SCIENCE

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*THE ATOMIC THEORY FROM THE CHEMICAL STANDPOINT.**

The Atomic Theory is the most fundamental hypothesis of the chemistry of to-day and plays a greater part in this than in any other science, and to give an account of all the classes of chemical phenomena which it is sought to explain by its aid would require far more time than I have at my disposal. I shall limit myself to giving as briefly as possible the main facts which have led chemists to adopt it and to stating which of the various properties which have been ascribed to the atoms are, and which are not, essential to its use in chemistry, and what properties may be attributed to them, solely on the basis of chemical experiments.

The question whether any given portion of matter is continuous, absolutely the same throughout, even if infinitely divided, or whether it consists of particles separated by comparatively empty space, is, of course, almost as old as philosophic thought. The beginnings of chemistry lie still further back; the first man who questioned why wood burns, or why grape juice turns to wine, was an incipient chemist.

About the middle of the seventeenth century, Robert Boyle, who originated our present conception of element and compound, applied the atomic theory to chemistry, in-

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terpreting chemical combination as a joining together of elementary corpuscles. Boyle's view had little influence on chemistry, and I think naturally. In the absence of more definite chemical knowledge than then existed, I should consider the conception that water and alcohol, for example, are perfectly continuous, and that their mixing is a perfect blending, quite as plausible as, and less contradictory to the evidence of the senses, than the view that they consist of discrete particles which mix, but do not penetrate each other. Up to the beginning of the present century those who adopted the atomic hypothesis did so from supposed physical or metaphysical necessity, rather than on the basis of any satisfactory chemical evidence.

The general acceptance of the atomic hypothesis by chemists was due to the experimental establishment of two laws, which are among the most fundamental principles of chemistry—the *Law of Constant or Definite Proportions*, and the *Law of Multiple Proportions*. For the benefit of those who have forgotten their chemistry I may state briefly in what these laws consist.

The Law of Constant Proportions.—Every chemical compound has an invariable composition, that is, the relative weights of the elements entering into it are invariable. On comparing the composition of numerous substances, it was soon found that to each element might be attributed a certain number, the *combining number*, which represents the proportion by weight in which that element enters into combination. If we compare, for instance, the compounds which the akali metals lithium, sodium and potassium form with the halogens chlorine, bromine and iodine, we find the following relations: 7 parts lithium unite with 35.4 parts chlorine; 80 parts bromine, or 127 parts iodine; similarly 23 parts sodium unite with 35.4 parts chlorine; 80 parts bromine, or 127 parts iodine, and so on.

Lithium.	Sodium.	Potassium.
7.	23.	39.
Chlorine.	Bromine.	Iodine.
35.4.	80.	127.

These figures, which merely express the results of analysis, are the combining numbers, and to each of the seventy-five or more elements belongs its own proper combining number.

The Law of Multiple Proportions.—Elements often combine in more than one proportion. When this is the case, the different weights of the one, which unite with a given weight of the other, bear a simple relation to each other. A good example of this is found in the chlorides of the metal molybdenum, of which four are known. The combining number of molybdenum is 96, and 96 grams molybdenum combine with respectively 2, 3, 4 and 5 times 35.4 grams chlorine, 35.4 being the combining number of the latter, the resulting compounds being represented by the formulas $MoCl_2$, $MoCl_3$, $MoCl_4$ and $MoCl_5$. A somewhat more complicated case is found in the paraffine series of hydrocarbons, CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12}, etc. Both laws apply as well when the compounds contain more than two elements.

These two laws hold without exception through the many thousands of known chemical compounds. They involve nothing hypothetical, being simply the expression of analytical results in a particular form. They were established mainly through the labors of Richter, Proust, Dalton and Berzelius, but to Dalton belongs the credit of having employed the atomic theory in explaining them.

If matter be absolutely continuous and capable of any degreee of subdivision, it is difficult to see why each element should have a definite combining number, which holds without exception, and why there should be distinct compounds well marked off from others, instead of different substances shading off into each other by infinitesimal differences. Why, for example, should there not exist a sodium chloride with 34 or 36 parts chlorine to 23 parts sodium, as well with 35.4 parts? It is true that we may bring these elements together in any proportion, but unless the ratio is just 23 to 35.4, the excess of the one or the other will be left unchanged, and we always obtain a chloride with 23 parts sodium and 35.4 parts chlorine. The hypothesis of continuity does not explain why, in the series of molybdenum chlorides just mentioned, the weights of chlorine combining with a given weight of molybdenum should be in the proportion 2, 3, 4, 5, without any or every intermediate figure. It is quite as difficult to explain on this view why the same combining number always adheres to the same element no matter into what combine it enters; the combining number of chlorine might be 35.4 with respect to sodium, and any other figure with regard to lithium or potassium.

