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CONTENTS.

SERIES A. VOL. CXXXIV.

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	PAGE
The Combination of Hydrogen and Oxygen on the Surface of Silica and its Relation to the Propagation of Reaction Chains in the Gas. By W. L. Garstang and C. N. Hinshelwood, F.R.S.....	1
The Atomic Weight of Xenon. By R. Whytlaw-Gray, F.R.S., H. S. Patterson and W. Cawood	7
The Diffusion of Colloidal Electrolytes and other Charged Colloids. By G. S. Hartley and C. Robinson. Communicated by F. G. Donnan, F.R.S.....	20
Arc Spectrum of Gold. By J. C. McLennan, F.R.S., and A. B. McLay	35
Spark Spectrum of Mercury, Hg II. By J. C. McLennan, F.R.S., A. B. McLay and M. F. Crawford	41
The Steady Broadside Motion of an Anchor Ring in an Infinite Viscous Liquid. By F. E. Relton. Communicated by S. Chapman, F.R.S.	47
The Thermal Conductivities of Certain Approximately Pure Metals and Alloys at High Temperatures. By L. C. Bailey. Communicated by C. H. Lees, F.R.S....	57
The Thermal Conductivities of the Saturated Hydrocarbons in the Gaseous State. By W. B. Mann and B. G. Dickins. Communicated by G. P. Thomson, F.R.S....	77
The Sorption Process in the Zeolite Chabazite. By M. G. Evans. Communicated by A. Lapworth, F.R.S. (Plates 1 and 2)	97
The Interaction Energy of Two α -Particles at Close Distances, determined from the Anomalous Scattering in Helium. By H. M. Taylor. Communicated by R. H. Fowler, F.R.S.	103
The Mobility of Positive Ions in Helium. Part I.—Helium Ions. By A. M. Tyndall and C. F. Powell. Communicated by A. P. Chattock, F.R.S.....	125
The Quantum Mechanics of Electrolysis. By R. W. Gurney. Communicated by Lord Rutherford, F.R.S.....	137
The Scattering of α -Particles by Light Elements. By W. Riezler. Communicated by J. Chadwick, F.R.S.....	154
The Formation of Vortices from a Surface of Discontinuity. By L. Rosenhead. Communicated by H. Jeffreys, F.R.S.	170
On Dirichlet's Divisor Problem. By J. R. Wilton. Communicated by G. H. Hardy, F.R.S.	192
Electron Scattering in Helium. By S. Werner. Communicated by N. Bohr, For. Mem. R.S.	202
The Kinetics of the Decomposition, in Carbon Tetrachloride Solution, of Ozone and of Ozone-Chlorine Mixtures. By E. J. Bowen, E. A. Moelwyn-Hughes and C. N. Hinshelwood, F.R.S.....	211

The Quantum Mechanics of Electrolysis.

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(Communicated by Lord Rutherford, O.M., F.R.S.—Received July 23, 1931.)

As quantum mechanics endows particles with entirely new properties, it enables us to deal with problems which have remained unsolved for many years. In electrolysis we have been unable to visualise the physical processes which underlie some of the most elementary phenomena. Thermodynamics gives a consistent account of them, independent of any mechanism; but when we try to unravel the actual processes their complexity is baffling. Quantum mechanics provides a new line of attack. One conception we find for our purpose particularly valuable—the idea that there always exists a finite probability of a particle making a spontaneous transition between any two states of equal energy.

In the Sommerfeld theory of metals the valence electrons of the metallic atoms are all free electrons, so that we may regard the atoms of the metallic crystal as ions. Applying this to the anode of a copper voltameter, for example, we may say that when a current is passed, ions from the crystal lattice are leaving the surface of the electrode and slipping away into solution. The same is true of reversible gas electrodes. In great contrast to this are the processes at the electrodes of a cell where an acid is being decomposed by electrolysis. Here ions from the electrolyte are being neutralised by actual capture and loss of electrons, evolving neutral oxygen and hydrogen. Thus the phenomena of electrolysis fall into two classes, both of which may be treated by quantum mechanics. In the electrolysis of acids we encounter the complicated phenomena of “overpotential,” which provides an elaborate test for our theory; for this reason we shall be dealing in this paper with only these irreversible processes.

§ 1. *Irreversible Electrolytic Phenomena.*

Suppose that we have two plane platinum electrodes of unit area dipping into a dilute acid, such as sulphuric acid, which has been carefully freed from dissolved oxygen. If we apply between these electrodes an e.m.f. of, say, 1.2 volts, the value of the steady current which will flow is only 10^{-6} amps. If we now increase the potential difference between the plates by steps to 1.4, 1.6 and 1.8 volts, the value of the steady current rises to about 10^{-5} ,

10^{-4} , and 10^{-3} amps. respectively. Since the resistance of the electrolyte is quite low, the ohmic drop of potential in the solution must at these low currents be very small. The whole drop of potential occurs at or near the two electrode-liquid surfaces of contact; we will denote these two "electrode-potentials" at the anode and cathode by V_a and $-V_c$ respectively. When we increase the applied e.m.f. the anode becomes more positive with respect to the electrolyte by a definite amount, and the cathode more negative with respect to the electrolyte by a definite amount. We do not know whether at the lowest currents the potential difference is divided equally between the two electrode-potentials, *i.e.*, whether $V_a = V_c$. But we do know that, when the electrodes are similar and have equal area, any increment in the applied e.m.f. is shared equally between them, *i.e.*, $\Delta V_a = -\Delta V_c$. If, instead of increasing the applied e.m.f., we raise the temperature at constant potential difference, the current increases exponentially, as before. For a rise of temperature of about 40° C. the current is increased by a factor of 10. The details of the effects collected from Bowden's papers,* are as follows:—

