ether $\text{C}_3\text{H}_5\text{ClO}_2$ must have double that molecular weight: for the reaction is a regular double decomposition, in which no indication of increase or diminution in the number of molecules takes place.

With the chloro-sulphuric acid there is a similar alternative. $\text{S}_3\text{O}_{12}\text{H}_6$ must be the molecular formula of hydric sulphate, if $\text{S}_3\text{O}_6\text{Cl}_6$ be that of the chloro-acid: for the above reaction is as normal as possible, and, moreover, we can recover the chloro-acid from the hydric salt by a couple of steps as normal, as far as the sulphate is concerned:—

In order to judge of the evidence of molecular weights obtained by a study of chemical reactions, we ought to consider, on the one hand, what properties must belong to compounds built up of atoms, and, on the other hand, what properties might belong to them if there were no limit to the divisibility of each kind of elementary matter.

Now the first and most essential characteristic of every molecule is that it possesses a weight equal at least to the sum of the atomic weights of its constituents, in such number as represents the simplest proportion consistent with a correct analysis. Thus a compound containing iron and oxygen in such proportions by weight as correspond to three atoms of oxygen to every two atoms of iron, must have at least as great a molecular weight as $2 \times 55 + 3 \times 16$. On the other hand, if iron and oxygen, when combined in this proportion, were infinitely divisible, one would be able to get smaller weights of the oxide to take part in reactions, than such as are 160 times as heavy as the unit weight of hydrogen. We can replace the oxygen in this oxide by chlorine; we can combine it more or less fully with sulphuric acid, or with other acids; we can decompose these salts by other compounds; we can combine them with other salts; and we can compare each of these products with the original oxide, quantifying the proportions of the materials which take part in each transformation: and the result of it all is that we get a chain of evidence proving that less than 160 parts of ferric oxide never take part in any reaction.

So again with other bodies.

Thus a base composed of carbon, hydrogen, and nitrogen was obtained, which could not be represented by a simpler formula than $C_6H_{15}N$. The atomic theory tells us that less than $72 + 15 + 14 = 101$ parts by weight of this base cannot possibly take part in any reaction. We bring it in contact with hydric chloride in varying proportions, beginning with very little of the chloride. By examining the product, we find it is a mixture of the unchanged base with a compound containing carbon, hydrogen, nitrogen, and chlorine, in proportions corresponding to the formula $C_6H_{16}NCl$, and containing exactly 101 parts of the base with one part by weight of additional hydrogen and 35.5 parts of chlorine. If we add our hydric chloride to the base, exactly in this proportion, we have nothing left of either material uncombined with the other; and if we add more hydric

chloride, such excess is left uncombined and unchanged. The base does react on hydric chloride in the proportions indicated by its atomic formula, and has not been found to react in any other proportion.

Take an acid salt like hydric citrate, $C_6H_8O_7$ being the simplest atomic formula representing its composition. By bringing it in various proportions in contact with a solution of potassic hydrate, we find that it is capable of reacting in three distinct proportions on that basic hydrate—

If we look through the reactions of well-known bodies with one another, we find that there are many which are not made out quantitatively; but not one of the enormous number that we know accurately and with certainty, has shown a combining proportion of molecules at variance with the atomic theory, and corresponding to the idea that matter is infinitely divisible.

The density of gases and vapours has afforded valuable independent confirmation of the truth of the atomic constitution of molecules, for every compound which evaporates without decomposition has a vapour-density proportional to its molecular weight.

The great benefits conferred upon our science by the doctrine of types would have been impossible without the doctrine of radicals. The two theories were for a considerable time held by different chemists, and were supposed to be inconsistent with one another. They have proved to be essential to one another; so that it may confidently be asserted that those who showed that NH_4 may replace an atom of hydrogen, of potassium, &c., and that C_2H_5 may also perform such functions, prepared the way for the comparisons of bodies of one type.

Another class of considerations which have done admirable work in establishing molecular weights, are those relating to the number of products of substitution obtainable by altering the proportion of materials.

Thus hydric sulphate not only forms the neutral potassic sulphate which we considered in relation to the neutral tartrate,

but it also forms a double salt containing hydrogen and potassium, according to the formula HKSO_4 , when it is brought in contact with half or less than half as much potassic hydrate as is needed to form the neutral salt; and the fact that the hydrogen in the sulphate can be replaced by potassium, in the proportion of half or all, gives an independent proof that the minimum formula of the hydric salt must be H_2SO_4 . So also the hydric tartrate forms, not only the neutral salt above mentioned, but also an acid double salt of hydrogen and potassium, for which the simplest formula is $\text{C}_4\text{H}_5\text{KO}_6$, and a double salt with sodium and potassium $\text{C}_4\text{H}_4\text{NaKO}_6$.

The common phosphates were proved by such evidence as this to be tribasic, and the oxalates, in like manner, to be bibasic. Other reactions confirm the conclusions thus arrived at. For instance, the bibasic salts yield two classes of amides—normal amides, such as oxamide $\text{C}_2\text{O}_2\text{N}_2\text{H}_4$, and compounds of amide and salt, like potassic oxamate $\text{C}_2\text{O}_2\text{OK}^{\text{NH}_2}$; and monobasic salts are distinguished from these not only by their inability to react in more than one proportion on potash or soda, but also by their inability to form compounds of amide and salt, like the oxamate. Again, bibasic hydrogen salts lose their water by heat, and monobasic hydrogen salts do not.