If, however, we assume that a given portion of each of the elements, instead of being capable of any degree of subdivision whatever, consists of minute parts, or atoms, each of which, while it may or may not be further divisible, nevertheless always acts in chemical reactions as if it were not, that is, acts as a whole; and if we assume that in the same elementary substance, these particles have the same weight, but that the weight differs in the case of each element, then we have a state of affairs which would necessarily lead to the two laws I have described. The combining numbers would represent simply the relative weights of these chemically ultimate particles; a sodium atom weighing 23, would unite with a chlorine atom weighing 35.4, or a bromine atom weighing 80, while a bromine atom weighing 80, would combine with one of potassium weighing 39. So, also, an atom of molybdenum, weighing 96, would unite with 2, 3, 4 or 5 chlorine atoms, each weighing 35.4.

It will be observed that this hypothesis involves no assumption as to the cause or manner of the union of these chemical atoms. Whether they simply lie side by side, each retaining its individuality, or whether they interpenetrate, fuse or blend together, and for the time lose their individual existence. We shall see presently that there are reasons for adopting the former view.

The *atom*, in a chemical sense, may be defined as the smallest portion of an element which acts as an independent unit in chemical changes; the chemical *molecule* is the smallest portion of any substance, elementary or compound, which retains all the chemical properties of the substance in mass and which can move to an unlimited extent, independently of other portions. The molecules of compounds, therefore, consist of several atoms; the molecules of elements, there is good reason to believe, are frequently composed of several like atoms, while in other cases they consist of but one. Each kind of atom, therefore, has a specific mass, represented by the combining number, and specific chemical qualities, by virtue of which the elements differ, as iron and sulphur. Of the relation of these little is known, except that the chemical qualities are to some extent periodic functions of the mass. It cannot be asserted that every atom has combining power, for a whole group of elements, the helium-argon group, shows no well-established tendency to form compounds.

Before proceeding to discuss the further properties which chemists have been led to attribute to the atoms, we may consider certain qualities which have from time to time been ascribed to them, but on which chemistry is silent. Speculators have often erred in attempting to elaborate their hypotheses too fully, and by making assumptions which have afterwards proved to be improbable or untenable, have brought discredit on views, which in their essentials, were of great value. Perhaps no hypothesis has suffered more in this respect than the atomic theory. In his book on the 'Concepts of Modern Physics' (p. 85), Stallo mentions certain points on which, he says, all atomists are agreed. Among others are these: "*Atoms are absolutely simple, unchangeable, indestructible; they are physically, if not mathematically, indivisible.*"

Without speaking for the physicists, I can assert most positively that none of these attributes are in the least essential to the conception of the chemical atom. Whether the atoms be *simple* or *complex*, *divisible* or *indivisible*, we have at present no satisfactory means of deciding, and whether they be one or the other, it in no wise affects the conception of the atom as the chemical unit. It is believed by some, on spectroscopic evidence, that atoms are decomposed at the high temperatures existing in certain stars, and a similar explanation has been offered for certain electrical phenomena exhibited by gases. All we can say at present is, that by no chemical or physical process known to us, do atoms undergo division or transformation to an extent appreciable by chemical methods. An atom of carbon always acts with the combining weight 12; if it consist of several independent parts, we do not know it, because in all reactions thus far known, these parts always act together. The idea of the transmutation of the elements, while resting at present on a very slender basis, is entirely justifiable as a working hypothesis.

The supposed *indestructibility* of the atom amounts merely to this, that with our limited range of experimental methods, we have not been able to cause any appreciable portion of matter to disappear as such permanently, but can always recover it unchanged in mass and chemical properties. To assert that matter cannot, under any circumstances, be made to disappear as matter, seems to me to be the most unjustifiable dogma imaginable.

