THE ATOM OF THE CHEMIST.

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The chemist has believed in the existence of the atom for more than one hundred years. The fact that the different elements combine to form compounds in certain definite proportions by weight can be most easily explained by assuming each element to be made up of discrete particles, all of the same mass in a given element but of different masses for different elements. But while this explanation of the laws of chemical combination was the only satisfactory one that could be offered, nevertheless, until a few years ago, not a single direct proof of the existence of atoms had been obtained. As a matter of fact, about twenty years ago a school of chemists arose, headed by Ostwald, who doubted the existence of atoms. They said the atomic theory was an attempt to explain nature by a crude mechanical analogy, and that matter was not the coarse grained sort of affair that these literal minded people made it out to be. They said that the people who believed in atoms did so because they had a psychological intuition which they got from observing dust particles. One can divide a dust particle into finer and finer particles, but the imagination balks at continuing this process of division indefinitely. So these literal minded people said that one must ultimately arrive at a particle of such fineness that it could not be further divided and hence is the indivisible atom. Likewise, said the antagonists of the atomic theory, these people think of a liquid like water not as a fluid but as a discontinuous medium made up of hard, solid molecules which were freer to slide over one another, for the reason that the human mind grasps the idea of particles of unchanging size and shape much more readily than it does that of fluid matter. And so a gas, instead of being a continuous medium able to expand indefinitely, must be made up of hard elastic particles flying about in space.

On the other hand, these literal minded chemists, and they comprised a great majority, went ahead serenely

building up a system of chemical combination based upon the assumption of indivisible atoms—a system which has proved extremely fruitful in bringing the facts of chemistry, especially organic chemistry, to light and which constitutes one of the most remarkable achievements of human intelligence. Within the last few years, by a series of brilliant experiments, the existence of the atom has been established beyond a doubt. For most of the direct evidence of the existence of the atom we are indebted to the physicist. But the physicist was not content with demonstrating the existence of the atom. He has gone ahead and shown that the atom is made up in turn of electrons and positive nuclei and is of such complexity as to defy our comprehension. His work has proved that both schools of chemists were wrong. Atoms exist, but they are not the hard, indivisible particles that the chemist thought them to be. They are perhaps nothing but systems of electrical particles. These particles themselves are nothing but centers of electrical force. There is nothing left for the man whose imagination works through his tactual sense to rub between his fingers and say, "This is matter." The man who was happy with hard, indivisible atoms is no more comfortable with this complicated atom that the physicist has forced upon him than he would have been in the old days without any atoms at all.

The chemist is interested primarily in the ability of atoms to combine with atoms of other elements to form chemical compounds. The numerical measure of the ability of an atom to combine with other atoms has been called its valence, and the force which binds one atom to another, as to the nature of which we have been until recently very much in the dark, has been designated as the valence bond. By ascribing to hydrogen one valence bond, oxygen two and carbon four, the organic chemist has built up a most extraordinary system of chemical valence which not only applies almost perfectly to several hundred thousand compounds, but which may almost be said to predict the existence and the properties of this vast number of compounds as well as innumerable

other compounds which yet await syntheses in the laboratory.

When we come to inorganic chemistry, the situation is different. In the first place, the valence of many of the elements is not a simple, definite number, but is a variable quantity, some of the elements having as many as seven different numerical valences. In the second place, the valence bond is a different sort of a thing than the one we met in organic chemistry. If we electrolyze sodium chloride which has been brought into a liquid condition by solution or melting, the sodium travels in the direction of the positive current, and the chlorine in the opposite direction, thus demonstrating that the sodium atoms are positively charged and the chlorine atoms negatively so. It has been recognized since the time of Faraday that the attraction of the positively charged sodium atom for the negatively charged chlorine atom would account fully for the valence bond in sodium chloride. It remained for the brilliant researches of Bragg and Bragg to show just how and why this was so. Physical experiments show that a sodium chloride crystal is made up of alternate positive and negative charges arranged in a so-called simple cubic arrangement, each positive charge surrounded by six negative charges, and each negative charge surrounded by six positives. These charges are not to be confused with the electron or elementary positive charge, however. For with the positive charge is associated a mass equal to that of the sodium atom and with the negative charge a mass equal to that of the chlorine atom. Evidently, then, we have the charged atoms acting as indivisible units and bound to each other by electrostatic forces alone. In valence bonds of this nature, therefore, number has lost its significance, for apparently one sodium atom may attract the six chlorine atoms which surround it with as much force as it would attract a single chlorine atom in a sodium chloride molecule in the gaseous state. Evidently, therefore, if we were to try to write sodium as we do carbon, oxygen and hydrogen in organic chemistry, with a certain number of dashes to represent its valence, we

should be at a loss whether to put one dash to represent the sodium atom, or six. With the understanding, however, which the physicist has given us of the structure of sodium chloride, the uncertainty of the valence number causes us no difficulty; rather, the new viewpoint of the matter makes easily understandable the many interesting properties of that large class of substances of which sodium is a conspicuous example, known as electrolytes.

