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CONTENTS:

*THE IONS OF ELECTROLYSIS.**

THE subject of electrolysis must always have a special interest for the Royal Institution. It was here that Davy showed its practical value by his brilliant discovery of the metals of the alkalies and alkaline earths; and it was here that Faraday laid the foundation of the scientific discussion of electrolysis; it was here that with his singular experimental skill and clearness of insight he discovered and expounded the laws of electrolysis which will always be known by his name. It is therefore with a good deal of diffidence that I stand here to continue the story. And there is much to be said, for, like all good work, Faraday's work has been fruitful, and in consequence of it, as well as of the genius and skill of subsequent investigators, we now know much about electrolysis which Faraday did not and could not know.

The great difficulty left was that of the mechanism of electrolysis. That the cation and the positive electricity travel together towards the cathode, and that the negative electricity similarly travels with the anion towards the anode, and that on their arrival at the electrodes the electricity is delivered to the metallic conductor and the matter is set free to appear as the ion itself, or to break up, or to act on the elec-

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* Lecture given before the Royal Institution of Great Britain.

trode, or on the solvent, or on something present in the solution; that the quantity of each ion so set free is proportional to the quantity of electricity transferred from the one electrode to the other and to the equivalent of the ion—that is, as we would put it now (if purists will allow us to speak of the *atomic* weight of NH_4 or of NO_3), to the atomic weight of the ion divided by its valency; all that was made out by Faraday. He had made some way in finding out how the liberated ions act, when they do act, on the things in the presence of which they find themselves; and where he led, others have followed, so that we have now many electrolytic methods of oxidation, of reduction and of synthesis, and great manufacturing industries depending on electrolysis. On this large field I do not now purpose to enter. What I wish to call your attention to this evening is the mechanism of electrolysis, or perhaps I should say the progress that has been made towards an explanation of the phenomena.

The earlier theories, from Grotthuss* in 1806, all assume that the decomposition is caused by the attraction of the electrodes or by the passage of the current, and that a definite electromotive force, different for each electrolyte, is required in order that decomposition shall take place. According to these theories, if the electromotive force is below that definite minimum no decomposition can occur and no current can pass.

And indeed at one time it was supposed that this was so. But Faraday, in a series of ingeniously devised and carefully executed experiments, showed that with electromotive force below the minimum necessary for the production of bubbles of gas on the electrodes, a perceptible current could pass for many days. He supposed that this small current was due to non-electrolytic conduction by the electrolyte. But the study of the phenomena of the polarization of the electrodes led ultimately to the complete explanation by Helmholtz* in 1873 of this apparently metallic conduction by the electrolyte, and to a proof that any electromotive force, however small, sends a current through an electrolyte and gives rise to separation of the ions proportional to the amount of electricity transmitted.

The phenomena of the polarization of the electrodes may be described shortly as follows: In the electrolysis of water (or rather of dilute sulphuric acid) it had been observed so long ago as 1802 that platinum or silver plates which had been used as electrodes acquired peculiar properties, so that for a short time the plate that had been the anode acted like the silver, and the plate that had been the cathode like the zinc of a voltaic cell, producing a short-lived and rapidly diminishing current. This observation was first made by Gautherot,† a teacher of music in Paris, who notes the effect of the current on the tongue and states that he had succeeded in decomposing water by means of his apparatus. Shortly after, J. W. Ritter, apparently without knowing anything of Gautherot's work, made a great many observations on the same subject. I cannot refrain from reading to you a passage from a letter from Christoph Bernoulli to van Mons. I take it from the translation published in *Nicholson's Journal*, October, 1805: "As Mr. Ritter at present resides in a village near Jena, I have not been able to see his experiments with his grand battery of two thousand pieces, or with his battery of fifty pieces, each thirty-six inches square, the action of which continues

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* Grotthuss, *Annales de Chimie*, LVIII., p. 54 (1806).

* Helmholtz, *Pogg.*, 150, p. 483 (1873); Faraday Lecture, *Chem. Soc. Trans.*, 39, p. 287 (1881); *Wied.*, 34, p. 737 (1888).

† Gautherot, *Annales de Chimie*, XXXIX., p. 203 (1801).

very perceptible for a fortnight. Neither have I seen his experiments with the new battery of his invention, consisting of a single metal, and which he calls *the charging pile.*

"I have frequently, however, seen him galvanize louis-d'or lent him by persons present. To effect this, he places the louis between two pieces of pasteboard thoroughly wetted, and keeps it six or eight minutes in the chain of circulation connected with the pile. Thus the louis becomes charged, without being immediately in contact with the conducting wires. If this louis be applied afterwards to the crural nerves of a frog recently prepared, the usual contractions will be excited. I had put a louis thus galvanized into my pocket, and Mr. Ritter said to me a few minutes after, that I might find out this louis from among the rest, by trying them in succession upon the frog. Accordingly I made the trial, and in reality distinguished among several others a single one in which the exciting quality was very evident. This charge is retained in proportion to the time that the piece has remained in the circuit of the pile. It is with metallic discs charged in this manner, and placed upon one another with pieces of wet pasteboard alternately interposed, that Mr. Ritter constructs his charging pile, which ought, in remembrance of its inventor, to be called the *Ritterian pile.* Mr. Ritter made me observe that the piece of gold galvanized by communication exerts at once the action of two metals, or of one constituent of the pile; and that the half which was next the negative pole while in the circle became positive, and the half toward the positive pole became negative."