- (a) For electrodes of different areas there is a relation between increment of current density and increment of electrode-potential which is independent of the area of the electrode.
- (b) This relation is given by $d(\log i) = C dV$, where C is a constant.
- (c) Over the small range of temperature which can be investigated the variation of the current density for a particular value of V is given by $d(\log i) = B dT$, where T is the absolute temperature.
- (d) The parameter C decreases with increasing temperature; in fact, it is inversely proportional to the absolute temperature. The relation is $d(\log i)/dV = A/T$, with $A = 5600$ if V is reckoned in volts, and $A = 1.7 \times 10^6$, if V is expressed in electrostatic units.
- (e) Although it is oxygen which is being discharged at the anode and hydrogen at the cathode, the same value of A, 1.7×10^6 , is found for both anodes and cathodes of platinum, within the experimental error.
- (f) For cathodes of silver, mercury, nickel, and platinum, the same value, 1.7×10^6 , is found within the experimental error.
- (g) The parameter B decreases with increasing V. For both anode and cathode its values are mainly between 0.05 and 0.06 over the range 0° to 80° C., at these current densities.

* Bowden, 'Proc. Roy. Soc.,' vol. 125, p. 446 (1929); and vol. 126, p. 107 (1929).

From the theory given in this paper numerical agreement is obtained on all these points.

Although the problem is more than 40 years old, and experimental papers on the subject are poured out every year, very little systematic work has been done at sufficiently low current densities to reveal the elementary processes. In 1899 the name *Ueberspannung*, or Overpotential, was given by Caspari* to this class of phenomena. In 1905 the linear relation between $\log i$ and V was found by Tafel.† The other relations given above are due to Bowden, who has made a comprehensive investigation by the passage of extremely small quantities of electricity.‡ To account for his results Bowden tentatively put forward a chemical theory of overpotential in which the phenomena are treated as a surface reaction due to activated dipoles. He supposed that when a small current is passed, a single layer of dipoles is deposited on each metal surface, consisting of hydrogen in some form at the cathode, and of oxygen in some form at the anode, the potential difference across the interface being controlled by the number and electric moment of these dipoles. Further changes in the electrode-potential were attributed to an increased deformation of the adsorbed dipoles, with consequent increase in electric moment. When electrolysis is taking place, it is supposed that the evaporation or collapse of these adsorbed dipoles is occurring continuously. Bowden assumed that the energy of the dipoles is distributed according to the Boltzmann law, and that only those dipoles which possess energy greater than W can leave the surface. "Energy of activation" can be supplied to the dipoles by raising the temperature or by increasing the electrical potential across the layer, which causes a further deformation of the dipoles with consequent increase in their potential energy, by an amount proportional to V . The total energy necessary is then given by $W = w - \alpha V$, where w and α are constants. The number of dipoles which possess sufficient energy to leave the surface will now be given by $N = N_0 \exp \{-(w - \alpha V)/RT\}$, which leads to $d(\log i)/dV = \alpha/RT$, similar to the observed relation.

In the present paper attention is focussed on the neutralisation of the electrolytic ions arriving at the electrodes. This is treated by quantum mechanics, and it is shown that we are led to just the effects given in the above list, without making any *ad hoc* assumptions.

* Caspari, 'Z. Phys. Chem.,' vol. 30, p. 89 (1899).

† Tafel, 'Z. Phys. Chem.,' vol. 50, p. 641 (1905).

‡ Bowden, *loc. cit.*; also Bowden and Rideal, 'Proc. Roy. Soc.,' A, vol. 120, p. 59 (1928) Bowden and O'Connor, *ibid.*, vol. 128, p. 317 (1930).

§ 2. *Application of Quantum Mechanics.*

The neutralisation of electrolytic ions will be more easily visualised if we first consider the neutralisation of a gaseous ion. When we say that the positive ions give up their charge to the electrode, we usually consider that they capture an electron by impact. But according to quantum mechanics no sort of contact is necessary, for an electron may make a spontaneous transition from the metal to a distant positive ion in the gas. What is more, to neighbouring ions these transitions take place so readily that positive ions cannot exist in the immediate neighbourhood of a metal except in special circumstances. Such neutralisation at a distance was first suggested by Compton and Van Voorhies* to account for certain experimental results obtained by them with gaseous ions. It has since been pointed out by Oliphant and Moon† that the process would be anticipated from quantum mechanics. The situation is illustrated in fig. 1, where is sketched the potential energy of an electron along a line perpendicular to the surface of the metal. Here MM represents the occupied

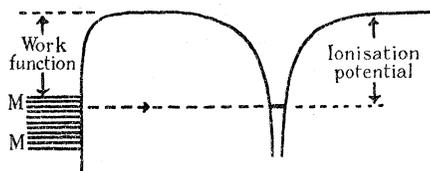


FIG. 1.

electron levels in the metal. According to the Sommerfeld theory, the valence electrons obeying the Fermi-Dirac statistics are distributed over a range of about 7, 9 and 12 volts in di-, tri-, and quadri-valent metals, respectively. The work-function of the metal, ϕ , is the negative energy of the highest occupied level with respect to the energy of an electron outside the metal. In fig. 1 is sketched also the Coulomb field and vacant level of a neighbouring ionised atom. Between the levels in the metal and those in the ion is a region forbidden by classical mechanics to electrons of these energies. If, however, the electrons in the metal are represented by a wave-function, this will not vanish at the surface of the metal, but will die away exponentially into the potential barrier. Since the number of electrons incident on unit area of the boundary from within is about 10^{30} per second, this penetration into the potential barrier is by no means negligible, but indicates a high probability of transition from

* Compton and Van Voorhies, 'Proc. Nat. Acad. Sci.,' vol. 13, p. 336 (1927), and 'Phys. Rev.,' vol. 30, p. 318 (1927).

