THE ELECTRON THEORY.

W. A. Noyes.

The first fairly comprehensive theory of chemical combination which bears some relation to modern views was proposed in a rather informal way by Lavoisier. Shortly after Priestly had discovered "dephlogistigated air," in 1774, the great French chemist came to recognize very clearly the fundamental part which the newly discovered element plays in nature. Finding that it is an essential element in the acids formed by the combustion of sulphur, phosphorus, nitrogen and carbon, he called it oxygen—the acid-former—a name still appropriate, though I think that most chemists to-day do not recognize how appropriate, so clearly as did the chemists who lived a century ago. Lavoisier also recognized that oxygen combines with metals to form what were then called metallic calxes, and with the assistance of De Morveau and others a nomenclature was introduced which was based on the view that the oxides of the non-metallic elements, called acids, combine with the oxides of the metallic elements, which had been called calxes, to form salts. This nomenclature still clings to us in such names as sulphate of potash. The thought expressed in this nomenclature, that there is a dual nature in the salts, furnished a very natural basis from which the electrochemical theory of Davy and Berzelius was easily developed. According to this theory, the atoms of the elements have two electrical poles, one positive and one negative, and the properties of the element depend upon whether the one or the other of these poles contains more electricity, chemical combination depending on the discharge of two poles of opposite signs when the atoms of two elements come together, the heat of combination being caused by this discharge. The resulting compound may still have an excess of positive or negative electricity, and so a positive oxide like that of potassium may combine with a negative oxide such as that of sulphur to form a salt. This theory dominated chemistry for nearly half a century.

The next important step toward an insight into the nature of chemical combination was the discovery of Faraday, in 1833, that the same current passing through a succession of electrolytes liberates equivalent quantities of elements or radicals at the electrodes immersed in the different solutions. This discovery points very clearly to a definite unit quantity of electricity which is directly connected with those primary units of matter which we call atoms. It is not a unit of energy, since the energy absorbed in the decomposition of the different electrolytes is different. The fundamental conception which we are forced to, was stated very clearly by Helmhotz in his Faraday lecture, in 1881: "If we accept the hypothesis that elementary substances are composed of atoms, we cannot avoid the conclusion that electricity, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity." Maxwell, too, spoke of a "molecule" of electricity in 1873, but evidently had little sympathy with such an idea. This idea is quite different from that in the theory of Berzelius, who considered that differences in affinity were caused by differences in the quantity of electricity in different atoms. The next advance, therefore, seems rather a step backward than forward, as it consisted in the overthrow and complete abandonment of the old electrochemical theory. In that theory chlorine was always negative and hydrogen was always positive in their compounds. But Dumas showed that three derivatives of acetic acid could be prepared in which one, two or three[1] atoms of the positive hydrogen could be replaced by one, two or three atoms of the negative chlorine, and yet the resulting compounds were monobasic acids resembling acetic acid in their salts and in their decompositions. In his attempts to explain these and other compounds on the basis of the electrochemical theory, Berzelius found himself more and more in conflict with well established facts of organic chemistry, and in spite of his tremendous authority as one of the greatest chemists of his time, the chemical world gradually abandoned the dualistic point of view and accepted a unitary conception of chemical compounds. Then, beginning in the fifties, there came the period of the rapid development of the theories of valence and of structural organic

[1] In the formulas used by Dumas, two, four or six atoms.

chemistry. During this period, which lasts, with very little change, to the present time, the attempt to connect the forces which hold the atoms in combination with electrical forces in any definite way was almost completely abandoned. It is true that the terms "positive" and "negative" have been frequently used throughout the period, but they have been used in a wholly vague and indefinite way, with no real thought of electrical properties in the groups.