Brugnatelli* suggested that the polarization of the plate which during the electrolysis had given off hydrogen was due to a compound of hydrogen with the metal of the electrode. But it was not until Schönbein discussed the question in 1839* that a systematic attempt was made to settle it by experiment. Schönbein's results were in favor of the view that the polarization is due to the formation on the surfaces of the electrodes of thin sheets of the products of the electrolysis.

Now the old theories assume that if we begin with very small electromotive force and gradually increase it, we have at first a state of tension, the electromotive force, so to speak, pulling at the ions, that this tension increases as the electromotive force increases till it becomes sufficient to pull the ions apart. If this were so there should be no current and no electrolysis till the electromotive force reaches a certain amount, and then suddenly a very great current and something like an explosive discharge of gas; for many molecules would be in the very same state of tension and all would give way at once.

When the electrolytic decomposition of water was first observed, as it was (by Nicholson and Carlisle) immediately after the publication of Volta's first description of the pile, the great difficulty felt by every one was that the hydrogen and the oxygen came off at different places which might be far apart. Grotthuss's theory no doubt explained this, but after the proof of a cause of polarization given by Schönbein, and the accumulating evidence that Ohm's law applies to electrolytic as well as to metallic conduction, no one could hold or defend Grotthuss's theory, although it was retained as a sort of makeshift until some one could think of something better. The something better was produced by Clausius in 1857.† Clausius was one of the eminent physicists to whom we owe the

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* Brugnatelli, *Gilbert's Annalen,* XXIII., p. 202 (1806).

* Schönbein, *Pogg.,* XLVI., p. 109; XLVII., p. 101 (1839).

† Clausius, *Pogg.,* ci, p. 338 (1857).

kinetic theory of gases, and his theory of electrolysis is derived from an application to solutions of the ideas involved in this kinetic theory. He supposes that the molecules of the electrolyte move through the solution as the molecules of a gas move, that they collide with one another as the gas molecules do, and that it must happen that here and there ions get separated and remain separated for a time, cation again uniting with anion when two of them meet under favorable conditions. There will thus always be some detached ions moving about just as molecules do. They will not always be the same ions that are thus detached, and a very small proportion of such loose ions will suffice to explain the phenomena. These loose ions retain in their separate condition the charges of electricity which they had when united, the cations being positively and the anions negatively charged. This is assumed to be the state of matters in any solution of an electrolyte. If now into such a solution we place two electrodes with any, however small, difference of potential, the cathode, being negative, will exercise an attraction upon the positively charged cations, and the positive anode will exercise a similar attraction on the negatively charged anions, and thus the loose ions, which before the introduction of the electrodes moved about in the liquid with no definite preferred direction, will on the whole, now that the electrodes have been introduced, move preferably, the cations towards the cathode, and the anions towards the anode, and those which are near the electrodes will be drawn to them and discharge their electric charge. This theory seems therefore to explain the phenomena. The essential difference between it and all previous theories is that Clausius does not attribute the decomposition to the current or to the attraction of the electrodes; what the attraction of the electrodes does is to separate the ions already disengaged from one another, and this the smallest electromotive force can do. The theory is so far adequate, but is it admissible? Can we suppose that hydrogen and chlorine atoms can move uncombined through the solution? It is to be noted that while Clausius does not give any opinion as to the proportion of loose ions to the total ions in any case, he assumes that this proportion increases as the temperature rises, on account of the greater briskness of the movements of the particles, and points out that this is in accordance with the fact that electrolytes conduct better as the temperature is higher. But he says, 'to explain the conduction of the electricity it is sufficient that in the encounters of the molecules an exchange of ions should take place here and there, and perhaps comparatively rarely.'

In this connection we may look at the views expressed by Williamson in his paper on the theory of etherification.* He says: "We are thus forced to admit that in an aggregate of molecules of any compound there is an exchange constantly going on between the elements which are contained in it. For instance, a drop of hydrochloric acid being supposed to be made up of a great number of molecules of the composition ClH, the proposition at which we have just arrived would lead us to believe that each atom of hydrogen does not remain quietly in juxtaposition with the atom of chlorine with which it first united, but, on the contrary, is constantly changing places with other atoms of hydrogen, or, what is the same thing, changing chlorine." Williamson founded this opinion on the observed facts of double decomposition. He made no application of this view to the case of electrolysis, and indeed does not explicitly mention the temporary detachment of the atoms during the process of ex-

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* Williamson, *Chem. Soc. Journ.*, IV., p. 111 (1852).

