THE ELECTRON THEORY.*

BY

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It is only twenty years since Prof. J. J. Thomson first characterized accurately those atoms of negative electricity which we call electrons, but, as with most great discoveries, many lines of work and of thought, reaching back for more than a century, culminated in this discovery. It seems worth while to go back and pick up some of these threads and look at their relations.

On August 1, 1774, Priestley discovered oxygen. He called it dephlogistigated air, and explained its properties on the basis of the old theory of phlogiston. Lavoisier, in Paris, when he learned of this discovery, repeated the experiments and soon came to a clear view of the important part which the element plays in nature. He considered that compounds of oxygen with the non-metallic elements are acids and that the compounds with metallic elements are bases. These acid oxides and basic oxides, in turn, combine to form salts. The point in which we are interested is the notion that the acid oxides and basic oxides are binary compounds, and that salts are also binary compounds of a second order. About 1790, according to a tradition which is questioned, some frogs' legs which had been purchased for an invalid wife of the Italian physician, Galvani, were hung on brass hooks attached to an iron railing. One of Galvani's pupils noted a peculiar twitching of the frogs' legs and called Galvani's attention to it. Thus began the discovery and study of current electricity. I have found in an old chemistry this cut (Fig. 1) to illustrate Galvani's experiments. When the pieces of copper and zinc are brought into contact the current flows and the frogs' legs twitch into the second position.

Soon after, Volta, in Paris, invented the voltaic pile, by means of which much stronger currents could be obtained. This

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figure (Fig. 2), taken from an old chemistry published in 1846, shows one of these early galvanic batteries. Sir Humphry Davy used one of these batteries in London, about 1804, when he made his great discovery of the decomposition of potash and soda by the electric current. This discovery attracted his attention to the very intimate connection between electricity and chemical action, and led him to the proposal of the old electrochemical theory. This theory was further developed by Berzelius, and it dominated the minds of chemists for half a century.

According to this theory, the atoms of the elements have two poles, one positive and one negative, and each element is positive or negative, according to the relative amounts of the two charges. When two elements combine, the discharge be-

FIG. 1.

FIG. 2.

tween the positive pole of one and the negative pole of the other causes an evolution of heat. The resulting compound may still be positive, as in the case of a metal united with oxygen, or negative, as, for instance, the acid oxides. The union of the positive oxide with a negative oxide gives a salt. The intimate relation between the theory and Lavoisier's ideas about oxides and salts is apparent.

In 1833 Faraday discovered a method of measuring an electrical current by determining the quantities of hydrogen and oxygen liberated by passing the current through dilute sulphuric acid. He soon found that if the same current is passed through two electrolytes, as through dilute sulphuric acid and through a solution of copper sulphate in successive cells, the amounts of the elements liberated in the two cells will be in proportion to

the chemical equivalents of the elements. Thus in the series of cells shown in Fig. 3, when one gramme (in round numbers) of hydrogen has been liberated in the first cell, 108 grammes of silver will have been deposited in the second, 63.6 grammes of copper in the third, 31.8 grammes of copper in the fourth, 65.7 grammes of gold in the fifth, and 29.5 grammes of tin in the sixth.

I do not think that Faraday grasped the full significance of this wonderful law which bears his name. It 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 not the same. Helmholtz stated the logical inference from the law very clearly in his Faraday lecture in 1881. He said, "If we accept the hypothesis that elementary substances are composed of atoms, we cannot avoid the conclusion that electricity, positive as well as

FIG. 3.

negative, is divided into definite elementary portions, which behave like atoms of electricity." This idea is very 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 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 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 leading 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 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

FIG. 4.

indefinite manner, with no real thought of electrical properties in the atoms or groups to which they are applied.