† Oliphant and Moon, 'Proc. Roy. Soc.,' vol. 127, p. 388 (1930).

the metal to a vacant level of equal energy in any neighbouring ion. The interaction matrix for such a transition has been worked out by Massey.* It appears that the chance of a positive ion remaining within a few molecular diameters of the metal for a millionth of a second without being neutralised is extremely small.

At first sight this effect appears inconsistent with the existence of an electrical double layer of positive ions on a negative metal surface, such as are known for caesium on tungsten.† But since the above considerations only apply to electron-transitions between levels of equal energy, no transition can occur if the ionisation potential, \mathfrak{I} of the ion (when neutralised) is less than the work-function of the metal, as is clear from fig. 1. It was in fact found that this condition must be satisfied.† The alkalis and heavier alkaline earths are the only elements whose ionisation potentials are less than 4 to 6 volts.

We have not yet considered the reverse transition from a negative ion, or neutral atom, to the metal. Evidently this transition is possible from an atom whose ionisation potential is less than ϕ ; for in this case the electron can find for itself a vacant level in the metal above the occupied levels. Langmuir and Kingdon, in fact, found that neutral atoms of alkali metals, incident on a filament, were all scattered as positive ions, when ϕ was greater than the ionisation potential \mathfrak{I} . But from atoms whose levels are lower, an electron-transition to the metal is almost impossible, since practically all possible states in the metal of equal energy are already occupied.

We have so far been considering the simple case of a gaseous ion in field-free space. The situation is very different if the ion possesses potential energy of its own, due to the interaction of its charge with some other charge. If in this case an electron makes a transition from the metal to the ion, neutralising the ionic charge, this potential energy is annihilated. But, of course, these electron transitions may only take place subject to the conservation of energy. Hence it is essential that the electron-level in the metal from which the electron comes shall be higher or lower according as the ion has negative or positive potential energy (fig. 2).

These considerations indicate an important difference between ions in liquid solution, and ions in a gas. For electrolytic ions, owing to their interaction with adjacent water molecules, are all in a state of having lost energy—namely, the “heat of hydration,” which has been given out. This negative potential

* Massey, ‘Proc. Camb. Phil. Soc.’ vol. 26, p. 386 (1930).

† Langmuir and Kingdon, ‘Proc. Roy. Soc.’ vol. 107, p. 73 (1925).

energy of the ion itself, which we shall denote by W , and which usually amounts to several ϵ -volts per ion, must be replaced when the ion is neutralised, in

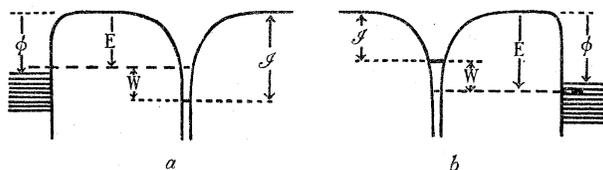


FIG. 2.—Showing the relations between W , S , and E for (a) positive ions, and (b) negative ions.

order to conserve energy. It is no longer true that the necessary condition for neutralisation of positive and negative ions is that ϕ be less or greater than the ionisation potential S . But we can define a quantity, instead of S , for which this is true; we shall call this quantity the neutralisation potential and denote it by E . Then the necessary condition for the required electron transition to be possible is for a positive ion $E_+ > \phi$ and for a negative ion $E_- < \phi$, where

$$E_+ = S_+ - W_+ \quad \text{and} \quad E_- = S_- + W_- \quad (1)$$

Fig. 2, *a* illustrates a case where transition to a positive ion would have taken place in a vacuum or gas, but is impossible in solution, because the required level is now an unoccupied level; similarly in fig. 2, *b*, the transition to the metal has become impossible because the required level is now an occupied level.

§ 3. *Electrode Potentials.*

It will now be clear that the presence of a rapid change of potential at the metal-liquid interface, *i.e.*, an electrode-potential such as we usually find, may well be the controlling factor in governing the neutralisation of ions. With regard to fig. 2, *a* and *b*, it is evident that in each case the electron-transition would become possible if the sign of the electrode-potential were such as to shift the level in the required direction. A moment's reflection shows that the sign of the electrode-potential which we find at cathodes is the sign which will promote the neutralisation of positive ions; while that which we find at anodes will promote the neutralisation of negative ions. In fact, the view which will be put forward in this paper is that the overpotential is not in this case due to an obstructive film of gas on the electrode, but, on the contrary, is an essential condition without which decomposition of the electrolyte cannot proceed. The effect of an electrode-potential V is to reduce the work-function

at the cathode effectively to $\phi - V$, or to increase that at the anode effectively to $\phi + V$. Hence the conditions to be satisfied are now

$$E_+ > \phi - V_c \quad E_- < \phi + V_a. \quad (2)$$

From the above discussion of neutralisation potentials it might be supposed that it would be possible at any rate to imagine an acid whose ionic levels were such that one could electrolyse it without the existence of electrode-potentials. A moment's consideration shows, however, that this is not so. For electrolysis to take place we need simultaneously $E_+ > \phi$ and $E_- < \phi$. But this implies $E_+ > E_-$, which is incompatible with ionic dissociation. The reason why electrolytes are dissociated into their ions, in the first place, is that the state of (ionisation + hydration) is a state of lower energy than the undissociated state. If the level occupied by the electron in the hydrated negative ion were not lower than the unoccupied level in the hydrated positive ion, electrons would immediately filter across from one to the other through the intervening potential barrier, until all the ions were neutralised. Thus in all highly dissociated electrolytes the neutralisation potentials of the ions are such that $E_+ < E_-$. And the necessary condition for decomposition by electrolysis can only be brought about by the presence of electrode-potentials. In § 4 we shall use this idea to predict the list of observed phenomena given above. But before we do this, we must make an excursion into electrostatics.