The classification of compounds by their analogies has been one of the most important operations for enabling us to see their distinctive resemblances and differences, and the establishment of series of homologous organic compounds has been, perhaps, the most perfect and useful case of such classification, as well as one of the most fruitful of benefit to the progress of science.

So well did the analogies and reactions among organic compounds serve to connect them with one another, by simple and natural principles, that the simpler part of the science has gained chiefly of late years by adopting methods and conclusions established in the more varied field of organic compounds. Thus, the chief arguments adduced by Gerhardt for the molecular weight of carbonic acid which we now adopt, and for the corresponding molecular weight of water, were to the effect that in no reaction between well known molecules is a smaller proportion of carbonic acid given off or taken up than that corresponding to the molecular weight 44; and, in like manner, less

than 18 parts, by weight, of water are never taken up nor given off in any well known reaction between molecules of known weight. The examples of molecules in each case were mainly taken from organic chemistry. The molecular weights of the gaseous elements, hydrogen, chlorine, nitrogen, oxygen, &c., were studied in great part with the aid of the light obtained from the comparison of organic reactions, in which they take part, especially the double decompositions which take place when chlorine normally replaces hydrogen.

A study of the phenomena of electrolysis, and some other inorganic processes, had led to metals being considered as possessing, in the free state, a molecular constitution analogous to that of compounds; and Brodie's reduction of oxides by oxygen gave evidence of combinations between atoms of oxygen in forming the free gas.

Amongst the general processes which were instrumental in judging of the correctness of molecular formulæ was Gerhardt's so-called law of even numbers. Among molecular formulæ which he considered well established, he observed that the sum of the atoms of a certain list which he supplied was always an even number; whereas, the sum of the atoms of elements not belonging to his list was sometimes an even, sometimes an uneven number.

The circumstance is now known to be one among several consequences of a difference in replacing value, which constitutes one of the most important characteristics of atoms, and we also know that many elements which Gerhardt classed with hydrogen, nitrogen, &c., do not belong to that class; but even in its original imperfect form the rule rendered very important services. Thus, such formulæ as $C_2H_3O_3$, $C_{10}H_{12}NO$, Gerhardt knew could not be molecular formulæ, and must be at least doubled. A study of their reactions amply confirms his verdict. We also know that such formulæ as $FeCl_3$, $HgCl$, $AlCl_3$, cannot represent molecules, and must be corrected so as to contain at least even numbers of chlorine atoms without including the metallic atoms in the account.

To do justice to the completeness of the evidence which is obtained respecting many molecular weights, by these purely chemical methods of research, it would be necessary to go into the full particulars of the operations and observations in the respective cases, and that would task, still more unduly than I

am now tasking it, the indulgence of the Society. But I feel convinced that the brief indications which I am able to give of the kind of evidence obtained under these various headings, will recall to the minds of chemists the particulars which it would be needful to describe specially to persons not intimately acquainted with the science.

There are, however, other properties of molecules which have been noticed since chemists discovered the existence of the molecules themselves, and these are of kinds to be more easily understood by all—properties which involve no change of composition in the molecules, but which belong to them as long as they subsist.

Of these physical properties, one of the most important is the volume of molecules in the state of gas or vapour. Whenever we examine perfect vapours composed of like molecules, we find that whatever the molecules may be, they occupy the same volume under like conditions. In other words, these little units of matter, found by the guiding aid of the atomic theory, are found also to be units of force when examined under those conditions. There have, in several cases, been important discrepancies between the chemical evidence of molecular constitution and the evidence afforded by vapour-volume. Thus, hydric sulphate and ammoniac chloride are among the compounds of whose molecular weights we have the best and most varied chemical evidence, yet the vapour formed from each of these occupies about double the volume of a gas molecule. A careful examination of the vapour formed from each of them showed, however, that it is a mixture of molecules of two sorts formed by the decomposition of the original compound. The fact that errors in the indications supplied by vapour-density could be thus pointed out by the chemical evidence of molecular weight is surely no slight confirmation of the perfection of the evidence of molecular weights obtainable by chemical methods; and, on the other hand, the immense number of coincidences between the indications obtained from the two independent sources is a strong evidence of the truth and parallelism of the two.

There are, also, crystalline compounds, which chemistry has founded be closely analogous, which occupy, in the crystalline state equal, or nearly equal, volumes.

Among other physical properties which confirm the truth of

the atomic views of molecular constitution are boiling points. Whenever truly analogous elements are comparable in respect to boiling points, it is found that those composed of heavier atoms boil at higher temperatures than those composed of lighter atoms. A comparison of the successive terms of the series—chlorine, bromine, and iodine, illustrates this difference very strikingly. So also a comparison of the several terms of the series—oxygen, sulphur, selenium, and tellurium, and not less so the elements nitrogen, phosphorus, arsenic, antimony, and bismuth.

Now, whenever volatile organic compounds belonging to a homologous series are compared, it is found that of two such compounds, the one having the higher molecular weight has also the higher boiling point. The glycols present, however, an exception to this general observation.

