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Transactions

OF

The Faraday Society.

FOUNDED 1903.

TO PROMOTE THE STUDY OF ELECTROCHEMISTRY, ELECTROMETALLURGY,
CHEMICAL PHYSICS, METALLOGRAPHY, AND KINDRED SUBJECTS.

VOL. III.

JULY, 1907.

PART I.

THE APPLICATION OF THE ELECTRON THEORY TO ELECTROLYSIS.

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*(A Paper read before the Faraday Society on Tuesday, January 15, 1907,
SIR JOSEPH SWAN, F.R.S., PAST-PRESIDENT, in the Chair.)*

The electron theory of electricity and magnetism may be fitly described as an extension of the ionic theory of electrochemistry to solids, gases, and a vacuum, inasmuch as it postulates material carriers of all electric charges, and reduces electric phenomena to the configuration and motion of these carriers. The application of the electron theory to electrolysis means, therefore, no revolutionary change in electrochemical conceptions, but simply an attempt to bring our extended knowledge of the properties of the elementary carriers of electricity to bear upon well-known phenomena, and thus to gain a clearer insight into the actual mechanism of electrolytic conduction and dissociation.

One of the most valuable achievements of the electron theory is the complete harmonisation of the processes of metallic and electrolytic conduction. Both processes depend upon the existence of minute charged bodies capable of threading their way through a mass of other bodies which are either uncharged or less mobile. If a body contains no such charged bodies—ions in the wider sense—or if its ions are fixed in position, it is incapable of conveying an electric current of any description. A current consists in the displacement of ions. The conductivity of a body is accurately and precisely defined by the number of ions it contains in unit volume and by their average mobility; this mobility, in its usual acceptation, excluding any measurable free path. The definition and physical interpretation of conductivity is thus the same in liquids and solids.

It is only when we consider the individual carriers themselves that a fundamental difference appears between metallic and electrolytic conduction. Compare a cm.-cube of copper with a cm.-cube of dilute hydrochloric acid,

each of them conveying a current of one ampere. The copper conveys its current almost solely by its free electrons, some 400 trillion in number, which possess a mobility some 100 million times greater than that of a hydrogen ion. The hydrochloric acid conveys the current by means of its hydrogen and chlorine ions, which, in a millinormal solution, amount to about 2 trillion. Since the current is the same in each case, the electrons in the copper must move some 200 times more slowly than in the electrolyte. But this is not usually the case, for in a copper wire 1 mm. in diameter conveying one ampere the speed of the electrons is of the order of 1 cm. per second. The greatly superior mobility of the free electrons brings it about that a much lower voltage is required to maintain an ampere in a copper conductor than in a liquid conductor of the same dimensions.

Whence this difference between solids and liquids? At first sight it seems strange that free electrons should be observable in a vacuum and traceable in a metal, but that there should be none in a liquid. The elucidation of this question would be of fundamental importance for the theory of electrolysis, and would constitute a valuable contribution from the general theory to the special field to which, as a matter of fact, it owes its origin.

It cannot be said that this question is anywhere near a complete solution. But since the whole range of electromagnetic phenomena has become unified under the sway of the electron theory, much additional material has become available upon which to base our judgment.

The existence of free electrons in metals is made possible by the close packing of their atoms, which brings about a frequent exchange of electrons between one atom and another. During the short period occupied by its change of allegiance—a period amounting to something like 1-5,000th of its average time of attachment to a metallic atom—the electron is free to fall along the potential gradient, and thus to constitute an electric current. When the metal expands by heat, this process of exchange naturally becomes rarer, and the metallic resistance increases. The positive atoms and neutral atoms are so tightly packed that they contribute nothing perceptible to the conductivity.

In an insulating solid or liquid the electrons are effectively bound up with atoms or molecular groups, and these are arranged in some structure, usually crystalline in the case of solids, which precludes the formation of mobile charged groups and the liberation of electrons.

In an electrolyte, on the other hand, such charged groups are formed, and they are sufficiently mobile to follow the E.M.F. That free electrons are not produced is capable of a simple explanation. Two copper atoms have equal attractions for an electron, but atoms of, say, hydrogen and chlorine have not. Hydrogen loses one of its electrons more easily than chlorine, and when the two atoms of a molecule of hydrochloric acid separate, the chlorine takes one of the normal hydrogen electrons away with it. The hydrogen atom thus remains positively charged, and the chlorine atom negatively. The two ions so produced act as condensation nuclei, like any other small charged particles. The study of electric condensation nuclei will, I believe, shed a flood of light on electrolytic problems. The fundamental researches of C. T. R. Wilson* have proved that in vapours, at all events, ions act as condensation nuclei, and that negative ions are slightly more effective than positive ions. Of this phenomenon J. J. Thomson† has furnished a simple explanation.