On the other hand, in the case of the organic compounds, where the number system of valence works so satisfactorily, we have no physical evidence as to the structure or arrangement of the atoms in the molecules except that the atoms do not seem to be charged as they are in the case of sodium chloride. We must still rely upon the intuition of the chemist rather than the direct experiment of the physicist for an explanation of the force which we call a valence bond. Many chemists still prefer to regard valence as an abstract numerical property of the atom and content themselves with taking it as it exists without worrying about why it is so. On the other hand, with the conception of the atom as a positive nucleus whose charge is its atomic number surrounded by electrons, a physical chemist believes that valence is not simply a number, but that it can be explained in all cases as due to electrostatic forces between the positive nucleus of one atom, and the outer electrons of the same and other atoms. The theory of G. N. Lewis has met with most remarkable success in explaining the combination of atoms in the molecules. This theory is based upon the conception of the atom which the physicist has given us, and I shall try to sketch for you its essential features.

Let us consider the elements from lithium to neon inclusive, which form the first row of eight in the periodic table. Lithium has an atomic number of three, glucinum, four, boron five, and so on, to neon with an atomic number of ten, the elements being placed according to their atomic number. The atomic number is the number of positive charges on the nucleus, and we represent the nucleus of the atom by writing the atomic number with

a plus charge after it. The neutral atom then must have as many electrons around the nucleus as it has positive charges on the nucleus. It should be observed that except in the cases of substances like sodium chloride where the atoms are alternately positively and negatively charged, the atoms must be on the average neutral. In our representation of the electrons, we have apparently arbitrarily placed two of the electrons close to the nucleus and the remaining electrons are arranged at some distance away from the nucleus. The following consideration, however, shows the justification for doing this. When lithium combines with fluorine to form lithium-fluoride, we get a salt which resembles sodium chloride. The lithium atom becomes positively charged and the fluorine atom negatively charged. This can be brought about only by an electron passing from the lithium atom to the fluorine atom. The lithium atom, however, never loses more than one electron. This is a fact which has been recognized for a long time. Even before the electron was discovered, it was thoroughly understood that the lithium atom could acquire only one positive charge while the glucinum atom combines with two fluorine atoms and acquires two positive charges. That is to say, the glucinum atom may lose two electrons. Since it has four electrons, however, apparently there are two electrons in it just as in the lithium atom which may not be lost. We find the same considerations to apply throughout the rest of this row of elements, and we assume that these electrons are closer to the nucleus than those electrons which take part in a chemical reaction Those electrons which take part in a chemical reaction we, somewhat arbitrarily perhaps, assume to be at a greater distance from the nucleus and designate them as valence electrons. A valence electron, then, is an electron in the periphery of the atom. Lithium has one, glucinum two, boron three, and so on up to neon which has eight. Lithium combines with one fluorine atom, beryllium with two fluorine atoms, boron with three and carbon with four. Lithium fluoride and glucinum fluoride are salt-like in their character, that is, they resemble sodium chloride, and the valence bonds

which hold them together may be ascribed to the electrostatic forces between the atoms when an electron passes from one atom to another leaving the one atom positively charged and causing the other atom to be negatively charged. Compounds of this type are called polar compounds because the molecule consists of a positive and a negative atom or atoms resembling a magnet with a north and a south pole. The reason that the electron passes so readily from the lithium atom to the fluorine atom appears to be because the positive charge upon the nucleus of the fluorine atom is so much greater than that upon the lithium atom. The recipe for making a polar compound, that is, one of salt-like character, then, is to take two atoms with a considerable difference in the positive charge upon their nuclei. This rule is subject to a modification which will be obvious a little farther on. When that modification is introduced, it is found to be verified absolutely by the facts of chemistry. When we consider boron trifluoride, we find that the difference in positive charges upon the nuclei of the two atoms in question is not so great. Therefore, the tendency for an electron to leave the boron atom and go to the fluorine atom will be very much less. As a matter of fact, boron trifluoride does not appear to be a polar substance, that is, of salt-like character, and when we consider carbon tetrafluoride, where the fluorine has only three positive charges more than the carbon, we have a compound which has no resemblance whatsoever to a salt. There is no reason to believe that the electron has left the carbon atom and gone to the fluorine atom, and we are forced to the conclusion that the valence bonds here must be quite different in character from those in lithium fluoride. G. N. Lewis has proposed the theory that the valence bond in a compound of this non-polar type consists of two electrons occupying a position somewhere intermediate between the two atoms. We do not have time to go into the detailed considerations which led Lewis to the idea that a non-polar bond consisted of two electrons. We can only try out the arrangement of a number of compounds to see how it will work out and, of course, that is in the last analysis the only consideration of importance in regard

to any theory. It may be noted at once, however, that if two electrons are to be placed between atoms for each valence bond, it will in general lead to an even number of electrons in any molecule. Remarkably enough, all but a very few of the hundreds of thousands of chemical compounds do contain an even number of electrons. It may be noticed that if we take the old valence theory of organic chemistry where carbon has four valence bonds and hydrogen one, and assume that these valence bonds link, not with each other, but from atom to atom, then the electron in the Lewis theory of valence simply replaces the valence bond in the old system. The application of this theory of valence to organic chemistry in general, then, becomes very simple.