Consider an ion in a gas. In the neighbourhood of a metal surface the ion is attracted to the metal by the mirror-image force. The potential energy falls slowly as in fig. 3, *a*; at contact with the metal the force becomes suddenly repulsive, and the curve rises rapidly. At room temperature the thermal kinetic energy of the ion is about 1/25 volt. But under the attraction of the mirror image the ion will acquire a kinetic energy 10 times this normal value at a distance of 15 molecular diameters from the metal surface; while near the surface the kinetic energy will be more than 100 times its normal value. If the ion make an elastic impact on the metal, it will retrace its path and move off into the body of the gas with its original energy of 1/25 of a volt.

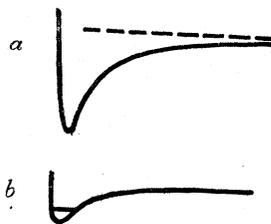


FIG. 3.

The ionisation potential of a hydrogen atom is nearly the same whether it happens to be dissolved in water or situated in a vacuum; that is to say, the forces between the proton and electron are nearly the same. At large distances, however, we know that in a medium of dielectric

constant K the force between charges is $1/K$ of its value in a vacuum. Applying this to the mirror-image forces near an electrode, we see that at large distances from the surface the mirror-image force will be only $1/K$ of its value in a gas. But at a distance of one or two molecular diameters from a clean metal surface the effective factor $1/K$ tends towards unity. The dip in the potential energy curve will therefore be confined to a small layer next to the metal, fig. 3, *b*.

The condition of escape of the gaseous ion considered above was that it retained at least some of its original $1/25$ volt of energy. If by colliding with a gas molecule it had given up more than $1/25$ volt, it would have been unable to escape. This is what will happen to an electrolytic ion. Owing to the extremely small free path, the chance of an ion *not* making a collision while it has its abnormally high kinetic energy is very small. The ion will be trapped in the potential pocket, as in fig. 3, *b*.

These considerations apply equally to positive and negative ions. When therefore an electrically neutral metal surface is exposed to a dilute electrolyte, the ions of both signs which happen to be near the surface will be trapped. Water molecules still cover the greater part of the metal surface, but since each ion which approaches the surface is liable to be trapped, we shall have these water molecules being ousted by ions of both signs, until finally there are perhaps no water molecules left in contact with the metal except those water molecules which are bound to the ions by the hydration forces. All that this means is that in contact with the metal the concentration of the electrolyte will be much greater than in the body of the solution. But suppose next that at the moment when the metal was exposed to the electrolyte it was electrically positive with respect to the latter; in this case there is a tendency for more negative ions to be trapped than positive, while if the metal were negative an excess of positive ions would be trapped. The charge of these ions distributed over the surface will give rise to a potential difference V , which we can calculate from $N\varepsilon = CV$, where C is the capacity of the double layer formed by the surplus ions and their mirror images. The excess number of ions N required to give a potential difference of 1 volt will be

$$N = \frac{K}{4\pi d300\varepsilon} \text{ per unit area.} \quad (3)$$

Writing $d = 2 \times 10^{-8}$ cm., and $K = 1$, we find $N = 3 \times 10^{13}$. As there may be more than 10^{15} ions per unit area in contact with the surface, it is clear that ions of one sign need be little in excess of ions of the other sign to give the observed electrode-potentials of one or two volts. The required excess is much

smaller than the number of ions in one monomolecular layer, so that the change of potential can take place in one molecular diameter from the metal surface. At each electrode the number of positive and negative ions in contact with the metal will never differ by more than a few per cent. If the potential of the metal is raised by means of applied e.m.f., those ions of the same sign which have at the moment the highest thermal energies will be repelled, and their places in contact with the metal taken by ions of the other sign, which are being attracted.

When two such metal electrodes are joined by an external circuit, as in an electrolytic cell, the equilibrium of the layer of ions on one electrode is not independent of that of the layer on the other. Any change in the electrode-potential at one electrode sends an electric charge through the external circuit, which, arriving at the other electrode, will disturb the equilibrium of ions there. If N positive ions are replaced by negatives on the surface of one electrode, and simultaneously N negatives are replaced by positives on the surface of the other electrode, then $2N$ electrons will meanwhile flow through the external circuit, producing a transient current. Neutralisation of ions plays no part in these transient currents. Bowden and Rideal measured the charge $N\epsilon$ passing through the external circuit during the establishment of a measured over-potential. At a smooth mercury cathode they found $N\epsilon = 3.6 \times 10^{13}\epsilon$ per volt rise in V . The value calculated above from (3) is in excellent agreement with this.

§ 4. Outline of the Theory.

In contemporary physics there are two ways of regarding the hydration of ions. One prefers to leave the state of hydration indefinite,* while the other postulates the formation of definite molecular ions, so that, for example, $(\text{H}_2\text{O} \cdot \text{H})^+$ and $(\text{H}_2\text{O} \cdot \text{OH})^-$ are formed by the hydration of H^+ and OH^- respectively.† The two views are not mutually exclusive; the former draws its conclusions from general considerations, but of recent years there is considerable support for the complex ion theory. In § 2 we have spoken of the hydration energy W as if it had one definite value for all the ions of one kind; but in neither theory is this true. In the general form of the theory the mean hydration energy is obtained from the virial by summing over all possible

* Born, 'Ver. D. Phys. Ges.,' vol. 21, p. 13 (1919); Fajans, *ibid.*, p. 709.