change; this is wholly due to Clausius, who arrived at his views as to the exchanges going on in a solution in a way quite different from that followed by Williamson, and quite independently. It was not then known how closely double decomposition and electrolysis are connected. We may perhaps get a clearer idea of Clausius's theory by imagining the phenomenon to take place on a scale such that we could see the individual ions. Let us then imagine a large field with a large number of men in it, each mounted on a horse. We shall further suppose that all the men are exactly alike and that all the horses are exactly alike. They are moving at random, most of them at about the same rate, but a few of them faster, a very few of them considerably faster, a few of them slower, a very few of them considerably slower, than the average. They move in straight lines until they meet an obstacle which makes them deviate. This obstacle will often be another man and horse. The collision will give both a shake, and will sometimes dismount one or both of the riders. When this happens each will look for a horse, and as all horses are exactly alike, the horse such a dismounted man finds and mounts will not always be the one he came down from. But in any case there will be always in the field some men without horses and some horses without men. And the quicker the average pace the larger will be the proportion of dismounted men and riderless horses to the total number of men and horses. And this not only because there will be more and, as a rule, more violent collisions, but also because the dismounted men will have more difficulty in catching horses, although to keep up the analogy of the ions we must suppose the horses to be as anxious to be caught as the men are to catch them. If it does not make my allegory too grotesque we might suppose places with attractions for men and for horses, respectively, to correspond to the electrodes, so that a man looking for a horse would on the whole rather go in the direction of lunch than away from it, and if he got near the refreshment room before he found a horse, he would look in there. An objection was made to Clausius's theory that the same thing which he supposed to happen in solution, say of hydrochloric acid, ought also to happen in the gas. We are not yet in a position to discuss this point with much prospect of obtaining a perfectly satisfactory explanation of the difficulty, although some progress towards an intelligible theory has been made, but at the risk of being tedious I may indicate that my allegory may show us that we need not despair of finding in due time an answer. Let us suppose that in the field there are not only men and horses, but also a large number of other moving objects, let us say, by way of example, cows. It seems plain that whether the presence of the cows would increase the chance of a man being dismounted or not, it would sensibly interfere with his chance of catching a horse if he were. And it will be admitted that the nature and size of these other moving objects must exercise an influence on the proportion of horseless men and riderless horses to the total number. But these other moving objects represent the molecules of the solvent, so that we need not be surprised when we find that the electrolytic conductivity is affected by the nature of the solvent and that where there is no solvent the conductivity is very small or even nothing.

A very important question was left only partially answered by Faraday. It is, What substances are electrolytes? Faraday considered the water in dilute acid as the electrolyte, and the acid as a substance having the power of increasing the conductivity of the water. When a solution of sulphate of copper was electrolyzed, he supposed that the water was primarily decomposed and that the metallic copper was a secondary product reduced by the nascent hydrogen. He says:* "I have experimented on many bodies, with a view to determine whether the results were primary or secondary. I have been surprised to find how many of them, in ordinary cases, are of the latter class and how frequently water is the only body electrolyzed in instances where other substances have been supposed to give way." From our present point of view many of us would rather say that the direct electrolysis of water very rarely occurs, except to a very small extent.

In 1839 Daniell began a series of ingeniously devised and skillfully executed experiments with the view of determining, in the case of salt solutions, whether it is the salt or the water which is primarily electrolyzed. The results appeared in two letters from Daniell to Faraday in 1839† and 1840,‡ and in a paper by Daniell and W. A. Miller in 1844,§ all published in the *Transactions of the Royal Society*. The purpose of these investigations was attained, and it was completely proved that in reference to their behavior as electrolytes there was no difference between say potassium chloride and potassium nitrate, except that in the latter some ammonia was formed at the cathode by the reducing action of the nascent hydrogen, and it was clearly shown that from an electrolytic point of view all the oxygen acids and their salts fell into line with hydrochloric acid and the chlorides, and the NH_4 was electrolytically perfectly analogous to K. There is, however, an interest in these papers beyond this important result. In the earlier part of the work the authors measured the amount of electrolysis not only by 'the amount of ions disengaged at either or both electrodes by the primary action of the current or the secondary action of the elements,' but also tried to obtain a check to this way of measuring, by using a diaphragm in the electrolytic cell, and analyzing the contents of the two parts of the cell, the one on the anode side and the other on the cathode side of the diaphragm. This check was 'founded on the hypothesis that the voltaic decomposition of an electrolyte is not only effected by the disengagement of its anion and cation at their respective electrodes, but by the equivalent transfer of each to the electrodes, so that the measure of the quantity of matter translated to either side of the diaphragm might be taken as the measure of the electrolysis.' They soon found that this hypothesis was unfit to give any such measurement, and in the paper of 1844 state that their results show that the hypothesis of equivalent transfer of the ions, 'although generally received, is itself destitute of foundation.'

The non-equivalent transfer of the ions, incidentally observed by Daniell and Miller, and imperfectly measured by them in a few cases, was made the subject of a long and elaborate series of experiments by Hittorf. The work extended over six years from 1853 to 1859* and is a monument of patient labor and of happy adaptation of means to a clearly perceived end. The importance of the work was not at first recognized by either physicists or chemists; indeed its meaning was scarcely understood. I shall try to put before you as shortly as I can an outline of the ideas involved in the work, and of the most important conclusions arrived at by Hittorf. As the anions and the cations are separated at their re-

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* Faraday, 'Experimental Researches in Electricity,' par. 751 (1834).

† Daniell, *Phil. Trans.*, 1839, p. 97.

‡ *Op. cit.*, 1840, p. 209.

§ Daniell, *Phil. Trans.*, 1839, p. 97.