As so often happens, the beginning of a return to an electrical theory of combination came from the study of phenomena in a different and, as it seemed at the time, wholly unrelated field. During the late seventies, Crookes busied himself with the study of electrical discharge through highly rarefied gases. The phenomena which he discovered were so strange and startling that he spoke freely of a "fourth state" of matter. The physicists and chemists of the time were disposed to look on the expression as somewhat sensational, but the event has shown that he was nearer right than his critics. The phenomena of most interest to us are those of the discharge from the cathode, or negative pole, through a tube in which the pressure of the residual gas has been reduced to one-millionth of an atmosphere. Under such conditions rays are shot out in straight lines perpendicular to the surface of the cathode and when they impinge on the glass opposite they produce a beautiful green fluorescence and give rise to the X-rays, though those rays were not discovered till some fifteen years later. Crookes showed that this "radiant matter," as he called it, almost with the vision of a prophet, travels straight across the tube, irrespective of the location of the anode. He showed that an opaque object in its path will cast a sharp shadow on the fluorescent glass; he showed that if it strikes the vanes on one side of a little wheel suspended in its path the wheel will rotate, and he showed that it can be deflected by a magnet. He found, too, that this radiant matter came always from the negative pole, never from the positive. He had discovered a stream of electrons, but the world had to wait some fifteen years before the X-rays emanating from the fluorescent glass were discovered, and nearly twenty years before the real properties of the electrons were established.

Meanwhile, during the eighties, the ionization theory of Arrhenius was proposed, and with Ostwald as its Nestor, gained rapidly in favor until it has become to-day the only logical basis which we have for the accurate discussion of the properties of solutions.

The development of the theory has demonstrated almost as certainly that atoms or groups of atoms carrying one or more units of an electrical charge exist independently in a solution of an electrolyte, as the study of gases has demonstrated that independent molecules of nitrogen peroxide exist in the gas which consists of a mixture of nitrogen peroxide, NO_2, and nitrogen tetroxide, N_2O_4. What becomes of these charges when the ions reunite, is a question which has scarcely been raised till recently.

From the idea that the reactions between electrolytes in solution take place between ions bearing electrical charges, it is a very simple and natural step to the thought that other reactions may occur in a similar manner. An application of this thought to the reactions of the elements soon leads to the view that the molecules of elementary substances may sometimes separate into positive and negative atoms. This conclusion was, perhaps, first expressed by Van't Hoff in 1895, in an attempt to explain the formation of ozone during the slow oxidation of phosphorus.[1] Similar views were expressed by myself[2] in 1901, and were quickly followed by a statement from Professor Stieglitz that he had presented the same idea some time before at the University of Chicago. Three years later Professor Abegg, of Breslau, published a remarkable paper in which he developed the idea of the electrical polarity of the atoms in considerable detail, and proposed his theory of normal valences and of contra valences, the sum of the two kinds of valences for any given atom being eight. Thus a nitrogen atom may develop toward hydrogen three negative, normal valances or toward oxygen it may assume five, positive, contra valences. In this paper Abegg points out for the first time a probable connection between his theory and the theory of electrons.

Lavoisier and many others of the earlier chemists seem to have considered an atomic or molecular constitution of matter as probable, but the first definite basis for an atomic theory was, of course, laid by Dalton's discovery of the laws of combining weights and of miltiple proportion, in the early days of the nineteenth century. He did not discover the law of constant proportion, and the evidence which he gave for the law of miltiple proportion was exceedingly crude from the quantitative standpoint; indeed, there is to-day, as far as I know, only a single case for which the law has been demonstrated with an accuracy of one part in a thousand, and the determinations for that single

[1] Z. physik. Chemie, *16*, 411 (1895).
[2] J. Am. Chem. Soc., *23*, 460 (1901).
[3] Ibid., *23*, 797 (1901).

case are recent. For a genuine experimental basis we must treat the law as a corollary of the law of combining weights. We all remember that Dalton was not successful in selecting true atomic weights, and while both Avogadro and Amprere suggested a correct basis for the selection very shortly after Dalton's first publication, their suggestion did not meet with approval. So it happened that for the first half of the nineteenth century chemists generally were confused about the atomic weights which they should use, and many of them became skeptical about any possibility of certain choice among the miltiples which might be selected and were disposed to content themselves with a system of equivalents. In the late fifties, Cannizaro, who died only two years ago in Italy, rescued the law of Avogadro from oblivion and contributed very much to the general acceptance of a rational system of atomic weights. A decade later the discovery of the periodic system by Mendeleef and Lothar Meyer confirmed in a most brilliant manner the truth and value of the principles on which the new table of atomic weights was based. At the same time the periodic system pointed, irresistibly, toward some common substratum or ultimate material from which the atoms have been built up or into which they might be disintegrated, but this remained for thirty years and longer only a tantalizing suggestion. Meanwhile the insight which the development of organic chemistry gave into the structure of molecules forced upon organic chemists, at least, a growing conviction of the actual existence of atoms and molecules. In spite of this, the close of the nineteenth century saw the rise of an important school of chemistry, under the lead of Ostwald, which apparently wished to abandon the atomic theory altogether and would have been glad to express all of the facts of chemistry in terms of energy and in the language of mathematical equations. The discoveries of the last decade seem to have convinced even the leader of this school, and I think that to-day we may accept atoms and molecules as actual existing entities with almost the same certainty with which we accept the existence of the sun, moon and planets. With the atomic theory goes, almost of necessity, the kinetic theory of gases. Indeed, some of the most convincing demonstrations of the truth of the atomic theory have come along the lines of the kinetic theory. I might say, in passing, that the second law of thermodynamics, that the entropy of a system always tends to increase, presupposes, almost of necessity, an atomic constitution of matter.