The melting points of homologous organic compounds also show differences running parallel in like manner to their differences of molecular weight.

The relative velocities of motion of particles, as shown by the processes of diffusion, afford another confirmation of the general truth of the molecular weights; for, on the one hand, it is known that heavy particles diffuse more slowly than light particles; on the other hand, a comparison of the relative velocities of movement of molecules of relative weights, previously determined upon chemical evidence, shows that the heavier molecule of chemistry is also the heavier molecule in diffusion.

At this point of my study of this question I am in a serious difficulty, for molecules have no *locus standi* in the absence of the atomic theory. They are, to use the words of Dumas, physical atoms; their existence is a necessary consequence of the atomic theory, and all chemical reactions agree in proving their existence. They are also discovered by an examination of the mechanical properties of gases.

The opponents of the atomic theory are bound to explain, in some other way, the facts which point so distinctly to the existence of molecules, if they wish to advance from the position of mere contradictors to that of chemists.

Hitherto they have not done so, and the case stands thus: on the one hand, we have a simple theory which explains in a consistent manner the most general results of accurate observation in chemistry, and is daily being extended and

consolidated by the discovery of new facts which range themselves naturally under it. On the other hand, we have a mere negation: for the statements of those who say that our evidence of the existence of atoms is not conclusive, and yet omit to show any alternative theory, are nothing more. In discussing the relative composition of carbonic acid and carbonic oxide, I have endeavoured to put the negation in a tangible form, as an affirmation that there are no limits to the divisibility of elements, and to represent compounds containing multiples of equivalent weights as containing sub-multiples corresponding to the same empirical proportions.

If elements, in combining with one another, merely undergo more minute subdivision, so that a compound, like amylic alcohol, CH_{15}O_3 , is formed from methylic alcohol by removing hydrogen and oxygen from the compound CH_4O , then we could expect a weight of it corresponding to a formula containing less hydrogen and oxygen to perform the functions of the molecule CH_4O .

Of two things, one: either the existence of molecules is denied, or it is admitted.

In the former case, the vast and consistent body of chemical evidence of the existence of molecules must be set aside and disproved, and the physical confirmations of their existence must also be proved to be erroneous.

In the latter case it must be shown by quantitative analysis that those complex molecules to which we attribute a great weight, are really lighter than their simpler analogues.

Now, the difficulty is to choose arguments for an opponent. It would probably matter little to us which they might select; but when they content themselves with saying that we are wrong, without either showing in what respect our evidence or our reasonings are at fault, and without showing any other evidence or any other reasonings which they consider preferable, it is difficult to know what else to do with them than to state our case and leave them to their reflections.

Atomic Values.

The most important and weighty chemical property of atoms as yet discovered, is one which can only be perceived by the aid of a knowledge of the equivalent weights of the elements and of the molecular weight of a considerable number of compounds.

Thus if we know the molecular formulæ of the following compounds, we can compare them with one another and perceive their differences of composition :

Hydric acetate has the molecular formula	$C_2H_4O_2$
Hydric monochloracetate	$C_2H_3ClO_2$
„ dichloracetate	$C_2H_2Cl_2O_2$
„ trichloracetate	$C_2HCl_3O_2$
Again,	
Marsh-gas has the molecular formula....	CH_4
Methylic chloride	CH_3Cl
Methylenic chloride	CH_2Cl_2
Chloroform	$CHCl_3$
Carbonic chloride	CCl_4

It is apparent from these series of formulæ that one equivalent weight of chlorine can take the place of one of hydrogen in a molecule, or two of chlorine can replace two of hydrogen, or three replace three, and so on. Hydrogen-compounds containing in each molecule a much greater number of hydrogen equivalents, have been found to allow, in like manner, the hydrogen to be replaced, one equivalent at a time, by chlorine, and to the extent of a great number of equivalents in each molecule.

In like manner, potassium replaces hydrogen in molecules, sometimes in the proportion of an even number of equivalents, sometimes in the proportion of an uneven number of equivalents, as will be seen by the following molecular formulæ:—

H_2O	H_2SO_4	H_3PO_4	H_3N	$H_2C_4H_4O_6$
HKO	$HKSO_4$	H_2KPO_4	KH_2N	$HKC_4H_4O_6$
K_2O	K_2SO_4	HK_2PO_4		$K_2C_4H_4O_6$
		K_3PO_4		

When, however, oxygen takes the place of hydrogen, without change of equivalent weight, it is only in the proportion of two equivalents of oxygen replacing two of hydrogen, four of oxygen replacing four of hydrogen, six replacing six, and so on; always an even number of hydrogen equivalents replaced in each reaction of the kind. Thus carbonic acid is formed from marsh-gas by the normal reaction $CH_4 + 2O_2 = CO_2 + 2H_2O$, in which four equivalent weights of oxygen replace four of hydrogen. Hydric nitrate has a constitution similar to ammoniac hydrate, the difference being that it contains four equivalent

weights of oxygen instead of four equivalent weights of hydrogen in the ammonia, as will be easily seen by a comparison of the formulæ HONH_4 and HONO_2 .