* Hittorf, *Pogg.*, LXXXIX., p. 177 (1853); XCVIII., p. 1 (1856); CIII., p. 1 (1858); CVI., pp. 337 and 513 (1859). *Arch. Néerland.* (II.), VI., p. 671 (1901).

spective electrodes in equivalent quantity, that is, in the case where the valency of anion and cation is the same, in equal numbers, it never occurred to any one to doubt that they traveled towards the electrodes at the same rate, until Daniell and Miller showed that this hypothesis is erroneous. To follow their reasoning and that of Hittorf we may take an imaginary case, and suppose an electrolyte *MX* with its cation *M* and its anion *X* of such character that these ions when separated at the electrodes can be removed from the solution completely and at once, and that the electrolysis is carried on in a vessel provided with two compartments, one containing the cathode and the other the anode, such that whatever happens at an electrode shall affect only the contents of the compartment containing that electrode, and so arranged that the liquid contained in each compartment can be completely removed from it and analyzed. Now, let us first suppose *MX* to be such that its ions travel at the same rate. In the time then in which one *M* has entered the cathode compartment one *X* has left it. There is at this moment an excess of two *M*'s in this compartment; these are deposited at the cathode, and now the concentration of the solution in this compartment is diminished by one *MX*. Similarly at the anode during the same time one *X* has entered and one *M* has left, two *X*'s have been deposited and the solution has lost one *MX*. In this case, then, where the two sets of ions travel at the same rate, the loss of solute is the same at the two electrodes. Let us now suppose an extreme case in which one of the sets of ions (say the cations) does not travel at all. In the time in which one *X* leaves the cathode compartment no *M* enters it, the excess of one *M* is deposited, and the solution here has lost one *MX*. At the anode one *X* has entered and no *M* has left, the *X* is deposited, and the solution here has lost no *MX*. Again, take the case that the anions travel twice as fast as the cations. Here in the time in which one *M* enters the cathode compartment two *X*'s leave it, the excess of three *M*'s is deposited, and the solution has lost two *MX*'s. At the anode during the same time one *M* has left and two *X*'s have entered, the three *X*'s have been deposited and the solution has lost one *MX*. Of course it will be seen that the excess of one kind in a compartment consists not only of what enters it, but also of the excess resulting from the departure of the other kind. Without taking any more cases we at once see that the speed of the cation is to that of the anion as the loss of solute at the anode is to that at the cathode. This non-equivalent transfer has sometimes been described in another way. It has been said that the ions go at the same rate, but that at the same time the solute as a whole is being moved towards one of the electrodes. But this really is the same thing. If we imagine two processions walking with the same length of step and the same number of steps a minute in opposite directions on such a moving platform as that in the Paris Exhibition, we might no doubt say that the two *walked* at the same rate; they could not be said to *travel* at the same rate. Hittorf's way of putting it is not only the simpler way, it is the only way that agrees with what has since been made out as to the rate of movement of the ions.

Hittorf's work had to wait long for recognition, but we now know its great importance, not only on account of the large number of accurate measurements, but also because of the general conclusions he drew from them. He deduced from the transfer numbers conclusions as to the nature of the solute, showing, for instance, that solution of stannic chloride electrolyzes as hydrochloric acid, the stannic chloride being completely hydrolyzed. He also showed that such double salts as KCN,AgCN, 2KCl,-

$PtCl_4$ and $KCl,AuCl_3$ have potassium for their only cation, the silver, the platinum and the gold forming part of the anion. He also showed that $2KI,CdI_2$ behaves as a single salt with K as cation when the concentration is great, but as two salts with cadmium as well as potassium as cation in dilute solution. In these and in similar cases, Hittorf made a valuable contribution to the theory of double salts. But perhaps the most striking generalization is that contained in the words 'electrolytes are salts,' and his very instructive comparison of the readiness with which a substance enters into double decomposition and the readiness with which it can be electrolyzed. With the fairness to his predecessors which is characteristic of him, he quotes an almost forgotten statement of Gay-Lussac to something like the same effect.

Ladies and Gentlemen,—I wish here to tell you that within the last three weeks Professor Hittorf entered on the fifty-first year of his professorship. The officials of the Royal Institution have authorized me to ask our Chairman, Lord Kelvin, to send your congratulations to Professor Hittorf on his jubilee.

We now come to another turning-point in the development of the theory of electrolysis, inseparably associated with the name of Kohlrausch.* It is to Kohlrausch and to those who worked with him that we owe the methods for the accurate determination of the conductivity of electrolytes. I need not give a description of the apparatus. It is now used in every laboratory, and by means of it a series of observations of the conductivity of an electrolyte can be made at different concentrations in a very short time. An early result of Kohlrausch's investigation was his discovery that 'all acids which have been examined in strong solutions show, for a definite proportion of water, a maximum of conductivity,' and he shows that for many other electrolytes there is a solution which conducts better than one either a little more or a little less concentrated. Thus the maxima of conductivity of the following acids are at the following percentages: HNO_3, 29.7 per cent.; HCl, 18.3 per cent.; H_2SO_4, 30.4 per cent.; $HC_2H_3O_2$, 16.6 per cent. "The maximal acetic acid conducts at least 38,000 times better than concentrated acetic acid." In connection with this he says, 'we do not know one single liquid which at ordinary temperature is, by itself, a good electrolytic conductor.' He refers the trace of conductivity in H_2SO_4 to the dissociation into water and SO_3 observed by Marignac and by Pfaundler, and observes that, as up to the present time we know only mixtures which at ordinary temperature conduct well, the supposition is not unnatural that it is mixture that makes electrolytes good conductors. And again, if what has been said is correct, we must, in order to have good conduction, protect the wandering constituents from frequent meeting with one another, and this service is performed by the solvent, which makes it possible for the ions to get over a part of their journey—and so much larger a part the more solvent there is—without reforming molecules. It is this suggestion which I ventured a little while ago to put into an allegorical form.