As Helmholtz pointed out clearly in 1881, the acceptance of the atomic theory forces upon us the recognition of a unit quantity of electricity which is just as definite as the atom itself and which Helmholtz very properly said "behaves like an atom of electricity." But the physicists of that day and for long afterwards were accustomed to think of electricity from the standpoint of energy, and the suggestion remained unheeded; indeed, it is very doubtful if Helmholtz himself grasped its full significance.

In 1897 Professor J. J. Thomson took up again the study of the cathode rays in a Crookes tube. These rays had then acquired an extraordinary interest from their use in the production of X-rays. Professor Thomson devised a very ingenious experiment in which he deflected the cathode rays into an insulated hollow vessel by an electromagnet. Knowing the capacity of the vessel, he could determine the quantity of electricity carried into it by the electrons in a given time. He also arranged to have the electrons fall on a thermocouple of known heat capacity, and determined the energy developed on stopping them. From the data obtained he calculated that the velocity of the particles was of the order of ten thousand miles a second, or even as high as 1/10 the velocity of light. The quantity of electricity carried by the particles was found to be very considerable in proportion to the heat energy shown by the thermocouple. These facts seemed to allow of only two alternatives: either the mass of the particles is extremely small or each particle must carry an enormous charge of electricity. Further experiments confirmed the choice of the first of these possibilities, and physicists are generally agreed that the mass of the electron is about one eighteen hundredth part of the mass of a hydrogen atom. Physicists are not altogether agreed, however, as to whether this electromagnetic mass is the same in nature as the mass of an atom which may be measured by reference to the force of gravity. If it is affected by gravity, an electron having a velocity of 10,000 kilometers a second would fall toward the earth possibly two millimeters in flying 800 kilometers, say, as far as from here to Pittsburgh. The difficulty of preparing a straight, evacuated tube of that length is evidently rather great, and we shall probably have to wait some time for experimental evidence on this point. The question has become one of unusual speculative interest in the light of the discussion by J. J. Thomson and the measurements of Kaufmann and Bucherer, which seem to show that the mass of the electron is wholly dependent on the velocity with which it moves.

I will not attempt to discuss how the theory of electrons explains the varied phenomena of electricity and magnetism. Before passing on to its application in chemistry, I will speak of only two or three of the conclusions which have been reached. The electron may be defined as an atom of negative electricity and the current through a metallic conductor seems to be an actual flow of electrons in one direction. In the vacuum tube the electrons or cathode rays fly also only in one direction, but if the cathode is perforated and a residual gas is present, positively charged atoms or molecules may be shot in the opposite direction, of course at a much lower velocity because of their enormously greater mass. These atoms form the canal rays of Goldstein. In electrolytes the electrons no longer move independently as in metallic conductors, but attach themselves to the so-called negative atoms or groups and move slowly in one direction, while the positive atoms or groups—those which have lost an electron—move in the opposite direction. We have long known the metals as the positive portion of electrolytes. It is only recently that this property has been connected with the electrical conductivity of metals. According to the electron theory, a metallic atom forms the positive portion of an electrolyte because it has lost one or more electrons. A metallic wire conducts electricity because it allows the electrons in or associated with the atoms to slip along easily from one atom to another, since the electrons easily escape from the individual atom.