Again, phosgene is methylenic chloride in which two equivalents of hydrogen are replaced by two of oxygen—

The compounds .. ammonia	$2\text{H}_3\text{N}$
nitrous acid.....	O_3N_2
glycoll.....	$\text{C}_2\text{H}_6\text{O}_2$
hydric glycollate	$\text{C}_2\text{H}_4\text{O}_3$
hydric oxalate.....	$\text{C}_2\text{H}_2\text{O}_4$

show a replacement of hydrogen by oxygen in steps, each one being two hydrogen replaced by two of oxygen. Now, it is not the existence of these compounds which proves any different value in oxygen atoms from chlorine atoms; it is the fact that no case is known of a molecule containing a single equivalent of oxygen in place of one of hydrogen, nor of three equivalents of oxygen in place of three of hydrogen, nor, in short, of any uneven number of hydrogen equivalents replaced by an uneven number of oxygen equivalents.

The same difference between oxygen and chlorine may be seen by comparing all well known molecular formulæ containing either one of those elements, apart from the particular process by which they may have been formed. Thus we have, by way of illustration, some bodies taken at random from various classes of compounds—

$\text{C}_2\text{H}_5\text{Cl}$	H_2O
$\text{C}_2\text{H}_4\text{Cl}_2$	CO
$\text{C}_2\text{H}_3\text{Cl}_3$	CO_2
$\text{C}_2\text{H}_6\text{ClN}$	$\text{C}_2\text{H}_2\text{O}_4$
$\text{C}_2\text{H}_5\text{Cl}_2\text{N}$	$\text{C}_2\text{H}_6\text{O}$
PCl_3	$\text{C}_5\text{H}_{12}\text{O}$
NH_4Cl	$\text{C}_4\text{H}_6\text{O}_4$
CrO_2Cl_2	$\text{C}_3\text{H}_8\text{O}_3$
SO_2Cl_2	$\text{C}_2\text{H}_3\text{OCl}$
SO_4H_2	$\text{C}_2\text{H}_4\text{OCl}_2$
PO_4HNa_2	
PbO_2H_2	
PbO	
PbO_2	

There are, however, some cases which at first sight do not agree with this general conclusion. Thus, on comparing potassic chloride with potassic oxide, it might be said that the equivalent weight of potassium in the former is combined with an equivalent weight of chlorine, and in the latter with an equivalent weight of oxygen; thus KCl , $\text{KO}_\frac{1}{2}$. But the answer is that this comparison is made in defiance of the known molecular formula of potash (K_2O), established by reactions and analogies which leave no doubt of its correctness. Whenever oxygen replaces chlorine in such a chloride, it binds together two basic equivalents, one from one molecule of the chloride one from another; and in like manner when chlorine replaces oxygen in any molecule, such as water H_2O or potassic hydrate, it loosens into two molecules what the oxygen held bound up in one. Thus, by passing oxygen and hydric chloride through a red-hot tube, we have a replacement of chlorine by oxygen, taking place, as far as it goes, according to the molecular equation $\text{O}_2 + 4\text{HCl} = 2\text{H}_2\text{O} + 2\text{Cl}_2$, half as many molecules of water being formed as molecules of hydric chloride are decomposed; and on the other hand if we send chlorine and steam through a hot tube, we break up a part of the steam, forming two molecules of chloride from every one of oxide.

When we apply the word atom to two equivalent weights of oxygen, and say that an atom of oxygen has a replacing value equal to that of two atoms of chlorine or of hydrogen, we give to a couple of equivalent weights of oxygen the name atom, as a record of the fact that we have never known them to divide, and that we must in all our considerations respecting oxygen bear in mind this peculiarity of it. In carbonic oxide it may be argued that an atom of oxygen takes the place of four equivalents of hydrogen of marsh-gas, and that it has there the equivalent weight 4, instead of its usual equivalent weight 8. But on the other hand the gas may be represented as containing carbon with an equivalent weight of double its usual one, viz., 6 instead of 3. In any case, the gas affords an instance of a change of atomic value, and if we describe the value of the atom of oxygen in disregard of this case, it is because we have to record its commonest value.

What has been here said of oxygen applies to sulphur equally. No molecule has ever been found containing an uneven number of equivalent weights of sulphur, and the atom of sulphur has

certainly the value of two chlorine or hydrogen. There are, however, strong reasons for believing that in some of its compounds its atom has a replacing value of four or even six. Selenium and tellurium are so closely allied to oxygen and sulphur in their reactions that their atoms are always classed together. In like manner bromine and iodine go with chlorine, and lithium, sodium, &c., go with hydrogen and potassium. Silver also has an atom of uneven value.

Nitrogen is found upon similar evidence to divide in no smaller proportion than that of three times $4\frac{2}{3}$, or 14 parts by weight, for whenever it has an equivalent weight of $2\frac{4}{5}$, as in NH_4Cl , its atom has five values.