Since carbon combines with four fluorine atoms, we might expect nitrogen to combine with five and oxygen with six. But no such compounds occur. The reason appears to be fairly obvious. The forces of repulsion between the nitrogen and fluorine nuclei are so great that the atoms refuse to remain in combination with each other. When we come to the neon atom, we find a peculiar state of affairs; neon does not combine with any other atom. We might explain its refusal to combine with nitrogen or oxygen as due to the repulsion of the positive nuclei, but there appears to be no reason why it should not take an electron away from a weak atom like lithium. The conclusion which we are forced to is this: Neon has eight electrons in its outer or valence shell. There must be something about the geometry of the arrangement of eight electrons about an atom which makes it peculiarly satisfactory to the forces between the electrons. Eight electrons may be comfortably arranged in the outer surface of the atom but no more electrons may be introduced into this arrangement. Sodium, with an atomic number of eleven, resembles lithium in its properties and can acquire only one positive charge. That is to say, it has only one valence electron. We must conclude then that in the sodium atom the eight electrons are in a condition similar to the two electrons in the lithium atom. We then represent the sodium atom as

having eleven positive charges upon its nucleus, two electrons close to the nucleus, eight more outside of these two, and the one valence electron still outside these eight forming the beginning of a new shell of outer or valence electrons. The second row in the periodic table thus becomes a repetition of the first row, the number of valence electrons increasing with the atomic number until we reach the rare gas argon, the only difference being that the second row has an inner shell of eight electrons The chemical properties of these elements bear out this conclusion absolutely. If time permitted, we could go on through the periodic table of elements, showing how the properties of these elements may be explained by assuming that the electrons are arranged in series of shells, one about the other, the outer shell always composed of the valence electrons.

Since this group of eight seems to be a peculiarly stable arrangement for the electrons about an atom, we should expect that those atoms which have less than eight electrons in their outer shells would try to acquire eight electrons when they enter into a chemical compound. This proves to be the case. It does not apply, of course, to those atoms which are relatively weak, that is, those atoms which have a small positive charge upon the nucleus, because we have seen that when they enter into chemical combination they lose their valence electrons entirely. But, for the atoms beginning with carbon, which do not lose their valence electrons to another atom in a chemical combination, we find in a vast majority of cases they combine with other atoms in such a way that they complete their shell of valence electrons up to the number eight. An inspection of such typical compounds as carbon tetrafluoride, methane, ammonia, water and hydrogen fluoride, will show that this is the case. The hydrogen atom, it may be remarked here, with only one positive charge upon its nucleus and only one electron of any kind, appears to be completely satisfied with two electrons instead of eight. But this is what we might expect since we have been led to the conclusion that all atoms have two electrons arranged very close to the nucleus. Hydrogen and helium with atomic numbers of one

and two, then, are to be placed in a series by themselves at the beginning of the periodic table—the hydrogen atom anxious to acquire two electrons by chemical combination and the helium atom, having two electrons already, refusing to combine chemically with anything. Helium gas is absolutely unreactive chemically.

The chemical properties of any atom, then, are to be explained by the number of valence electrons it possesses and the pull upon these valence electrons exerted by the positive nucleus. If the pull exerted by the nucleus is very strong, as in the case of chlorine, which not only retains its valence electron with great force but strives to acquire additional ones, we say that the element is electronegative. If the force upon the valence electrons is weak, as in the case of sodium, we say that the element is electropositive, meaning, of course, only slightly electronegative since all atoms must be regarded as exerting some pull on their valence electrons and hence being electronegative to some degree. Now the concept of atomic number would lead us to expect that the atoms would increase continuously in electronegativety from hydrogen, with an atomic number of one, up to uranium with an atomic number of ninety-two, since the force upon the valence electron should be proportional to the atomic number by the ordinary laws of electrostatics. As a matter of fact, the electronegativety is a periodic function of the atomic number. The atoms may be arranged in the well known periodic table in periods of two, eight, eight, eighteen, eighteen, thirty-two and thirty-two. The electronegativety rises to a maximum at the end of each period and drops almost to zero at the beginning of the next period, and the greatest electronegativety in the whole periodic system is reached in the element fluorine[1] with an atomic number of nine. It was to explain this periodicity of the elements that Lewis and Kossel introduced the concept of shells, concentric about the atomic nucleus. Each period ends in an inert gas where presumably a shell of electrons is completely