Several authors have discussed the nature of chemical combination in the light of the electron theory. The most elaborate discussion is that of J. J. Thomson.[1] His fundamental assumption is that atoms are composed of a group of electrons within a uniform sphere of positively electrified matter. A single electron would go to the center of such a sphere. Two electrons, owing to their mutual repulsion, would be in equilibrium at a distance from each other equal to the radius of the sphere. Three electrons would form an equilateral triangle, four a tetrahedron, six an octohedron; but Professor Thomson says that he has been unable to solve the general problem for *n* electrons distributed in a sphere. He gives, however, a rather remarkable solution on the supposition that the electrons are situated in a plane. In that case they will arrange themselves in concentric rings and for a given number of electrons there is only a single stable arrangement. Further than this, with a given number in the exterior

---

[1] Philosophical Magazine, March, 1904.

ring, the number which can be placed within is limited by two extremes. The most suggestive case of this kind is that with 20 electrons in the outer ring. The total number of electrons with such an outer ring can never be less than 59 and can not exceed 67. This might be supposed to correspond to a group of nine elements of the periodic system from helium to neon or from neon to argon. The arrangement with 59 electrons, if it lost one, would be compelled to rearrange to a form having only 19 electrons in the outer ring, but owing to the positive charge acquired by the loss of the electron, it would immediately acquire another and go back to its original form. Such an element would have a valence of 0 for a positive charge, and Professor Thomson suggests that this would correspond to such an element as helium or neon. But he goes on to say that the element would have a valency of 8 for a negative charge, which does not, of course, correspond to the properties of the zero group. A group of 60 electrons might lose one electron and acquire a permanent positive charge of one valence, which would correspond to such an element as lithium or sodium. It ought, however, to be capable of gaining 7 electrons; that is, it should have a valency of seven for a negative charge. Here, again, the facts do not correspond to the theory. It seems evident that the theory needs to be supplemented by some explanation why electropositive elements lose electrons but do not readily take them up, while it would seem that the electronegative elements can do both. The facts seem to be connected with the properties of metals as conductors and of non-metals as non-conductors.

Lorenz in his explanation of the Zeeman effect seems to assume that the electrons revolve around a nucleus of matter having a positive charge. It seems possible that the idea of Lorenz is true for metals, that of Thomson for non-metals.

Whichever theory is accepted, the notion that atoms may acquire positive or negative charges by the loss or gain of an electron and that the charged atom may then attract another atom bearing a charge of the opposite sign seems likely to be a fruitful one. I will give an illustration of possible application to well-known facts. An atom of nitrogen may receive four electrons from four hydrogen atoms if at the same time it gives one to the oxygen atom of a hydroxyl group. But the hydroxyl group is loosely held by the nitrogen atom with its four electrons and the compound ionizes and reacts as though consisting of ammonium and hydroxyl. One atom of nitrogen may also give five electrons to three oxygen atoms in forming nitric acid. Here the nitrogen atom, which has become strongly positive, holds the oxygen of the hydroxyl group firmly, but the positive hydrogen is repelled. And so nitric acid ionizes and reacts as though composed of hydrogen and nitrate ions. This will be clearer from an inspection of the following formulas:

The *facts* referred to have, of course, been long known, but as far as I know, this is the first attempt at a rational explanation.

In the development of the electron theory, the intimate connection between electrical phenomena and light, foreshadowed by Maxwell's electromagnetic theory, more than forty years ago, becomes more and more apparent. The spectrum lines are, of course, to be traced back to the motion of electrons, and it is not an impossible dream that these lines may enable us to decipher the structure of the atoms—that the atoms have a complex structure no one can doubt in the light of radiochemistry.

The color of compounds and the rotation of the plane of polarization are also connected with the electrons. Dr. Fry, of Cincinnati, has shown how the theory may help to a solution of intricate phases of the benzene problem.[1] It seems very certain that it is a theory with which we must reckon for some time to come. In studying it we still feel keenly the need of some more fundamental explanation. The elementary idea of attraction is just as difficult to accept when applied to atoms bearing positive and negative charges as when applied to the heavenly bodies at distances of millions of millions of miles. In both cases the thoughtful mind finds it impossible to believe in action at a distance without some medium or mechanism to connect them. And so I can not do better than to close with the words of Professor Thomson: "The theory is not an ultimate one; its object is physical rather than metaphysical. From the point of view of the physicist, a theory of matter is a policy rather than a creed. Its object is to connect or coördinate apparently diverse phenomena, and above all to suggest, stimulate and direct experiment. It ought to furnish a compass which, if followed, will lead the explorer further and further into unexplored regions. Whether these regions will be barren or fertile, experience alone will decide; but, at any rate, one who is guided in this way will travel onward in a definite direction and will not wander aimlessly to and fro."

1 Z. physik. Chem., *76*, 385, 398, 591.