As to the *unchangeableness* of the atoms, we are equally in the dark. That an atom of oxygen in water is similar in every respect to one in iron rust, we cannot assert. There are certain physical properties of the elements which persist in their compounds, among which are the optical properties. Every transparent compound has a definite molecular refractive power, and it has been found that the figure representing this may be divided up in such a way as to assign a definite portion to each atom in the molecule. If we once know the atomic refractive powers of the several elements, we can calculate with considerable accuracy the molecular refraction of any compound containing these elements. For example, the molecular refraction of alcohol, C_2H_6O, is the sum of twice the atomic refraction of carbon, six times that of hydrogen and once that of oxygen. Now remarkably there are certain exceptions. For instance, oxygen combines in either of two ways, which are called single and double union, which are symbolically represented in the case of carbon compounds, by $C = O$ and $C - O$. Its atomic refraction is different in these two forms, and we cannot positively state that the difference is not due to a temporary change of some kind in the atom itself. At the same time (with the above qualifications and some others of a similar nature) the persistence of the atomic refraction and certain other physical properties through all the combinations of an atom, affords some indication that its nature remains essentially unchanged.

Finally, questions as to the shape, size, hardness or penetrability of the atoms, are matters of indifference to the chemist at present. For his purposes they may be regarded simply as centers through which energy manifests itself, of like properties in the same element, but differing in mass and certain other respects in the different elements.

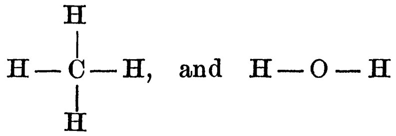
We may now consider some of the properties which the chemist does ascribe to the atom in addition to mass and specific chemical nature.

In recent years much has been learned about *chemical affinity*, a great part of which is susceptible of mathematical expression, and is independent of the atomic theory, only the experimentally determined combining numbers coming into consideration, the *gram atom* and *gram molecule* taking the place of the atom and molecule. As to the real cause or nature of affinity we are still totally in the dark. Very elaborate researches, however, have brought to light certain important facts to which I may properly refer, as they are at present incapable of interpretation apart from the hypothesis of atoms.

Each unit of an element is capable of uniting with but a limited number of other units, which differs in different cases. This may be illustrated by the hydrogen compounds

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

The carbon atom can hold four hydrogen atoms, the nitrogen atom but three, the oxygen atom but two, and the chlorine atom but one. The combining power of carbon, nitrogen and oxygen atoms may be regarded as divisible into four, three and two parts respectively (with regard to hydrogen), while that of the chlorine atom is indivisible. The number of parts into which the combining power is thus divisible is termed the *valency* of the element, and each of these parts is termed a *valence*, *bond*, or *affinity unit.* Without going further into detail (for the subject is an elaborate one), it may be stated as a general law, that combination takes place by a valence of one atom acting on a valence of another atom, or by the several valences of one, acting on the corresponding number of valences of another atom or atoms. This is conveniently represented by lines joining the atomic symbols. Thus CH_4 and H_2O may be represented by the formulas



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H, \\ & & | & & \\ & & H & & \end{array} \quad \text{and} \quad H-O-H$$

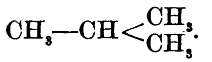
as the oxygen atom has two valences, these may combine each with a valence of carbon, thus

$$O=C=O.$$

This law holds invariably in the case of carbon compounds, and in general, but whether combination takes place only in this way in all classes of compounds is as yet an open question. The number of valences has nothing to do with the strength of affinity ; a pentavalent atom has not five times the affinity of a univalent atom.

It was long ago discovered that there could exist several substances of the same percentage composition and molecular weight, but differing in chemical and physical properties, the so-called *isomeric* compounds. Sometimes as many as twenty distinct compounds of the same composition are known. This difference is inconceivable if the atoms are indiscriminately arranged, like a lot of different colored balls thrown together at random ; there must be in each a definite arrangement of the atoms which cannot be changed without changing the nature of the compound. A comprehensive study of compounds, aided by the conception of valency, has led to the idea of the linkage of atoms in the molecule and to the so-called structural or constitutional formulas. The structural formulas of the two forms of butane, C_4H_{10}, are given, as illustrating the linkage of atoms, as well as the nature of isomerism.

$CH_3-CH_2-CH_2-CH_3$,



$CH_3-CH<\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$.

Such formulas are not intended to represent the actual form of the molecule; they are schematic merely; they are not fanciful, but are based on innumerable experiments, which do not concern us here. The innumerable facts of organic chemistry tally so well with the assumption of chemical units or atoms, linked together in definite ways, as to give to the hypothesis a very great degree of probability.