It seems to me of paramount importance to the due understanding of the functions of this element, to state in the most direct and matter of fact way possible, the actual proportion in which its atom replaces hydrogen. If the replacing value of an atom be measured by the number of hydrogen atoms needed to replace it, then nitrogen has in ammonia the atomic value three, for three atoms of hydrogen are needed in order to replace one of nitrogen in NH_3 , forming three molecules of hydrogen H_3H_3 ; and in sal ammoniac it has just as distinctly the atomic value five, for five atoms of hydrogen are needed in order to take the place of one of nitrogen, forming one molecule of hydric chloride and four molecules of hydrogen: ClNH_4 becomes $\text{ClH} + \text{H}_4\text{H}_4$. Sal-ammoniac is as well known a molecule as ammonia itself; each of them undergoes decomposition at high temperatures, the complex molecule not requiring so high a temperature for its decomposition as the simpler one. Those chemists who represent sal-ammoniac as containing one atom of nitrogen of the same value as in ammonia, seem to me to incur the disadvantage of stating rather what, according to their own theoretical notions *ought* to be, than what actually *is*, and thereby to lose sight of one of the most important of all properties of atoms, viz., the property of changing value under particular chemical and physical conditions which it is our business to study and describe.

I shall return to this important point somewhat later, and endeavour to trace an outline of the conditions of these changes.

Together with nitrogen are always classed the elements phos-

phorus, arsenic, antimony, and bismuth. Their atoms have frequently the value of three, but frequently also that of five. Boron has in its chloride and fluoride the value three, but in its double fluoride the value five— BCl_3 , BF_3 , KBF_4 . Gold is not proved to have any smaller atomic value than three, for we have no evidence of the molecular weight of the compound AuCl . Compounds corresponding to AuCl_3 and NaAuCl_4 , are common and tolerably well known.

Carbon is at present perhaps that element of which the compounds are best investigated. A comparison of the composition of an immense number of carbon-compounds has not led to the discovery of a single molecule containing a number of its equivalent weights, other than such as can be divided by four. Its atom is accordingly considered to weigh 12, and to have the value 4. In carbonic oxide, the atom of carbon has a somewhat uncertain value, according as we consider oxygen to vary in value or not. Silicium, titanium, and tin are in many respects so closely allied to carbon that it is to be expected that their atomic weight must be such as to give the atoms the value 4 in their ordinary compounds. The atom tin in stannous chloride appears at first sight to be worth 2, but the molecular formula of the compound is not known, and may possibly be Sn_2Cl_4 like olefiant gas. Silicium in its double fluoride, SiF_6K_2 , is evidently worth 8, and titanium and tin have also doubtless a higher value than 4 in their double salts.

Platinum seems to vary from four values to eight, as in the compounds PtCl_4 and PtCl_6K_2 . Its lower chloride PtCl_2 ought probably to have a higher molecular formula.

Not only does the empirical comparison of the number of equivalent weights of each element contained in well-known molecules lead to a discovery of the relative weights of atoms, but there are other chemical evidences which concur with these. Thus the univalent alkali-metals have long been known to be unable to form basic salts, whereas many multivalent metals form such salts with peculiar facility; witness antimony and bismuth, mercury and lead, in the compounds SbOCl , $\text{Bi}_2\text{O}_2\text{SO}_4$, $\text{Pb}(\text{HO})(\text{NO}_3)$. In such compounds as these, the metal performs the function of binding together several radicals or simple atoms, just as in water or potassic hydrate the oxygen binds the two atoms together; and when such a metal is removed, and an equivalent quantity of a single-

value metal supplied in its place, the atoms which had been bound together pass off, each in combination with its own atom of metal. Thus, in the reaction $\text{Pb}^{\text{HO}}_{\text{NO}_3} + \text{Ag}_2\text{SO}_4 = \text{PbSO}_4 + \text{AgOH} + \text{AgNO}_3$ we have a severance of AgOH from AgNO₃, which would not take place if silver were of double its atomic weight, and, like lead, of the atomic value 2.

Double amides, such as $\text{Hg}^{\text{Cl}}_{\text{NH}_2}$, and double salts, such as $\text{Ba}^{\text{NO}_2}_{\text{C}_2\text{H}_3\text{O}_2}$, $\text{Cu}^{\text{AsO}_2}_{\text{C}_2\text{H}_3\text{O}_2}$ are also evidences of the biacid character of the base, just as $\text{KNaC}_4\text{H}_4\text{O}_6$ is an evidence of the bibasic character of the acid.

Again, compounds of metals with organic radicals have furnished admirable evidences of the atomic weights of various metals whose equivalent weights are known. Thus the compounds $\text{Zn}(\text{C}_2\text{H}_5)_2$, $\text{Zn}^{\text{C}_2\text{H}_5}_1$, $\text{Hg}(\text{C}_2\text{H}_4)_2$, $\text{Hg}^{\text{C}_2\text{H}_5}_1$, $\text{Sn}(\text{C}_2\text{H}_5)_4$, $\text{Sn}^{\text{C}_2\text{H}_5}_3$, $\text{Sn}^{\text{C}_2\text{H}_5}_2$, $\text{Pb}(\text{C}_2\text{H}_5)_4$, $\text{Pb}^{\text{C}_2\text{H}_5}_3$, &c., have been among the best chemical evidences of the atomic values of the respective metals.

Similar proofs of the value of the atom of silicium have been given by the formation of molecules containing atoms of ethyl and chlorine together numbering *four*, just as in the molecule of marsh-gas the hydrogen can be replaced by chlorine in four distinct proportions.

Atomic Heat.