† Hund, 'Z. Physik,' vol. 32, p. 13 (1925); Brönsted, 'J. Phys. Chem.,' vol. 30, p. 777 (1926); Hunt and Briscoe, 'J. Phys. Chem.,' vol. 33, p. 1509 (1929); Goldschmidt and Mathiesen, 'Z. Phys. Chem.,' vol. 121, p. 156 (1926); Kendall and Gross, 'J. Amer. Chem. Soc.,' vol. 43, p. 1424 (1921).

configurations. In the complex ion theory the molecular ion will have a large number of vibration levels in which the ions will be distributed according to Boltzmann's law. (We shall suppose that these vibration-rotation levels are sufficiently close together and sufficiently blurred by the interaction with adjacent molecules to be treated as forming an almost continuous spectrum of levels.) It is clear that the single level of fig. 2, *a* or 2, *b*, and the single value of the neutralisation potential must be replaced by a wide band of levels, labelled in excellent agreement E_0^+ and E_0^- in fig. 4.

The hydration energy W_0 of those molecular ions which are in their lowest vibration-rotation level is equal to the full dissociation potential of the molecular ion. But for a molecular ion in its n th vibration-rotation level $W_n < W_0$, since the work required to dissociate the ion is less by an amount equal to the excess vibration-rotation energy. Since for a positive ion $E = \mathfrak{S}_+ - W$, it is clear that $E_n > E_0$, and that $N_+(E)$, the number of positive ions with neutralisation potential between E and $E + dE$ will be given by the Boltzmann law, $N(E) = N_0 e^{(E_0 - E)/kT}$. On the other hand, for negative ions the neutralisation potential is given by $E = \mathfrak{S} + W$; hence $E_n < E_0$, and $N_-(E)$ will be an inverted Boltzmann distribution. These two distributions are labelled E_0^+ and E_0^- in fig. 4, which will be explained in detail later.

We can now return to the consideration of electrode-potentials which was begun in § 3. It was there pointed out that the essential condition for a large current flowing is that there should be a large overlapping between the ionic and metallic electron-levels between which transitions can take place. We find now that the conditions which must be satisfied for neutralisation to take place are for positive ions at the cathode

$$E_n > \phi - V_c, \quad (4)$$

and for negative ions at the anode

$$E_n < \phi + V_a, \quad (5)$$

and these cannot be simultaneously satisfied with $V_c = V_a = 0$. The number of ions for which (4) is satisfied at the cathode is given by

$$\int_{\phi - V_c}^{\infty} N_+(E) \cdot dE.$$

And if $P(E)$ is the probability of an electron making a transition from the metal to an ion through a potential barrier of height E , the current flowing will be given by

$$\int_{\phi - V_c}^{\infty} N_+(E) \cdot P(E) \cdot dE. \quad (6)$$

When a steady current is flowing, the number of electrons which are making transitions through the potential barrier from the cathode to the positive ions must be equal to the number of electrons making transitions from the negative ions to the anode. This integral must therefore be equal to the corresponding integral at the anode. Suppose now that we wish to pass a larger steady current through the cell; both of these integrals must obviously be increased. But at constant temperature $N(E)$, $P(E)$, and ϕ are already fully determined. Therefore to produce the necessary increment there remains only the possibility of change in V at each electrode. This is the explanation of the familiar fact that any increment in applied e.m.f. is almost entirely taken up in increasing the potential differences at both the metal-liquid interfaces. It is just this necessary change in V which shows itself as the overpotential which is automatically set up by the replacement of ions, as described in § 3. Turning next to variation with temperature at constant potential difference, we see that the exponential increase of $N(E)$ will cause the current to rise exponentially with the absolute temperature, in agreement with observation. We shall show that the theory leads to numerical agreement with experiment.

§ 5. Theory and Results.

In the foregoing outline we have treated the familiar work function ϕ as if it had a precise meaning. It would be properly defined if the dividing line between occupied and unoccupied levels in the metal were sharp. At room temperature, however, this is far from true. In accordance with the Fermi-Dirac statistics the number of free metallic electrons with energies between w and $w + dw$ is given by

$$n(w) = \frac{A\sqrt{w}}{1 + \exp\{(w - w_1)/kT\}} \quad (7)$$

where A is a constant. As will appear later, at the low current densities with which we are dealing, levels for which w differs little from w_1 make a negligible contribution to the current. Outside a narrow range of energies ($w_1 \pm 0.01$ e-volt) we can replace (7) by

$$n(w) = A\sqrt{w} \cdot e^{(w_1 - w)/kT}, \quad w \gg w_1, \quad (8)$$

$$n(w) = A\sqrt{w} (1 - e^{(w - w_1)/kT}). \quad w \ll w_1. \quad (9)$$

This distribution is illustrated diagrammatically by the blackened area in the anode and cathode in fig. 4. Above w_1 the number of electrons falls off exponentially with the same Boltzmann factor as that of the ionic levels.

Making use of this distribution, the integral (6), representing the current flowing, must now be replaced by

$$\int_{E_0^+}^{E_1 - \epsilon V} n(E, V) \cdot N_+(E) \cdot P(E) \cdot dE, \tag{10}$$

where E_1 is the value of E corresponding to w_1 when V is zero. The corresponding integral at the anode will be

$$\int_{E_1 + \epsilon V}^{E_0^-} \nu(E, V) \cdot N_-(E) \cdot P(E) \cdot dE, \tag{11}$$

where $\nu(E, V)$ is the number of vacant levels in the metal, which falls off below w_1 exponentially with the same Boltzmann factor. The similarity of the phenomena at anode and cathode is due to this fact.