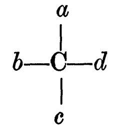
Some atoms can manifest a different valency according to circumstances; thus iron forms two chlorides, $FeCl_2$ and $FeCl_3$, in the former of which the iron atom is believed, for good reasons, to have but two valences (Fe''), and in the latter three (Fe''').

Of the cause of valency we know nothing, and in addition to what I have said we know but little, except that there is an intimate relation between the valences and the power of carrying electric charges, and that (in some cases at least) there is a definite geometrical relation between the valences.

If a salt, for example, sodium chloride, be dissolved in water, and an electric current be passed through the solution, the sodium atoms move to the negative pole, carrying charges of positive electricity, and the chlorine atoms to the positive pole, carrying negative electricity. These electrically charged atoms (or groups of atoms) are termed *ions.* If the chlorides of iron be similarly treated, a similar result follows, the iron transporting positive electricity. There is this difference, however, that the divalent iron atom in $FeCl_2$ transports but two units of electricity, while the trivalent atom in $FeCl_3$ carries three. More complex molecules are frequently broken up into a mixture of simple and complex ions, the latter carrying a unit of electricity for each free valence, thus K_2SO_4 gives two positive K ions and the negative ion $= SO_4$, which carries two units; with regard to the amount of electricity carried the valences are therefore equivalent. What the cause of the relation between valency and electrical phenomena is, we do not know.

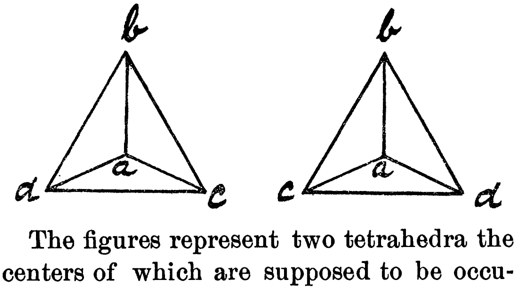
There is still another property of valency which has been discovered in recent years, and which is of the highest importance. It may be asked whether in the case of the carbon atom, for example, the division of the attractive power into four valences implies action in four distinct and fixed directions, that is, whether the atom possesses a sort of polarity, or whether the action may be in any direction. Thanks to the recent labors of organic chemists, it now seems tolerably certain that the carbon atom tends to exert its attraction in four distinct and tolerably fixed directions, rather than in all directions equally.

It has long been known that there exist certain pairs of organic compounds which have identical composition and molecular weight, which show identical chemical behavior and which agree in all physical properties except two. These bodies cannot be regarded as isomeric in the ordinary sense, as their structural formulas as usually written, are identical. The two respects in which they differ are these: in solution one rotates the plane of polarization of light to the right, the other to the left; when crystallized, they frequently show hemihedral faces, differing only in this, that the crystals of the one cannot be brought to coincide with those of the other, but are as an unsymmetrical body and its reflected image in a mirror. I have said that the ordinary structural formulas are schematic merely, they do not claim to show the actual relation of the atoms in space. Two molecules, whose geometrical forms are identical except in being right- and left-handed or as object and reflection, would be represented by the same structural formula, and would have the same chemical, and in general the same physical properties; their action on polarized light, however, would be the same, but in opposite directions, and their crystalline form, if unsymmetrical, would be so in opposite senses. In short, the isomerism would not be chemical, but *physical* or *geometrical*, like the pairs in question. It was further observed that in every case of this kind the molecule contains an 'asymmetric carbon atom,' a carbon atom united with four atoms or groups each differing from the others:



$$\begin{array}{ccc} & a & \\ & | & \\ b - & C & - d \\ & | & \\ & c & \end{array}$$

If we regard the groups a, b, c, d as interchangeable in position, or as rotating independently about the central carbon atom, we cannot explain the apparent right- and left-handedness of the molecule; there could be no fixed difference between the two compounds. If, however, as van't Hoff and Le Bel pointed out, we suppose the four valences to extend in the directions of the apices of a tetrahedron and to be fixed in these directions; then when the combined groups are all different, we obtain two forms of molecule which are identical in every respect except that the one is like the reflected image of the other.