In order to compare the conductivity of one electrolyte with that of another, it is necessary that we choose comparable quantities of the two, and there is no difficulty in seeing that such comparable quantities are those decomposed by the same current of electricity—that is to say, the electro-chemical equivalents of the

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* Kohlrausch and Nippoldt, *Pogg.*, CXXXVIII., p. 280 (1869); Kohlrausch, *Pogg.*, Jubelband, p. 290 (1874); Kohlrausch and Grotrian, *Pogg.*, CLIV., pp. 1 and 215 (1875); Grotrian, CLVII., p. 130 (1876); Kohlrausch, CLIX., p. 233 (1876). *Göttinger Nachrichten*, 1876, p. 213. *Wied.*, VI., p. 1 (1879); XI., p. 653 (1880).

electrolytes. Accordingly, instead of expressing the concentration in percentage of the solute, Kohlrausch uses 'molecular numbers.' The molecular number of a solution is the quantity, in grams, of the solute contained in a liter of the solution divided by the equivalent of the solute. Dividing the conductivity of a solution by its molecular number gives its molecular conductivity. It will be seen that 'molecular' is not used here in its ordinary chemical sense, but as the meaning is quite distinctly stated no confusion need arise. Kohlrausch showed that the molecular conductivity increases as the solution becomes more dilute, and with extreme dilution approaches a constant value.

I now show an experiment to illustrate this.

The apparatus* consists of an electrolytic cell in the form of a tall rectangular trough, the back and front being broad plates of glass, while the sides are composed of narrow strips of wood completely lined with silver-foil. The bottom of the cell is made of non-conducting material. The two sheets of silver serve as electrodes, being connected to binding screws by means of external wires. The cell is introduced into a battery circuit along with a galvanometer of low resistance. If the cell be filled with pure water there is scarcely an appreciable current transmitted. On removing the water and pouring in 20 c.c. of a 4-normal silver nitrate solution, so as to cover the bottom to a depth of a few millimeters, a current passes as indicated by the galvanometer. If pure water be now added in successive portions and the solution stirred after each addition, an increase in the strength of the current is observed, the increase being greatest after the first dilution, and becoming less with each succeeding dilution, so that a maximum is approached. In this experiment the distance between the electrodes is constant, and the area of the electrodes and of the cross-section of the conducting solution is proportional to the volume of the solution, and the quantity of the salt is constant; therefore any change in the strength of the current means a corresponding change in the molecular conductivity of the dissolved salt. The molecular conductivity, therefore, increases with the dilution, and asymptotically approaches a maximum.

I cannot here enter into a description of the great experimental difficulties connected with the determination of the conductivity of extremely dilute solutions, but I may refer to one of them, namely, the small but variable conductivity of the water used in preparing the solutions. There seems now to be no doubt that water is in itself an electrolyte. But the purest water that has been obtained has a conductivity of only about 10^{-10} as compared with that of mercury as unit. The minutest traces of salts greatly increase the conductivity, so that ordinary distilled water has a conductivity of 3×10^{-10} or more. With solutions of moderate dilution the variation of this very small quantity is of little consequence, but with extremely dilute solutions the conductivity to be measured is of the same order as that of the water.

For our present purpose the most important conclusion drawn by Kohlrausch from his observations is his law of the independent rate of motion of the ions in dilute solutions. The rate of motion of any ion towards the electrode depends on the gradient of potential. But Kohlrausch shows that the rate of motion of each ion in dilute solution is proportional to a number, the same whatever be the other ion of the electrolyte. Thus the rate at which the cation K moves towards the cathode in dilute solution is the same in solutions

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* From a paper by Noyes and Blanchard, in the *Zeitschrift für physikalische Chemie*, XXXVI., p. 9 (1901).

of KCl, KNO_3, $KC_2H_3O_2$, etc. Kohlrausch gives these numbers for six cations and ten anions. The results calculated from these numbers agree well with the observed conductivities.

Methods have been devised for directly observing and measuring the rate at which ions travel. In this connection I may specially mention the names of Oliver Lodge, Whetham and Masson. These measurements agree very well with the rates calculated by Kohlrausch.

I now show an experiment indicating a way in which such measurements can be made.

The apparatus* consists of a glass U-tube, with a long stopcock-funnel connected to the lower part of it. The tube is nearly half filled with a dilute (about 0.03 per cent.) solution of potassium nitrate, and then about the same quantity of a solution of potassium permanganate, of the same conductivity as the other solution, is slowly introduced by means of the funnel. The permanganate solution is loaded with urea (a non-electrolyte) so as to make it denser than the nitrate solution; the permanganate solution now lies in the lower part of the U-tube with a sharp interface between it and the nitrate solution above it in each limb of the tube. If now we connect the electrodes, which were preliminarily inserted into the upper parts of the limbs of the tube, with a battery with high difference of potential, a current will pass, and a transference of ions will take place, cations (K) towards the cathode and anions (NO_3 and MnO_4) towards the anode, and the column of pink color will rise in the limb containing the anode and fall by an equal amount in the other. By this means an approximation can be made to the rate of travel of the ions.