The correct limits of the integrals (10) and (11), and their physical significance will be understood from fig. 4, which is a developed form of fig. 2. Ordinates

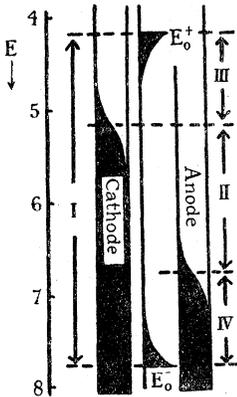


FIG. 4.—Abscissæ are $N(E)$ in the central strip, and $n(E, V)$ in the anode and cathode.

are energies, E being reckoned downwards from the top of the diagram; a rough scale of volts has been indicated. The figure consists of three strips, representing levels in the cathode, electrolyte and anode. It has already been explained that in the central strip the blackened areas represent $N_+(E)$ and $N_-(E)$. In the cathode and anode the blackened areas represent $n(E, V)$. The representation of the exponentials is, of course, merely schematic, since in reality they fall to 10^{-8} of their value in a range of half a volt.

The range of energies marked I is a fixed property of the electrolyte; its boundaries are E_0^+ and E_0^- . We may take the potential of the electrolyte as the standard to which energies are referred; the cathode is displaced upwards by an amount V_c , while the anode is displaced downwards by an amount V_a . This displacement has brought an appreciable number of high energy electrons in the cathode to overlap the positive ion levels in region III, and at the same time has brought some appreciably unoccupied levels in the anode to overlap the negative ion levels in region IV. The range of energies marked II represents the magnitude of the applied e.m.f., which in this case is supposed to be sufficient to cause a detectable but not a large current to flow. The boundaries of region II are $E_1 - \epsilon V_c$, and $E_1 + \epsilon V_a$, the dotted lines having

been drawn through the displaced metallic level w_1 of expressions (7), (8), (9). Region III is just the region of energies over which the integral (10) has to be taken; its boundaries are E_0^+ and $E_1 - \epsilon V_0$. From E_0^+ the number of vacant ionic levels falls off exponentially, but in the same region the number of metallic electrons is rising exponentially with the same Boltzmann factor, so that the product of the two exponential factors is everywhere the same. Thus the product $\{n(E) \cdot N_+(E)\}$ is almost constant until we come near to the metallic electron-level of energy ($w_1 + 0.01 \epsilon$ -volt); here the number of metallic electrons ceases to rise exponentially, so that the product falls very rapidly to a negligible value. We shall show later that the range of energies over which we have to integrate has for low-current densities a value about 1ϵ -volt; since this is large compared with 0.01ϵ -volt, we may use the level corresponding to w_1 in the limit of the integral (10). Region IV is for the same reasons the range over which the integral (11) has to be taken. It will be understood from the diagram how any increase of temperature, or any small increase in the applied e.m.f., will cause the value of the product $\{n(E) \cdot N(E)\}$ to rise exponentially. In so far as the metallic electrons are concerned, the rise of current with temperature takes place for the same reason as in the thermionic effect; here, however, the ionic levels co-operate.

Let $N(E, x)$ be the number of ions per unit area at a distance x from the metal, having neutralisation potential E . When a steady current is flowing this distribution will, apart from thermal agitation, be steady. In an interval of time dt in any slab of the solution a certain number of ions will be neutralised, and their places taken by ions flowing in. Thus the total current density is given by

$$\iint n(E, V) \cdot N(E, x) \cdot P(E, x) \cdot dE \cdot dx.$$

To investigate orders of magnitude we shall take $P(E, x)$ to be the probability of transition through a rectangular potential barrier of height E and width x , and we shall suppose that all the ions are being neutralised at the mean distance x' . The essential part of $P(E)$ will then be the factor $\exp(-4\pi x'/h \cdot \sqrt{2mE})$.* Thus each of the terms in the integral (10) contains an exponential factor; and the integral is to be taken over a small range of E where the other factors are relatively constant in comparison with the rapid variation of these exponential factors; retaining only the latter, we have that the integral (10), representing the current density, is proportional to

$$\int_{E_0}^{E_1 - \epsilon V} e^{(E - E_1 + \epsilon V)/kT} \cdot e^{(E_0 - E)/kT} \cdot e^{-4\pi x'/h \cdot \sqrt{2mE}} \cdot dE. \quad (12)$$

* Gurney and Condon, 'Phys. Rev.', vol. 33, p. 131 (1929).

On integrating, we find

$$\log i = \frac{E_0 - E_1 + \epsilon V}{kT} + \log \left\{ (ax' \sqrt{E_0} + 1) e^{-ax' \sqrt{E_0}} - (ax' \sqrt{E_1} - \epsilon V + 1) e^{-ax' \sqrt{E_1 - \epsilon V}} \right\} + \text{const.}$$

Hence

$$\frac{d(\log i)}{dV} = \frac{\epsilon}{kT} + \frac{\epsilon a^2 x'^2 \cdot e^{-ax' \sqrt{E_1 - \epsilon V}}}{(ax' \sqrt{E_0} + 1) e^{-ax' \sqrt{E_0}} - (ax' \sqrt{E_1} - \epsilon V + 1) e^{-ax' \sqrt{E_1 - \epsilon V}}} \quad (13)$$

where $a = 4\pi\sqrt{2m}/h$, and the value of E_1 is the work-function ϕ of the electrode. For the anode we have an identical expression if we take the appropriate sign for V . The values of E_0^+ and E_0^- must be about 4 ϵ -volts, and 8 ϵ -volts, respectively. The value of x' must be about 5×10^{-8} cm. Substituting these values in (13), we find that the second term is small compared with the first. We are left then with the simple term ϵ/kT , which will apply to both anode and cathode, and will be independent of the nature of the metal. It will be recalled that the term found by experiment is α/T , where α has the same value at anode and cathode, and is independent of the nature of the metal.