Perhaps the most direct confirmation of the atomic weights established upon evidence of the various kinds which we have been considering is afforded by the capacity for heat of elementary bodies. A comparison of the relative capacity for heat of solid elements showed that all atoms have nearly the same capacity for heat. Thus 23 grammes of sodium absorb, when heated from 0° C. to 1° C., almost exactly the same quantity of heat as 39 grammes of potassium when heated from 0° C. to 1° C.; and 210 grammes of bismuth absorb that same quantity when heated from 0° C. to 1° C. Silicium, carbon, and boron form exceptions to this law, but in all other cases the approximation

to equality between the numbers found for the several solid elements is admitted to be as close as can be expected from determinations involving so many difficulties, and including so many sources of error.

Like every other confirmation of the atomic theory, the law of atomic heat has contributed to the development and systematisation of that theory. It is well known that a considerable number of metals, such as lead, mercury, iron, tin, barium, &c., appeared, according to the atomic weights originally assigned to them, to have about half the atomic heat of the metals before mentioned, and that this circumstance was urged by an illustrious Italian chemist as an argument for doubling their atomic weights, so as to bring them within the law. It is also too well known to need illustration to you, that the chemical properties of those metals amply confirm the truth of Cannizzaro's proposition, that their atomic weights are twice as great as was formerly supposed. Indeed so much chemical evidence has now been accumulated, that we should certainly retain the higher atomic weights for lead, tin, iron, barium, &c., even if we knew nothing of atomic heat.

Atomic values are not so variable as equivalent weights. A most important light has been thrown on the phenomena of equivalence by our knowledge of atomic values and the general principle of their changes. The foundation of this consideration was laid by those chemists who proved that the molecule of chlorine consists of two atoms of chlorine combined with one another, and that the molecule of oxygen consists of two atoms of oxygen combined with one another.

It is well known that free carbon at high temperatures unites with hydrogen, forming acetylene, which has the molecular formula C^2H_2 . I will write the number belonging to each atomic symbol above, as an exponent, when I wish to represent the atoms so numbered as combined with one another, O^2 , &c., meaning a compound of an atom of oxygen with an atom of oxygen; C^2 a compound of an atom of carbon with another atom of carbon. On the other hand, I will write the number belonging to any atomic symbol below, when I wish to represent the atoms as not combined with one another. Thus H_2 means two atoms of hydrogen, and OH_2 means a compound of one atom of oxygen with two atoms of hydrogen, each of

which atoms of hydrogen is merely united with the atom of oxygen. It is merely an abbreviated form of writing HOH or

$\begin{array}{c} \text{HO} \quad \text{H} \\ \text{H} \quad \text{or O \&c.} \end{array}$
 By adding two atoms of hydrogen to acetylene

we get olefiant gas, C^2H_4 , and this again, in its turn, can be transformed into methyl C^2H_6 . These bodies, C^2H_2 , C^2H_4 , C^2H_6 , are well known to have molecular weights corresponding to two atoms of carbon in each, and the hydrogen is held in each molecule by being combined with the carbon. With more hydrogen the double atom of carbon cannot combine, for the next hydrocarbon to methyl is marsh-gas CH_4 containing a single atom of carbon.

Again, if we remove hydrogen from marsh-gas in the smallest possible proportion, we find that the atom of carbon in one molecule combines with one atom of carbon in another molecule, while they are losing their hydrogen. Methylic iodide reacts on zinc-iodomethide by a normal interchange of iodine for methyl $\text{H}_3\text{CI} + \text{IZnCH}_3 = \text{H}_3\text{CCH}_3 + \text{ZnI}_2$. It is admitted that the explanation of the molecular weight of methyl lies in the fact that it contains two atoms of carbon combined with one another to the extent of one-quarter of their value, and that this combination of carbon with carbon is the essential condition for the formation of such a complex molecule. But, if this be true, the other terms of the series are explained by a mere extension of the same principle. Ethylene contains two atoms of carbon H_2CCH_2 , each combined with two atoms of hydrogen, and each one combined with the other to the extent of two of its values. Acetylene, HCCH , is in like manner a compound of two atoms of carbon, each one combined with the other to the extent of three values.

It was known that an atom of carbon may combine partly with hydrogen, partly with some other element or elements, and it was also known that like atoms combine with one another; so that it was quite consistent with known facts to suppose that an atom of carbon may combine partly with another atom of carbon, partly with some other element. The simplification introduced into the chemistry of the compounds of carbon by this theory is, however, truly admirable, and, by itself, entitles the distinguished author of the idea to the high rank among theorists which he holds.

Carbon in all its compounds may have the same atomic value consistently with our present knowledge of those compounds. In carbonic oxide alone we are compelled to represent it as having only the value two, unless we attribute to oxygen the value four.

Among the instances of increase of equivalent weight in elements, there are a great number in which the element exhibiting that increase, by giving up some of the unlike with which it was united, unites with the like while doing so.