We now come to a new chapter beginning with 1887; but before entering on it we must turn aside for a little to a subject which does not at first sight seem to have a very close relation with the matter we have in hand. The subject is that of what may be called the osmotic phenomena. These are all connected with the concentration or with the dilution of solutions. They all involve the idea of the work done in concentrating a solution. We need not discuss the theory of these phenomena, we are interested in them now only as they give us methods of ascertaining the molecular concentration of a solution. In 1883* Raoult showed that in the case of a great many substances, equimolecular solutions (with the same solvent) have the same freezing-point In 1886† he showed that equimolecular solutions with the same volatile solvent have the same boiling-point. Molecular is here used in its ordinary chemical sense. These discoveries were eagerly taken up by chemists as promising an important addition to the means at their disposal for determining the molecular weights of substances. Convenient arrangements for applying the methods were devised by Beckmann,‡ and soon came into use in nearly every laboratory. They were almost exclusively used for the determination of the molecular weight of organic substances, and have been found trustworthy in such cases. When, however, van't Hoff§ in his study of the theory of solutions concluded from theoretical considerations that the depression of the freezing-point and the rise of the boiling-point are proportional to

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* Experiment from a paper by Nernst, in the *Zeitschrift für Elektrochemie*, III., p. 308 (1897).

* Raoult, *Compt. rend.*, XCIV., p. 1517; XCV., pp. 187 and 1030 (1882); XCVI., p. 1653; XCVII., p. 941 (1883).

† Raoult, *Compt. rend.*, CIII., p. 1125 (1886); CIV., pp. 976 and 1430; CV., p. 857 (1887). *Zeitschrift f. physik. Chemie*, II., pp. 353 (1888).

‡ Beckmann, *Zeitschrift f. physik. Chemie*, II., pp. 638 and 715 (1888); IV., p. 532 (1889); VIII., p. 223 (1891).

§ van't Hoff, *Zeitschrift f. physik. Chemie*, I., pp. 500–508 (1887).

osmotic pressure in the case of dilute solutions, the observations made by Raoult and others furnished a number of facts ready for testing the theory. He found that, while in many cases the osmotic pressure calculated from his formula $PV=RT$ agreed, within the limits of experimental error, with the value calculated from the observation, there were a very considerable number where the observed value differed from that given by the formula. He accordingly modified the formula by the introduction of a factor i, so as to make it $PV=iRT$. This factor i is unity in the cases where observation by Raoult's method gives results agreeing with the formula $PV=RT$; in other cases it is greater or less than unity, and indicates the extent of the disagreement. Arrhenius, to whom van't Hoff showed these numbers, pointed out that all the substances which had i greater than unity were electrolytes, and that the deviation had to do with their splitting up into ions. Arrhenius* had before this time (1887) been working at the subject of electrolysis and of the relation between the readiness with which substances undergo electrolysis and the readiness with which they enter into chemical reactions. He had been looking for an explanation of the fact that the conductivity of a solution of an electrolyte is not proportional to its concentration, and had come to the conclusion that this must depend on some of the molecules of the solute being 'active,' that is, taking part in the conduction—while others were inactive, behaving like molecules of a non-electrolyte, and that the proportion of active molecules increases with dilution.

van't Hoff's factor i enabled Arrhenius to give precision to these ideas, and in 1887† he formulated the theory that the 'active' molecules were those which were split into ions. It was now possible to calculate i in two ways and compare the results. Arrhenius gives a list of eighty-four substances, for which there existed at that time data for such calculations, and, calculating the value of i as deduced on his new theory from the conductivity, compares it with the value of i derived from freezing-point observations in each of the eighty-four substances. The agreement does not at first sight strike one as very close, but there are several circumstances which have to be considered in judging them. The whole mass of published observations was taken, the limits of probable error are very different in different cases, and the freezing-point measurements were all made at temperatures a little below 0°, while the conductivity measurements were made at 18°. The comparison was made, not as a demonstration of the theory, but rather as a preliminary trial with such materials as were at hand. The real testing of the theory necessarily came later. So I think we may agree with Arrhenius that, considering all the circumstances, the agreement is not unsatisfactory, except in the case of nine of the substances, and that most of these nine cases are liable to suspicion on other grounds. In 1887, almost at the time when Arrhenius published the paper of which I have just been speaking, Planck* discussed the subjects of the diminution of the vapor pressure and the lowering of the freezing-point in dilute salt solutions from the thermodynamic point of view, and starting from the principle of the increase of entropy, deduced formulæ connecting these quantities with the molecular weight. He says, in conclusion: "This formula claims exact numerical validity. It gives for most substances a greater molecular number than that usually assumed, *i. e.*, a partial or complete chem-

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* Arrhenius, *Bihang till kongl. Svenska vetensk. Akad. Handlingar*, 1884, Nos. 13 and 14.

† Arrhenius, *Zeitschrift f. physik. Chemie*, I., p. 631 (1887).

* Planck, *Wied.*, XXXII., p. 495 (1887).

ical decomposition of the substance in the solution. Even if the consequences of this proposition should require an essential modification of the generally prevailing views as to the constitution of solutions, I do not know any fact which shows it to be untenable. Indeed, many observations in other departments (the proportionally strong affinities of dilute solutions, which remind one of the properties of the nascent state, the easy decomposability by the weakest galvanic current, the phenomena of internal friction), are directly in favor of the view that in all dilute solutions a more or less complete decomposition of the molecules of the dissolved substances takes place. Besides, this conception adapts itself well to the opinions developed by L. Meyer, W. Ostwald and S. Arrhenius on the state of the molecules of dissolved substances, as it only goes a step further and fixes numerically the degree of the decomposition.''