In order to present a more complete theory, we have to introduce a modification into the idea of the neutralisation potential. The elementary point of view taken in § 2 was that the mutual potential energy of the ion and adjacent water molecules was before neutralisation negative and equal to $-W$, and after neutralisation was zero. This is not quite correct, for if neutralisation takes place with stationary nuclei, as in the Franck-Condon principle, the mutual

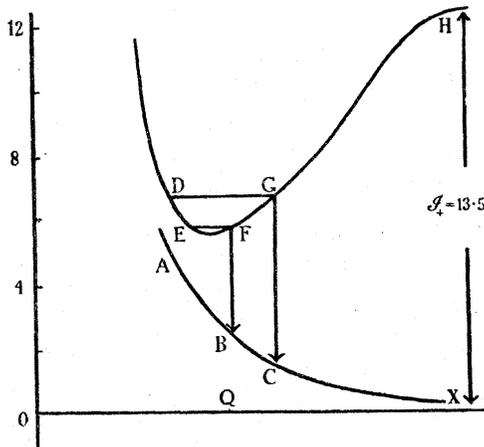


FIG. 5A.—Abscissæ are distances apart, the origin being the centre of gravity of the H_2O molecule.

potential energy immediately after neutralisation will be positive. This modification will be more easily made clear in terms of molecular ions. In 1925, investigating the molecular structure by the methods then available, Hund found a stable configuration for the $(\text{H}_3\text{O})^+$ ion with a dissociation potential of about 8.3 e-volts . Though this was done in the days before quantum mechanics, it may be of the right magnitude. Now $(\text{H}_3\text{O})^+$ is one of those peculiar ions, like H_3^+ , to which there is no corresponding neutral molecule. The symmetry properties of H_2O and neutral H are such that the force between them is repulsive at all distances, as in the antisymmetrical form of H_2 . When neutralisation of $(\text{H}_3\text{O})^+$ takes place, the components then fly apart evolving atomic hydrogen; the same is true of the complex negative ion, evolving oxygen. The potential energy of the neutral state of such ions must, therefore, be represented by a curve such as ABC, fig. 5A, similar to that which gives rise to the continuous spectrum of hydrogen. The curve for the stable vibrational levels of $(\text{H}_3\text{O})^+$, represented by DFH will lie above the axis so that HX is the ionisation potential of the hydrogen atom, 13.5 e-volts . The curve KMP, fig. 5B, for the negative complex ion will lie below the axis, so that PX is the ionisation potential of the unhydrated negative ion, which is usually only 2 to 4 e-volts.* EF represents the lowest vibration-rotation level of $(\text{H}_3\text{O})^+$ and the vertical distance of EF below H is the dissociation potential of the ion; the value, 8.3 e-volts , deduced by Hund is in fair agreement with the hydration energy, From Born's theory† Fajans deduced a value of 11.5 e-volts ,‡ but in his calculation he used too small a value for the work function of the electrode; the correct value of the hydration energy must be nearer to 9 e-volts .

Now it is clear that the transition representing neutralisation of an ion in its lowest vibration-rotation level is on this diagram FB for the positive ion, and MB' for the negative ion; and this is in each case the neutralisation potential that must be used when we are considering the electron transition. From fig. 5 we see much more clearly than from fig. 2 how it comes about that for any hydrated positive ion the neutralisation potential, represented by FB, is less than ϕ for any electrode, in spite of the fact that \mathfrak{S} is greater than ϕ ; while for a negative ion the neutralisation potential, represented by MB', is greater than ϕ , although \mathfrak{S} , represented by PX, is less than ϕ . In accordance with the Franck-Condon principle, BQ represents the positive mutual potential energy of the molecular components before they have moved apart. If R_n

* Foote and Mohler, "Origin of Spectra," chap. 8.

† Born, *loc. cit.*

‡ Fajans, *loc. cit.*

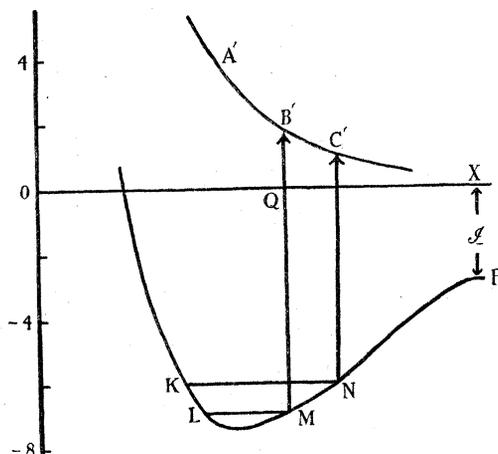


FIG. 5B.

is the value of this repulsive potential energy resulting from neutralisation of an ion in its n th vibration-rotation level, the correct expression for E_n is now,

$$\text{and } \left. \begin{array}{l} \text{for positive ions } E_n = \mathfrak{S} - W_n - R_n \\ \text{for negative ions } E_n = \mathfrak{S} + W_n + R_n \end{array} \right\} \quad (14)$$