The figures represent two tetrahedra the centers of which are supposed to be occupied by a carbon atom, the four groups a, b, c, d being located in the direction of the apices. It is easily seen that the one corresponds to the reflection of the other in a mirror. It is to be distinctly understood that it is intended to represent only the direction of the valences, not the shape of the carbon atom. As, in general, these geometrical isomers are not readily transformed into each other, it follows that the combined groups or atoms have a strong tendency to retain their relative positions; in short, that the direction of the valences is practically fixed. The same holds true in the case of pairs of compounds in which there are two doubly united carbon atoms as

$$\genfrac{}{}{0pt}{}{a}{b}\!> C = C <\!\genfrac{}{}{0pt}{}{c}{d} \quad \text{and} \quad \genfrac{}{}{0pt}{}{a}{b}\!> C = C <\!\genfrac{}{}{0pt}{}{d}{c}$$

a simple rotation of one half the molecule about its axis, or an interchange of position on the part of a and b or c and d in one of these forms would convert it into the other, yet in reality this does not occur, and in general, the two forms represent distinct compounds. The theory has been applied with great success in predicting new compounds and in explaining the nature of substances containing several asymmetric carbon atoms in the same molecule, notably the sugar group. It does not imply that the molecule is rigid, but merely that there are certain fixed directions of attraction, about which, within limits, the combined atoms may vibrate. The concordance of a very great number of facts with this hypothesis, and the absence of any noteworthy exceptions, lend to it a high degree of plausibility. Whether the fixed direction of the valences is true of other atoms than those of carbon, is as yet uncertain. Carbon compounds lend themselves with especial ease to such studies, and the valency of carbon is practically fixed at four. The effect of varying valency, as in the case of iron, is unknown, but in the case of nitrogen, and to some extent in that of certain metals, some evidence has been accumulated, tending to show that the rule is a general one.

It will be seen that the theory of the

structural formula involves an extension of the older atomic hypothesis, in that it asserts definitely that the combining atoms do not blend, but come into juxtaposition in some orderly and systematic fashion, while stereochemistry, or chemistry in space, asserts that the parts of these systems are to a certain extent fixed in relative position, not rotating about each other after the manner of the members of the solar system. As to the inner nature of the atom itself, however, it says absolutely nothing.

To sum up, the laws of Constant and Multiple Proportions have led the chemist to regard matter as not continuous, but composed of units or atoms, these having the same mass and specific chemical properties in the same element, but other masses and other chemical properties in other elements. Innumerable facts lead him to believe that the atoms in the molecule are not blended, nor so juxtaposed as to have an arbitrary and constantly varying relation, but combined in such a manner that there is a more intimate relation between some atoms than others, some forming connecting links between the rest, a relation which is schematically represented by structural formulas. Finally, stereochemical phenomena indicate that the molecule possesses a certain definite geometrical structure, not necessarily rigid, but not having a mobility of its parts analogous to that of the parts of the solar system. As to the further divisibility of the atoms, their unalterableness, indestructibility, form, origin, and, in short, their absolute nature, the chemist knows nothing and has no opinion of real weight—for him they are merely centers through which energy manifests itself.

If those who adopt the atomic theory would carefully distinguish between essentials and non-essentials, and if those who deny the possibility of interpreting vital phenomena in terms of physics and chemistry would bear in mind that we know scarcely more of the inner nature of the fragment of carbon than of the protoplasm into whose composition it enters, and that affinity is after all is as great a mystery as consciousness, we might possibly hear less of the impossibility of gross, inert, dead matter containing within itself "the promise and potency of every form and quality of life."

H. N. STOKES.

*SOME OBJECTIONS TO THE ATOMIC THEORY.**

FOR the purpose of this discussion, all metaphysical conceptions or discussions are ruled out, and it is explicitly confined to that definition of the atom or molecule connoted by Dalton's famous hypothesis with such amplifications or modifications as have been brought about by the subsequent advance of physical science. In its inception the hypothesis was not without objectors, and properly so.

The efforts of Wallaston and others to insist upon the importance of considering 'combining numbers' or 'reacting masses,' things which one could really know about and determine experimentally, rather than hypothetical atoms, the existence of which in the nature of things was beyond physical proof, was philosophically sound, as far as it went. But the historical vicissitudes of the hypothesis, interesting though they be, can not be considered here, but rather, attention must be given to the comparatively recent discussions on this subject as they have appeared in contemporaneous epistemological writings.

The attempt will be made to present the present status of the subject with due regard to relative perspective values, rather than to cite article and authority in an historical retrospect. Dalton's hypothesis

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*Paper read before the joint meeeting of the Chemical and Philosophical Societies of Washington. Time allotted for this contribution to the program, 15 minutes.