[1] Actually, neon may be supposed to be more electronegative than fluorine, but since it does not combine with any other element it is not ordinarily so considered.

filled. With the first element in the next period, then, there must be the beginning of a new shell. Thus sodium has one valence electron forming the beginning of the second shell of eight around the first shells of two and eight, each in the interior of the atom. The first question, then, that arises, is why does the positive nucleus exert so slight a retaining force upon this valence electron? The answer seems to be this: The valence electron is at a considerably greater distance from the nucleus than the inner shells. The electrons in the inner shells tend to neutralize the attractive force of the positive nucleus for this valence electron. The whole sodium atom, then, exclusive of this valence electron, may be regarded as having a net positive charge of one only, which acts as though it were centered in the nucleus. The force exerted, then, upon the valence electron will be relatively weak. Futhermore, the valence electron of sodium is farther from the nucleus than the valence electron in the lithium atom. Thus, according to Coulombs law, the force exerted upon an electron by a positive charge is inversely proportional to the square of the distance between them. The electron in the sodium atom is then at a greater distance from the nucleus than in the lithium atom and should be retained with less force. This is the case. Sodium is less electronegative than lithium. This explanation may be applied consistently to the properties of the elements throughout the periodic table. The electronegativety rises to a maximum at the end of each period, but each maximum is actually less than the preceding as we go from one period to another, because of the increasing distances of the electrons from the positive nucleus.

This application of the laws of electrostatics to explain the properties of the atom must be recognized as being only qualitative. The unsolved problem is why this arrangement of electrons in shells around a positive nucleus is stable at all. Undoubtedly there is something in the geometry of arrangement of electrons which determines how many electrons may be crowded into any shell. When we study the properties of the more complex

atoms, we find evidence that the outer shells are no longer perfectly definite arrangements in number, but that they are more or less variable in their makeup. Electrons may apparently shift from one shell to another. But the geometry of the atom can hardly explain why the electrons do not fall into the powerful positive nucleus. That they do not is a fact. Why they do not is a problem for the physicist rather than the chemist.

The importance of symmetry in the stability of electron arrangement should be emphasized. We have already mentioned Lewis' observation that so comparatively few of the many thousands of compounds contain a total number of electrons (measured by the sum of their atomic numbers) which is odd. Those which do are relatively unstable and almost without exception highly colored. Apparently when the number of electrons is odd, instead of each electron's having a definite position, one or more electrons are able to oscillate between two or more positions, thus absorbing light of some wave length in the visible spectrum and causing the phenomena of color. It has been noted that the complex atoms have a variable structure in their electron shells. These atoms are all colored.

To repeat, the most important question is, why the shells of electrons do not collapse into the positive nucleus.

The physicist has offered an explanation, and a natural enough one. He says that the electrons are rotating around the positive nucleus in orbits just as the planets rotate around the sun, and that they do not fall into the nucleus for the same reason that the planets do not fall into the sun. The chemist has a very grave objection to this dynamic atom of the physicist. The chemist has reason to believe that the atoms are combined in molecules of extraordinary complexity and rigidity of structure. These molecules retain their structure unchanged throughout the ordinary processes of fusion, evaporation and chemical reaction. The chemist believes that the atoms are held together in these molecules by electrons which occupy definite positions between the different

atoms. It is almost incomprehensible how these electrons can be rotating around these atoms in orbits and at the same time bind the atoms together in fixed and definite arrangements of molecular structure. Many chemists therefore have preferred to believe in the static atom, that is, one in which the electrons are arranged in stationary shells, preferring to leave the stability of the shells unexplained rather than adopt an explanation which appears to destroy the chemical property of the atom we call valence.

The physicist is concerned mainly with the explanation of such phenomena as radiation, and this dynamic theory of the atom explains radiation very well, provided the physicist discards a considerable portion of the classical theory of electrodynamics. He has the same justification in doing this that the chemist has in discarding Coulombs law as being operative at small distances between electrons and positive nuclei. That is, each explanation seems to fit the facts. The facts which the physicist and the chemist are trying to explain are thus of a different sort. To the chemist an atom which is radiating light is in a pathological condition. It appears to be impossible for an atom to be brought into a condition in which it radiates, without destroying the molecule of which that atom is a part. The dynamical theory of the atom, then, explains the properties of the atom in one condition; the static theory explains the properties of the atom when it is in another condition. The two theories may not be contradictory—they may simply apply to two different states of affairs. The problem to be answered, then, in the immediate future is not whether these two theories may be reconciled, but rather, whether they are dealing with the same phenomena.