Let DG be a vibration-rotation level about 1 ϵ -volt higher than EF; it is only levels between EF and DG which concern us; if U is the vibration-rotation energy, the distribution is given by $N(U) = e^{(U_0 - U)/kT}$. From fig. 5 we see that $(GC - FB)$, representing $(E - E_0)$ is greater than $(U - U_0)$; let $(E - E_0) = \gamma(U - U_0)$. Between E and E_0 we have the same number of levels as between U and U_0 , but they are distributed over a larger range of energy. Therefore we have that $N(E) = N_0 e^{(E_0 - E)/\gamma kT}$, where γ is greater than unity and to a first approximation constant. The value of γ depends on the relative slope of FG and BC; if, for example, BC is sloping downwards at the same rate that FG is sloping upwards as in fig. 5, γ has the value 2. The same argument applies to the slope of MN and B'C' for negative ions.

Since the term in (13) contributed by the potential barrier turned out to be small, we may treat $P(E)$ as a constant. Instead of the integral (12) we have now

$$\int_{E_0}^{E_1 - \epsilon V} e^{(E - E_1 + \epsilon V)/kT} \cdot e^{(E_0 - E)/\gamma kT} \cdot dE \quad (15)$$

$$= e^{(E_0/\gamma + \epsilon V - E_1)/kT} \left\{ e^{(E_1 - \epsilon V)(1 - 1/\gamma)/kT} - e^{E_0(1 - 1/\gamma)/kT} \right\} \cdot \frac{\gamma kT}{\gamma - 1} \quad (16)$$

Of the two terms in the bracket the second has a value only 10^{-4} of that of the first when $\gamma > 1.3$, as here. Retaining only the first term in the bracket, we find

$$\log i = \frac{E_0 - E_1 + \varepsilon V}{\gamma k T} + \log T + \text{constant.} \quad (17)$$

As our final result we obtain the two relations

$$\frac{d(\log i)}{dV} = \frac{\varepsilon}{\gamma k T} \quad \gamma > 1, \quad (18)$$

$$\frac{d(\log i)}{dT} = \frac{E_1 - E_0 - \varepsilon V}{\gamma k T^2} + \frac{1}{T}. \quad (19)$$

Excellent agreement with experiment is found with a value $\gamma = 2$. It will be recalled that the observed relation is $d(\log i)/dV = A/T$, with $A = 1.7 \times 10^6$. Since the value of k is 1.37×10^{-16} ergs, we have with $\gamma = 2$

$$\frac{\varepsilon}{\gamma k} = 1.7 \times 10^6.$$

Over the small range of absolute temperature which is open to experiment it will be recalled that $d(\log i)/dT = B$, where the value of B decreases with increase in V . It will be seen that the numerator in (19) will be diminished by any increase in V , in agreement with observation. This numerator, $(E_1 - \varepsilon V - E_0)$ will be recognised as the range of energies over which the integral (15) has been taken; throughout the investigation we have been supposing that this range of energies is about one ε -volt, or 1.6×10^{-12} ergs. It will be recalled that for both anode and cathode the observed values of B are between 0.05 and 0.06, for the temperature range 14° to 80° C. If we use the same value of γ as before, we shall have at 320° K., to compare with this,

$$\frac{1.6 \times 10^{-12}}{2 \cdot 1.37 \cdot 10^{-16} \cdot 102400} = 0.057.$$

§ 6. Conclusion.

The analysis of the problem has brought out clearly the important rôle played by the quantities E^+ , E^- , E_0^+ , E_0^- , which we have called the neutralisation potentials. In deriving these quantities we have used the only available vocabulary—that of molecular spectroscopy. The existence of definite molecules is not, however, a necessary assumption. Provided that the hydration energy is distributed according to the Boltzmann law, and has a relation corresponding to (14), indefinite molecular configurations would probably

give the same results. Agreement with experiment has been obtained for all of the seven relations tabulated in § 1.

The writing of this paper would not have been undertaken but for the welcome instruction in the experimental data volunteered to me by Dr. F. P. Bowden, to whom I wish to express my thanks.

The Scattering of α -Particles by Light Elements.

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It is well known that the scattering of fast α -particles by light elements shows very remarkable deviations from the classical law of scattering deduced from the assumption that the nuclei behave as point charges, surrounded by a Coulomb field of force. The first anomalous effects of this kind were obtained in 1919 by Rutherford* in an investigation of the collisions of α -particles with hydrogen nuclei. Chadwick and Bieler† found in later experiments that the number of H-particles observed at small angles, which, seen from the centre of gravity of the colliding system, correspond to α -particles scattered through large angles, was for the fastest α -particles about 100 times larger than the number calculated on the assumption of Coulomb forces between the colliding particles. They suggested that this effect was due to an oblate spheroidal shape of the α -particle. This assumption also agreed with subsequent experiments by Rutherford and Chadwick‡ on the scattering of α -particles in helium. They found that for high velocities of the incident α -particles the number of particles scattered through 45° was about twenty times larger than expected. For smaller initial velocities and smaller angles this ratio became much less, for certain velocities only one-third.

The scattering of α -particles by the nuclei of other light elements has been observed only in two cases, those of magnesium and aluminium. The first investigations of this kind were those of Bieler.§ He found that the ratio of

* Rutherford, 'Phil. Mag.', vol. 37, p. 537 (1919).

† Chadwick and Bieler, 'Phil. Mag.', vol. 42, p. 923 (1921).

‡ Rutherford and Chadwick, 'Phil. Mag.', vol. 4, p. 605 (1927).

§ Bieler, 'Proc. Roy. Soc., A,' vol. 105, p. 434 (1924).