An objection was taken to Planck's argument. It was said that as his formula contains the ratio of the molecular numbers of the solute and of the solvent, it could not be inferred that that of the solute is greater than its formula leads to, for it might be that the molecular number of the solvent is less than that indicated by its formula. Planck's answer was immediate and obvious. In any expression in which the molecular number of the solvent appears, there also appears as a factor the molecular weight. For instance, in the formula for the depression of the freezing-point the molecular number of the solvent is multiplied by the latent heat of one molecule of the solvent, and similarly in other cases. So that it makes no difference what molecular weight we assume for the solvent, and the use of its molecular number is merely a convenient way of expressing its quantity.

This increase in the number of the molecules, or splitting into ions, was called 'electrolytic dissociation.' It will be seen that it is what Lodge in 1885, in speaking of Clausius's theory, called dissociation. But while it has some obvious resemblances to the dissociation of a gas, there are very striking differences between the cases, and perhaps some of the difficulties in the way of the acceptance of the theory may have arisen from the use of the same word for two things differing so much. We need not, however, discuss the name, but it is well to look for a little at the essentially different nature of the things. This essential distinction consists in the products of the electrolytical dissociation being charged, the one set with positive, the other set with negative, electricity, so that, while in the body of the solution they can move about independently, they cannot be separated by diffusion as the products of the dissociation of a gas can. It is true that the quicker moving ions can, to a small extent, forerun the slower moving ions, and diffuse a little further into pure water or into a more dilute solution, as is shown by the fact that when two solutions of the same electrolyte of different concentration are in contact there is a difference of electric potential between them, but they cannot be separated to any weighable extent in this way. In order to separate from one another two gases uniformly mixed, a certain calculable amount of work has to be done, so that after a gas has been dissociated and wholly or partially converted into a mixture of the two gaseous products, some work has still to be done to get them separately. So it is also in the case of electrolytic dissociation; but while in the former case the decomposition work is the main thing, and the separation work very small, in the latter it is quite the other way. Here the heat of dissociation, that is, the work spent in decomposing the electrolyte into its ions, is small (indeed sometimes negative), while the work to be done to *separate* the ions is always very much greater. Indeed we may quite correctly say that in most highly dissociated solution of hydrochloric acid the hydrogen and the chlorine are still very firmly united, not indeed atom to atom, but each atom of the one kind to all the atoms of the other kind within a certain distance from it. A man does not lose his money when he takes it out of his pocket and puts it into a bank. He does indeed lose his relation to the individual gold and silver coins, and does not know and does not care where these particular pieces of metal are, but he is interested in knowing that they or their like are at his command, and the same sort of work will be required to impoverish him whether his money is in the bank or in his pocket. (I assume, of course, that the bank of our present imagination cannot become insolvent.)

I have said that the test of the theory would come later. It has been going on since 1887, and if time would allow I could give you many cases in which deductions from the theory have been found to agree with close quantitative accuracy with experimental observations. I shall mention only the first, still among the most important, namely, Ostwald's determination of the affinity constants, and his application of Guldberg and Waage's principle to the ions. I could also give you instances in which there have been discrepancies, or apparent discrepancies, and show how in some of these cases the difficulties have been cleared up. The history of this theory has in fact so far been that of every useful theory, for it is in this way only that a theory does its work. I shall select two points for illustration, not because they are more important than others, but because I can illustrate them by means of experiments which do not occupy much time, and can be made visible in a large room. The first has reference to the question, What are the ions in the case of a dibasic acid? As HNO_3 gives as its ions H and NO_3 so we might expect H_2SO_4 to give 2H and SO_4. But we find that until the dilution has advanced to a considerable extent the ions of sulphuric acid are mainly H and HSO_4. This is quite in harmony with the chemical action of H_2SO_4, for, as every chemist knows, at moderate temperatures we have the action $H_2SO_4+NaCl=HCl+NaHSO_4$, and the temperature has to be raised in order to get the action $NaHSO_4+NaCl=HCl+Na_2SO_4$. In the first of these experiments we take as the electrolyte a concentrated solution of potassium hydrogen sulphate $KHSO_4$. This gives the ions K and HSO_4. The latter go to the anode and there, on being discharged, form persulphuric acid, or its ions, and potassium persulphate $K_2S_2O_8$, being sparingly soluble, crystallizes out. This is the method by means of which Dr. Marshall discovered the persulphates. The next experiment will illustrate the formation and discharge at the anode of the anion SO_4. We have here dilute sulphuric acid with which is mixed a little manganous sulphate $MnSO_4$. The ion SO_4 when discharged, adds itself to $2MnSO_4$ and forms manganic sulphate $Mn_2(SO_4)_3$, recognized by its red color. This, even in acid solution, is quickly hydrolyzed, giving insoluble manganic hydrate.

The other point I wish to illustrate is the application of Guldberg and Waage's principle to ions. Without entering into any general discussion of this question, I shall merely say that theory leads to the result that the addition of a soluble acetate to a solution of acetic acid diminishes the concentration of H ions, and so makes the solution less effectively acid. This was experimentally proved by Arrhenius in 1890,* by measuring the rate at which cane-sugar

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* Arrhenius, *Zeitschrift f. physik. Chemie*, V., p. 1 (1890).

is inverted by acetic acid alone, and with varying quantities of sodium acetate added to it. But as such an experiment cannot be made visible to a large number of spectators at once, I thought of a way of showing the same thing, which, while not capable of the same degree of accuracy, would prove the principle qualitatively. I have here a solution of ferrous acetate to which I have added enough acetic acid to prevent the precipitation of ferrous sulphide on the addition of sulphuretted hydrogen. I add sulphuretted hydrogen; of course no precipitate is formed. I now add a solution of sodium acetate mixed with rather more than three equivalents of acetic acid, so as to make it plain that the effect is not due to the formation of an acid acetate, and you see that we have at once a precipitate of ferrous sulphide. To show that the addition of the water has not produced the result, I add to another portion of the same solution as much water, and you see that no precipitation takes place.