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 discharges 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

FIG. 5.

matter," as he called it almost with the vision of a prophet, travels straight across the tube, irrespective of the location of the anode. Thus in the bulb containing rarefied air, shown at the left in the figure (Fig. 4), the current from an induction coil will pass in a curved path from the negative pole *a* to any one of the positive poles, *b*, *c*, or *d*, to which the positive pole of the coil is connected. When the pressure within the bulb is reduced to a millionth of an atmosphere or less, the cathode rays are shot

FIG. 6.

out at right angles to the surface of the negative pole and impinge on the glass opposite, irrespective of the attachment of the positive pole of the coil to the top, bottom, or side of the bulb. This effect is shown at the right of the figure. Crookes also showed that an opaque object in the path of the rays casts a shadow, as shown in Fig. 5. By a very ingenious apparatus he caused the stream of "radiant matter" (electrons) to drive a little windmill (Fig. 6). When a magnet is brought near the

a prophecy of the doctrine of modern physicists that the mass of an electron is dependent on its velocity. Indeed, some physicists seem to say that the *whole* of the mass is due to the velocity, though I confess to some difficulty in understanding what is meant by such a statement. Crookes also predicted that some of the most important discoveries of the future would be made in connection with the study of "radiant matter"—a prediction which has been fully verified.

In 1887 Arrhenius published his classical paper on electrolytic dissociation. This laid the foundation for a new electrochemistry which has avoided many of the difficulties of the older theory and which furnishes the only rational means we have for the study of many of the properties of solutions of electrolytes. It is now clear that in such solutions electrolytes separate more or less completely into atoms or groups bearing positive or negative charges.

In 1897 Prof. J. J. Thomson took up again the study of the

FIG. 9.

cathode rays in the Crookes tubes. By means of the apparatus shown in Fig. 9 he showed that when static charges of opposite sign are applied to the plates *D* and *E*, the cathode rays passing through the narrow slits in *A* and *B* are attracted toward the positive plate, and this can be shown and measured by the motion of the spot of light falling on the scale at the end of the bulb. He then 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 then 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 one-tenth 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 for 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 kilometres a second would fall toward the earth possibly two millimetres in flying 800 kilometres, say as far as Cleveland. 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.

In the light of Thomson's experiments, we may now say that Crookes's "radiant matter" consists, in reality, of atoms of negative electricity. Professor Thomson called these atoms corpuscles, but they are now universally known as electrons. A knowledge of the properties of these new atoms has given us quite a new conception of the nature of a current of electricity in metallic conductors.

It has become clear that atoms of the elements contain electrons, and that metals allow these electrons to pass readily from one atom to another in a regular flow which furnishes the current of electricity in metallic conductors. In electrolytic conduction, on the other hand, electrons are associated with the negative ions, and these pass slowly through the liquid in one direction, while groups or atoms which have lost electrons and which have thereby become positive pass through the solution, usually at a different rate, in the opposite direction. In the wire the current consists in the flow of electrons; in the electrolyte it consists in the flow of two sets of ions in opposite directions.

My own interest in the chemical side of the electron theory arose from an accident. Some twenty years or so ago I had oc-

casion to perform the old Hofmann experiment with the use of a tube such as I hold in my hand. The tube is filled with chlorine, and when a solution of ammonia is added this chlorine should combine with an equal volume of hydrogen and liberate the nitrogen with which the hydrogen was combined. As ammonia is a compound containing one volume of nitrogen gas combined with three volumes of hydrogen, when water is allowed to enter, as you see it is doing, the tube should be left, at the end of the experiment, one-third full of nitrogen. I happened to use, on the occasion referred to, a dilute solution of ammonia and a smaller amount than usual. At the end of the experiment the tube contained one-sixth of its volume of nitrogen, as you see. I explained the result to the class as best I could, and tucked the matter away in my mind as something that would bear looking into. Several years later, in 1901, I had to find thesis subjects for a number of seniors at the Rose Polytechnic, and remembered the failure in the lecture experiment as a suitable topic. We found that when a solution of ammonia acts on chlorine, nitrogen trichloride (NCl_3) is formed. I explained the action at the time by the following diagram:

DIAGRAM 1.

Professor Bray has recently pointed out that a ninth-order reaction, such as is implied in this diagram, is, to say the least, highly improbable, but the suggestion that atoms may retain a positive or negative character in reactions which are not usually considered ionic has met with increasing favor. Van't Hoff¹ had made a somewhat similar suggestion about another reaction in 1895, and Professor Stieglitz published a note, shortly after the appearance of the paper by Lyons and myself, saying that he had presented the same idea some time before at the University

¹ *Z. physik. Chem.*, 16, 411 (1895).

of Chicago. Neither of us, at the time, thought of any connection between these facts and the electron theory. 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 valences, or toward oxygen it may assume five, positive, contra valences. In this paper Abegg pointed out for the first time a probable connection between his theory and the theory of electrons.