When a charged drop evaporates its electric charge remains, and its potential increases as its diameter diminishes. More energy is therefore

* C. T. R. Wilson, *Phil. Trans.* 189, p. 265, 1897.

† *Conduction of Electricity through Gases*, 2nd ed., p. 179.

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required to evaporate a charged drop than an uncharged drop. Condensation on the drop involves an expenditure of available electric energy, and thus condensation is facilitated. This fact has an important bearing on the theory of electrolysis. It explains the low mobility of the ions, the drop of potential at the electrodes, and the liberation of uncharged products at the latter. The different mobilities of the ions can, I think, only be attributed to their different degrees of normal hydration. That hydroxyl should have a mobility over four times that of lithium, points to the lithium atom as a particularly efficient condensation nucleus when deprived of one electron. It moves so slowly through the water under the influence of the potential gradient because it has to drag a number of water molecules (probably not more than half a dozen) along with it. The number must be the same for each ion at a given temperature, but cannot be very large, to judge from the actual mobility (347×10^{-6}) compared with that of the electron in copper (about 5×10^4).

When these hydrated ions reach the electrodes the E.M.F. tends to drive them into the metal of the electrodes. But the atoms of the latter are so closely packed, as a general rule, that no other atoms can force themselves between them. There arises a deadlock, which is only released when electrons are able to pass from the solution into the metal, or *vice versa*. The mobility of electrons, though comparatively great inside a metal, is very small at its surface, where the close packing of the metallic atoms loses its effect. But when the E.M.F. exceeds a certain minimum an electron may pass, say, into a hydrogen ion, and neutralise its positive charge. The immediate consequence will be that the hydrogen loses its condensing power. The link between it and the water molecules is broken, and the hydrogen is liberated as an uncharged gas. The converse process goes on at the anode. The chlorine atom passes its superfluous electron into the anode, thereby becoming neutral and free from its aqueous encumbrance.

In the further theoretical investigation of electrolytic action on the basis of the electron theory the study of mobilities will have to play a prominent part. Bredig's laws of mobility are of special interest in this connection. We require a quantitative determination of the hydration of the ions. This determination should not be very difficult, since a number of data, such as heats of solution, melting- and boiling-points, are ready to hand. It should be possible to determine the diameter and bulk of the ions, and their shape from stereochemical considerations. The fact, noted by Bredig, that the strongly electropositive and electronegative metals have a high mobility points to a superior facility of reaction.

A high mobility implies a low degree of hydration of the ion. This low degree of hydration enables such ions, when of opposite signs, to combine more freely and rapidly than is the case in ions having a larger bulk. The heats of reaction, the heats of ionisation, and the electro-affinities or electrode potentials of the majority of elements are fairly well known, and afford valuable data for determining the sizes of the ions. We already know that isomeric and metameric ions have the same mobility; that the mobility of an ion of a given sign is the smaller, the greater the number of atoms it contains; and that the effect of any change in the constitution of an ion is the greater, the smaller the number of atoms contained in the ion.

These facts leave the road clear for a determination of the actual constitution of a single ion on kinetic principles. When an ion contains 50 or 60 atoms it appears to have a minimum mobility which is not preceptibly diminished by a further addition of atoms. Such an ion must have a diameter of about a micromillimetre, and therefore comes within the range of

Szigmondy's ultramicroscope. There is, therefore, a possibility that the motion of such heavy ions may be studied by actual observation, and that they may be watched as they cover a distance of 1 cm. in an hour and a half under the influence of a potential gradient of 1 volt per cm. It then becomes a comparatively simple calculation to find the diameter of such an approximately spherical ion moving through a viscous liquid, or, in the last resort, threading its way among molecules of perhaps half its diameter. Such calculations have been made in connection with metallic conduction, and have led to the conclusion that the carriers of the current in a wire are almost solely the free electrons.

A difficulty is presented by the circumstance that ions of the higher valencies exhibit mobilities which are neither "independent" nor constant for different concentrations.* The extraordinarily high mobility of lead is not easily harmonised with our notions of the physical constitution of the ions. But it is interesting to note that the influence of hydration increases with the valency and the concentration, which is what we should expect.

The future development of electrolytic theory will lie, I think, in the direction of statistical analysis on kinetic principles. Such analyses have yielded most suggestive results in gas discharges, more especially the electric arc, in the vacuum tube, the Zeeman phenomenon, and, quite recently, in metallic conduction. Thomson's famous "counting experiment" must be followed up. He produced ions in a moist gas, and watched them as they settled down under the influence of gravity. We must follow their motions along the potential gradient in a liquid, and follow the fate of the electrons they convey through the liquid into one electrode, and back into the liquid through the other. The complete determination of the energy absorbed or emitted at the various stages of this transmission means the complete mastery of the problems of electrolysis.