Thus, SCl_2 , by the mere action of heat, decomposes with evolution of chlorine, and by an atom of sulphur combining with another atom of sulphur, $2\text{SCl}_2 = \text{S}_2\text{Cl}_2 + \text{Cl}_2$. Water and hydric peroxide are doubtless related to one another, in the same manner, each of the two atoms of oxygen in the molecule of the peroxide being half combined with oxygen, half with hydrogen. Mercuric chloride loses half its chlorine, forming calomel, while the mercury unites to the extent of half its value with mercury, and cupric chloride is reduced to cuprous chloride by a similar process. On the other hand, phosphoric chloride loses chlorine, and forms phosphorous chloride, without any combination of phosphorus with phosphorus taking place. The equation $\text{PCl}_5 = \text{PCl}_3 + \text{Cl}_2$ represents the process; and until it can be shown that the molecule of phosphorous chloride is a multiple of PCl_3 , the reaction must be accepted as direct evidence of a change in the atomic value of phosphorus from 5 to 3. In like manner, if ammonia be admitted to have the molecular formula NH_3 , the decomposition of sal-ammoniac by heat, according to the equation $\text{ClNH}_4 = \text{NH}_3 + \text{HCl}$, must be admitted as evidence of a change of atomic value in nitrogen from 5 to 3. When auric chloride is decomposed, with evolution of chlorine and formation of aurous chloride, the interpretation of the reaction requires evidence which we do not possess respecting the molecular weight of the lower chloride. If aurous chloride has the molecular formula AuCl , its formation is accompanied by a change of atomic value in the gold; but if its molecule contains more than one atom of gold, the metal may exist in both compounds with the same atomic value.

Among complex organic molecules there is, of course, considerable room for variety in the arrangement of atoms, which we may consider consistently with the empirical equivalent weight of the carbon.

The hydrocarbon benzole is of so much interest from its derivatives, that it has attracted a good deal of attention, and to explain its molecular constitution, the six atoms of carbon have been represented as arranged in a ring, each atom being combined with the atom of carbon at one side of it to the extent of two values, and with the atom of carbon on the other side of it to the extent of one value.

Another arrangement, which was mentioned a good many years ago at this Society, is to consider each atom of carbon combined with three others, and with one atom of hydrogen. Such an arrangement is easily represented in space. Let the accompanying formula represent as unfolded in one plane, the group which would be formed by the carbon atom at one end of each line moving back through the paper until equidistant from the two others in the line.

I put bars between symbols of elements, which, for convenience, are juxtaposed, but which I do not wish to represent as combined with one another.

Naphthalin may, in like manner, be represented by the formula C^6H_4 , as containing four atoms of carbon, each united with two of the others and with one atom of hydrogen, while the fifth atom of carbon is combined with each of the first four.

With respect to the conditions under which changes of atomic value take place, some valuable information may be gained by comparing molecules known to exist in different states. Let any chemist write for himself a list of molecules known to exist in the liquid state alone, and not volatile without decomposition. Let him compare with that, a list of molecules known to evaporate unchanged; and thirdly, let him look at the molecular formulæ of the hitherto uncondensed gases. He will notice that in passing from the non-volatile to the uncondensed, he goes from complex molecules to simpler and

simpler ones. Let him compare the formulæ of products formed by destructive distillation with those of the materials from which they are formed. The examples may be taken from mineral and from organic chemistry. He will find some cases of the formation of a more complex molecule by distillation; but for one such he will find an enormous number of cases of the breaking up of complex molecules into more and more simple ones. Take, for instance, the series CO_3H_2 , SO_3H_2 , NH_5O , SbCl_5 , PCl_5 , SO_4H_2 , PO_4H_3 , $\text{C}_2\text{O}_4\text{H}_2$, NH_3 , CH_4 , H_2O , CO_2 , beginning with compounds so exceedingly unstable, that, working at ordinary temperatures, we hardly know them; and finishing by compounds of great stability, which are only broken up into simpler molecules at the most intensely high temperatures. The fact stares us in the face, that simple molecules correspond to high temperatures, complex molecules correspond to low temperatures. Several of these changes of composition are certainly accompanied by changes of atomic value. Whenever there is a change of atomic value effected by change of temperature, the lower atomic value corresponds to the higher temperature. These phenomena have attracted some attention of late, in consequence of Deville's researches on dissociation. I will give an example of the application of this principle to the study of reactions in illustration of the importance of seeing and recording differences of atomic value in elements.

I will again use the notation which I referred to above. The following formulæ give samples of nitrogen-compounds in which nitrogen has the atomic value 5: ClNH_4 , HONH_4 , $\text{HON}(\text{C}^2\text{H}_5)_4$, $(\text{H}_4\text{NO})_2\text{CO}$, $(\text{H}_4\text{NO})_2\text{C}^2\text{O}_2$, H_4NOCCH_3 . The action of heat

O

upon them gives rise to NH_3 in two cases, $\text{N}(\text{C}^2\text{H}_5)_3$, $(\text{H}_2\text{N})_2\text{CO}$, $(\text{H}_2\text{N})_2\text{C}^2\text{O}_2$, H_2NOCCH_3 . In each case the nitrogen-atom is

O

reduced to the value of 3. In fact it will be seen that in ammonium-salts nitrogen is worth 5, in amides only worth 3. Ammonia is an amide in this sense.