In the same year, 1904, Prof. J. J. Thomson proposed a hypothesis that atoms consist of electrons within a uniform sphere of positive electricity. He discussed the arrangement of the electrons on this supposition. A single electron would go to the centre 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 octahedron; 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 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 cannot 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.

This paper of Professor Thomson's is of special interest be-

cause it contains, for the first time, the suggestion that two atoms may be held together by the electrical forces resulting from the transfer of an electron from one atom to another. The hypothesis of an arrangement of electrons within a sphere of positive electricity has been almost entirely abandoned in favor of the belief that atoms contain a positive nucleus which is very small in comparison with what may be called the effective size of the atom, and that electrons rotate around this nucleus at a considerable distance. Rutherford has been one of the leading supporters of this idea, and he bases an argument for it especially on the fact that when positively charged helium atoms are shot through a thin metallic film many of them pass through without deflection, while a few are scattered through a wide angle.

FIG. 10.

The reason for the scattering will be understood from this figure (Fig. 10),² which represents an atom with a small positive nucleus around which two electrons are rotating. If a positive helium atom were shot through the orbit of the electrons at a high velocity it would not be deflected appreciably unless it were to pass very close to the central nucleus. In case it came near the nucleus, however, it would be repelled and thrown off at an angle.

Since Prof. J. J. Thomson first suggested that atoms may be held in chemical combination by the electrical forces resulting from the transfer of an electron from one atom to another a number of chemists have used the electron theory in discussing chemi-

² A similar figure has been used by Prof. W. D. Harkins in an address which he has given.

cal problems. Thus Hentschel pointed out that the three atoms of chlorine in nitrogen trichloride are equivalent to six atoms (three molecules) of free chlorine in oxidizing power. In terms of the electron theory this is easily explained by assuming that in nitrogen trichloride the nitrogen atom has gained three electrons, becoming negative, while each chlorine atom has lost an electron, becoming positive. In order to convert the chlorine of the trichloride to the form in ordinary chlorides each chlorine atom must gain *two* electrons. In free chlorine, on the other hand, one chlorine atom has lost an electron, while the other has gained one, hence the two atoms of free chlorine require only two electrons to convert both atoms to the negative form. Professor Stieglitz pointed out, several years before the electron theory was used in discussing chemical problems, that in reacting with water the negative atom of a molecule of free chlorine combines with the positive hydrogen of the water, while the positive chlorine atom combines with the negative hydroxyl of the water to form hypochlorous acid.

The ordinary valence theory, which takes no account of the electrical forces, gives no satisfactory reason why ammonium hydroxide (H-O-NH_4) should in ionization, give hydroxyl ions, while nitric acid (H-O-NO_2) gives hydrogen ions. When we write the formulas in the light of the electron theory, as shown in this diagram, we see that the negative oxygen of the

DIAGRAM 2.

hydroxyl may be held strongly by the positive nitrogen atom of the nitro group (NO_2), while it is not held so strongly by the nitrogen atom of the ammonium group (NH_4). The nitrogen atom of the latter group has lost four electrons and gained one, if we assume a localization of valence electrons within the atom.

I have referred to the X-rays which are generated when the stream of electrons in a Crookes tube impinges on the glass of the bulb. For a long time there were great differences of opinion among physicists as to the real nature of these rays. It is now pretty well established that the X-rays are of essentially the same nature as light-waves, but have an exceedingly short wave-length.

Most of you have learned of the so-called gratings produced by ruling ten thousand or more lines to the inch on a smooth surface. A spectrum is produced by the reflection of light from such a surface, and if the distance between the lines is known it is a simple matter to calculate the wave-length of a bright line of the spectrum found at a particular angle with the surface of the grating. Conversely, if we know the wave-length of the light of the bright line and the angle, it is possible to calculate the distance between the lines of the grating. Laue, the Braggs, Mosely, and others have applied a similar, though not quite identical, principle to the study of X-ray spectra. They have used as gratings the regular rows of molecules in crystals of salt, the diamond, and other substances.

FIG. 11.