I have not spoken of non-aqueous solutions. At the rise of the dissociation theory, these were generally supposed to be non-conductors, but many of them have now been examined both by scientific workers in the old world, and very specially by our colleagues on the other side of the Atlantic, and have been found to conduct electrolytically. It seems likely that these investigations will throw much light on the influence of the solvent on the conductivity of the dissolved salt. Particularly interesting is the relation, indicated in some cases, between the specific inductive capacity of a solvent and the dissociation of the dissolved salt. But this is one of the questions not yet ripe for treatment in a discourse such as this.

I had also thought of saying something as to the atomic character of electricity, and the compounds of electricity with what we may venture to call the other chemical elements, and had even some idea of poaching on Lord Kelvin's domain of 'Aepinus atomized,' but time has saved me from this.

I have been describing the history of the theory of electrolysis from the time of Faraday, in such a way as is possible within the limits of an hour. I have necessarily omitted mention of many active, able and successful workers, and I cannot in every case justify the omission except by referring to the time limit. I have as far as I could explained the evidence which we have for the theories described, but I have not intended to argue for or against the essential truth of them. I have sometimes been asked in reference to the theory of electrolytic dissociation, Do you really believe it to be true? My answer to that question is, I believe it to be an eminently useful theory. It has led to a great deal of most valuable experimental work. It has enabled us to group together things that without its help seemed very little connected. It has led to the discussion of problems that could scarcely, without its suggestion, have occurred to any one. It does not seem to be exhausted, and I look forward to much good to be got from it yet, and therefore I am willing to take it as a guide. But I do not look on it as an infallible guide; we cannot expect, we do not need, an infallible guide in physical science. A long life may be anticipated for this theory; if that be so, we may be sure that it will undergo modifications, for if it is to act, it will be acted on.

Nothing but good can come from the fullest discussion, either of the theoretical basis or of the experimental evidence for or against a theory. No great principle in science or in law can be satisfactorily settled without full argument by competent advocates on both sides, and the eager hunt for evidence by those who attack and by those who defend will lead to a more complete investigation of the whole field than would be attained without such—shall we call it partisan?—interest.

A. CRUM BROWN.

THE BOTANICAL SOCIETY OF WASHINGTON.

BOTANICAL development at the national capital has been so rapid within the last few years that few outside of Washington comprehend that it has become the leading botanical center of America and is rapidly taking position as one of the leading botanical centers of the world. Probably no city in the world can boast of a larger number of well-trained professional men devoting their entire time to the study of botany in some one of its various branches. The aggregation of so large a number of professional botanists has finally led to the formation of a general botanical society which is of more than passing interest, as there is hardly a university of any note in the country that is not represented by graduates among its members.

The Biological Society of Washington was the first society organized in Washington which gave any attention to botanical matters. This society was too formal and did not allow of sufficient discussion to suit some of the botanists, and as a result in 1893 the 'Botanical Seminar' was organized, the original membership including Messrs. F. V. Coville, D. G. Fairchild, B. T. Galloway, Theo. Holm, E. F. Smith and M. B. Waite. The main aim of the Seminar was to discuss general problems of plant physiology and pathology and to promote a friendly spirit of criticism. In the early days of the Seminar no member published a paper until it had been read or summarized before the Society and had run the gauntlet of criticism which, the writer can testify, was frequently so severe as to be perilous to the peace of mind of the member under criticism. In no other society which the writer has ever attended was criticism so freely indulged in, or, it may be remarked, so pleasantly received. As it is axiomatic that no two minds ever think exactly alike, so it came to be an understood thing that no paper would suit everyone and many a lively discussion and tilt of warm words resulted.

The organization of the Seminar was somewhat novel, being mainly remarkable for its lack of organization. The Seminar had no officers and no constitution and its membership, though very exclusive, existed only as tradition or in memory. The meetings were held at the residences of members, the host of the preceding meeting acting as chairman. The membership was limited to twenty-five and unanimous consent of all members was required for election to membership.

In the nine years of its existence the Seminar filled an important place in Washington's botanical development, both scientifically and socially. A light lunch was served at each meeting and these light lunches, which sometimes became heavy, served as they were at 11 P.M., became famous among the members. It may be said that the fire of scientific enthusiasm requires no midnight lunch to feed upon, but it is certain that no matter how keenly the scientific fire burns a lunch during the evening adds to the flow of ideas and is conducive to 'that satisfied feeling' which makes all members regular attendants.

Within a few years the number of botanists in Washington became too large to be accommodated in the botanical seminar, meeting as it did in private houses, and in 1898 the Washington Botanical Club was organized particularly to consider the problems of systematic botany and furnish a means of communication between botanists interested in systematic and ecological studies. The organization of this club was largely brought about through the activity of Mr. C. L. Pollard and the late Gilbert H. Hicks. The general plan of this organ-