Among chemical evidences of atoms, the discovery of the distinction between direct and indirect combination is worth consideration, more especially as it is independent of the quantitative comparisons which have hitherto guided us. Many elements which have never been obtained directly combined, are bound together by a third; thus we have no direct com-

pound of hydrogen and potassium, but in potassic hydrate an atom of hydrogen is united with oxygen, and an atom of potassium is united with this same oxygen HOK. Hydrogen in this hydrate is indirectly united with potassium, an atom of oxygen being the connecting link between them.

Some elements can be either directly or indirectly united with one another, and exhibit different properties in each condition. In organic compounds we know an immense number in which hydrogen is directly united with carbon. Thus, methylic oxide H_3COCH_3 has all its six atoms of hydrogen united with carbon directly, whilst vinic alcohol H_3CCOH has five of its

H_2
atoms of hydrogen united with carbon directly, and one atom indirectly, through oxygen.

In consequence of this difference, we find that the hydrogen, which is indirectly united with carbon through the intervention of oxygen, separates from it as soon as by any process the oxygen is replaced by chlorine or bromine; whereas the hydrogen which is directly united with carbon undergoes no change by such replacement. H_3COCH_3 by the action of PCl_5 becomes $\text{H}_3\text{CCl} + \text{ClCH}_3$, whereas H_3CCOH becomes H_3CCCl

H_2 H_2
+ ClH . When the hydrocarbons are liberated from these compounds, it is well known that a direct combination of carbon in one atom with carbon in another takes place, as in the formation of C^2H_6 from a methyl-compound, or $\text{H}_3\text{CCCCCH}_3$ from an ethyl-compound.
 $\text{H}_2|\text{H}_2$

In like manner to oxygen, an atom of zinc holds two atoms of ethyl in combination in the molecule $\text{H}_3\text{CCZnCCCH}_3$, and by the action of water, the atom of zinc is replaced by two atoms of hydrogen, each atom of ethyl getting an atom of hydrogen in exchange for the half atom of zinc which it held at first.

These and many similar reactions are now so familiar to chemists that I only allude to them to recall their bearing on the order of combination of atoms.

Not only are they known and admitted to be due to differences of arrangement, such as I have alluded to, but the idea which they have established is found a sure and faithful guide in the investigation of the intricate varieties presented by isomeric organic bodies in their varied reactions.

Thus it is well known from Hofmann's admirable researches on the isomeric cyanides and sulphocyanates, that, by the action of ethylia on chloroform, an ethylic cyanide is formed, isomeric with the compound formerly known. It breaks up by the action of hydric chloride in presence of water, into hydric formate, and the compound of ethylia and hydric chloride, instead of breaking up, as the other cyanide does, under the influence of alkalis, into ammonia and a propionate.

The following equations represent the two reactions:—

And in like manner his new sulphocyanates break up under the influence of nascent hydrogen, according to the equation—

whilst their isomerics on the SH_2 type break up thus:—

In the new cyanides, the carbon of the cyanogen is indirectly united with the carbon of the ethyl through an atom of nitrogen of the value 5; whereas, in the old cyanide of ethyl, the carbon of the cyanogen is directly combined with the carbon of the ethyl, and in the sulphocyanate carbon is indirectly combined with carbon through the intervention of sulphur.

What concerns us in these reactions is to see the evidence which they afford, that the binding element is an atom. The very fact itself amounts to that. In potassic hydrate, oxygen is combined with hydrogen; it is also combined with potassium, but the hydrogen cannot pass off, even at a red heat, in combination with its half of the oxygen. The two halves are inseparable, and when I say that in the molecule of potassic hydrate there is a single atom of oxygen, I merely state that fact.

I would gladly proceed now to other and certainly not less interesting considerations based upon the atomic theory, which

have received verification from experiment, consideration for which I think it would be at least rather difficult to find any equivalent if matter were not composed of atoms; but I must content myself with indicating them at present, and reserving for a future occasion the task of giving more development to them. I allude to atomic motion—the dynamics of chemistry. It has been shown that heterogeneous molecules, when mixed with one another in the fluid state, interchange their analogous constituents, and that the products thus formed, if they remain mixed in the fluid state, also exchange their analogous constituents, reproducing the original materials. In a solution of two salts there are formed two new salts by the exchange of bases; and it depends on the relative velocities with which the decomposing change and the reproducing change go on in the liquid, what proportion the quantity of the original materials bears in the final mixture to that of the new products.

In using the atomic language and atomic ideas, it seems to me of great importance that we should limit our words as much as possible to statements of fact, and put aside into the realm of imagination all that is not in evidence. Thus the question whether our elementary atoms are in their nature indivisible, or whether they are built up of smaller particles, is one upon which I, as a chemist, have no hold whatever, and I may say that in chemistry the question is not raised by any evidence whatever.

They may be vortices, such as Thomson has spoken of; they may be little hard indivisible particles of regular or irregular form. I know nothing about it; and I am sure that we can best extend and consolidate our knowledge of atoms by examining their reactions, and studying the physical properties of their various products, looking back frequently at the facts acquired, arranging them according to their analogies, and striving to express in language as concise as possible the general relations which are observed among them.

In conclusion I must say that the vast body of evidence of the most various kinds, and from the most various sources, all pointing to the one central idea of atoms, does seem to me a truly admirable result of human industry and thought. Our atomic theory is the consistent general expression of all the best known and best arranged facts of the science, and certainly it is the very life of chemistry.