Two results of extreme interest have already come from this study. It has been discovered that each chemical element has a characteristic two-line X-ray spectrum. From these spectra what are known as atomic numbers have been deduced, which fix the position of each element in the periodic system. It is well known that some elements, such as tellurium, have atomic weights which do not fit into the proper place in the periodic system. The atomic numbers of all of the elements so far studied are in the proper order, and we can now say that the atomic number of an element is even more characteristic than its atomic weight.

The X-ray spectra have also been used by the Braggs, especially, to decipher the structure of crystals. This slide (Fig. 11) shows the structure of a crystal of potassium chloride as demon-

strated from the results of these experiments, and the next (Fig. 12) gives the very different structure of a diamond.

I think almost nothing has given me such a feeling of the loss which is coming to the world from this dreadful war as the knowledge that Mosely, one of the most brilliant workers in this field, though a young man of only twenty-six, was killed at the Dardanelles.

There must surely be a very close relation between the structure of atoms and the motion of the electrons within them and the spectra of the elements. Some years ago an element called nebulium was discovered by its spectrum in the great nebula of Orion. The element has not been found in the earth. Nicholson, from a study of the spectrum of nebulium, came to the conclusion that the atom of the element contains four electrons rotating

FIG. 12.

about a positive nucleus. At the same time he said that there were two of the spectrum lines of the nebula which he could not account for by this hypothesis. The same day that he presented his paper in England an astronomer, Wolff, gave a paper in Heidelberg in which he showed that the nebula consists of two parts, and the two lines which Nicholson could not explain came from a different part of the nebula from the rest. The two workers were entirely independent and were interested in different problems, so that the coincidence is remarkable, to say the least.

The work of physicists during recent years has led to the conclusion that the electrons within the atoms of the elements are in a very rapid rotation about positive nuclei. Chemists, on the other hand, have spoken of the transfer of valence electrons from one atom to another without any reference to the motion

of the electrons. It seems possible to unite the two points of view by the following hypothesis.³

Let us suppose that two atoms which have an affinity for each other are brought close together. A valence electron which is rotating around a positive nucleus in the first atom may find a positive nucleus in the second atom sufficiently close so that it will include the latter in its orbit, and it may then continue to describe an orbit about the positive nuclei of the two atoms. During that portion of its orbit within the second atom that atom would become, on the whole, negative, while the first atom would be positive. During the other part of its orbit each atom would be electrically neutral, and the atoms might fall apart. When

FIG. 13.

we remember, however, the tremendous velocity of the electrons and the relatively sluggish motions of the atoms, it seems evident that the motion of an electron in such an orbit might hold two atoms together. In ionization the electron would, of course, revolve about the nucleus of the negative atom, leaving the other atom positive. It seems impossible to explain ionization otherwise than on the supposition of the complete transfer of the electron. This complete transfer in ionization is one of the strongest arguments against the magneton theory as the only explanation of chemical combination.

³ This has now been published in the *Proceedings of the National Academy of Sciences* and in the *Journal of the American Chemical Society*.

An interesting feature of the hypothesis proposed is that it may be used to account for that localization of affinities in particular parts of atoms which is indicated by many of the properties of organic compounds. Thus if we suppose that there are four (or eight) positive nuclei in a carbon atom, around which valence electrons may rotate, an atom of hydrogen may be held to the neighborhood of one of these nuclei as indicated in the figure (Fig. 13).

A few years ago we were accustomed to think of atoms as "manufactured articles," indivisible and unchangeable. The phenomena of radio-activity and the electron theory have demonstrated that atoms are extremely complex entities which may disintegrate into simpler parts. The conclusion is almost irresistible that they may also be formed from simpler parts. The atoms are also tremendous storehouses of energy for which we have not yet found the key. During the last sixty years chemists have deciphered the structure of thousands of compounds of carbon. A hundred years ago this knowledge would have seemed an impossible dream. To-day it is a practical reality, lying at the very foundation of our manufacture of dyes and explosives. Our knowledge of the structure of atoms is still a dream with very shadowy outlines, but I think we may be confident that a not very distant future will see this dream translated into definite details.

I think we may be quite certain that the electron theory is with us to stay, although the theory has found many changes and a very rapid development during its short life, and I cannot 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."