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GURNEY AND JACKSON
LONDON: 33 PATERNOSTER ROW
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THE MECHANISM OF OVERVOLTAGE AND ITS RELATION TO THE COMBINATION OF HY- DROGEN ATOMS AT METAL ELECTRODES.

BY J. A. V. BUTLER, D.Sc.

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In a recent paper on the Quantum Mechanics of Electrolysis,¹ Dr. R. W. Gurney has calculated the rate of transfer of electrons between an electrode and dischargeable ions in a solution, and has developed on this basis a general theory of overvoltage. His calculation is based on the postulate that "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 $\phi + V$." I made use of this concept in 1923 in a "Kinetic Theory of Reversible Oxidation Potentials at inert Electrodes"² and, employing classical statistical mechanics, gave the rate of transfer of electrons to reducible ions present in the vicinity of the electrode at a concentration x as

$$\theta_1 = kxe^{-\phi + EF/RT} \quad . \quad . \quad . \quad (1)$$

(where E has the opposite sign to V). At the reversible electrode potential, I pointed out that electrons must be returned to the electrode from the reduced material at the same rate, and regarding the reversible potential difference as that required to effect the balance of these two processes, and taking account of the possibility of adsorption of the electromotively active substances, I derived by statistical methods the thermodynamic relations between the electrode potential and the concentrations of the substances or ions taking part in the exchanges.

Under conditions in which the rate of the reverse process is relatively slow, (1) might have been expected to give the relation between the current density and the overvoltage, but the difficulty was encountered that the exponential term required by the experimental data was half that which appears in (1). Dr. Gurney has recently applied the principles of Quantum Mechanics to elucidate the rate of transfer of electrons, and taking into account the forces between the discharged hydrogen atoms and the solvent, has deduced the expression

$$i = kTe^{E_0 - E_1 + FV/\gamma RT} \quad . \quad . \quad . \quad (2)$$

which may be written, since k contains the concentration of hydrogen ions in the solution

$$i = k'[H^+]Te^{E_0 - E_1 + FV/\gamma RT}, \quad . \quad . \quad . \quad (3)$$

where E_0 and E_1 are constants, and i is the current density for the potential difference V . γ is a constant which is greater than unity; if its value is 2, the experimental findings³ are accounted for.

¹ *Proc. Roy. Soc.*, **134A**, 137, 1931.

² *Trans. Faraday Soc.*, **19**, 734, 1924.

³ *Proc. Roy. Soc.*, **120A**, 59, 1928 (Bowden and Rideal); **126A**, 107, 1929 (Bowden).

In this expression no account is taken of the rate at which electrons are returned to the electrode by hydrogen atoms. By analogy with (3) we may write this in the form

$$i' = k''[H]T e^{E' - FV/\gamma RT}, \quad . \quad . \quad . \quad (4)$$

where $[H]$ is the concentration of hydrogen atoms at the surface of the electrode. When no current is passing $[H]$ will be governed by the concentration of hydrogen molecules in the solution, and will be determined by the dissociation of molecular hydrogen as in the equation $H_2 = 2H$. We can represent this equilibrium provisionally as governed by the equation $[H_2] = k'''[H]^2$. When a current is passing hydrogen atoms will accumulate at the electrode until their rate of recombination to form molecular hydrogen (and loss by diffusion, etc.) is equal to their rate of formation.

The total current of electrons passing from the electrode to the solution is therefore

$$i = k'[H^+]T e^{E_0 - E_1 + FV/\gamma RT} - k''[H]T e^{E' - FV/\gamma RT}, \quad . \quad (5)$$

where $[H]$ is thus determined. Collecting the constants and putting $\gamma = 2$ in each term, we may write this in the form

$$i = K[H^+]e^{FV/2RT} - K'[H]e^{-FV/2RT} \quad . \quad . \quad (6)$$

Therefore, if $V_0 = 0$ when $i = 0$, we have

$$FV_0/RT = \log K'[H]K[H^+], \quad . \quad . \quad . \quad (7)$$

$$\text{or} \quad V_0 = RT/F \log K' \sqrt{[H_2]}K[H^+], \quad . \quad . \quad (8)$$

which is the usual thermodynamic expression.

As V increases the first term in (6) increases rapidly, and the second diminishes, and unless $[H]$ becomes very great the second term cannot be of any importance in the determination of i for comparatively large currents. But it becomes important for very small values of i . When V is not far removed from the equilibrium potential V_0 , we have approximately

$$i = K[H^+]e^{FV_0/2RT} \cdot F(V - V_0)/RT \quad . \quad . \quad (9)$$

i.e., overvoltage varies linearly with the current density for very small values of the latter.

In collaboration with Mr. G. Armstrong, experiments have been made in this laboratory on the overvoltage produced at platinum cathodes by small currents of the order of 10^{-6} to 10^{-7} amps./cm.², and we have found that in this region the overvoltage varies linearly with the current as is required by this expression. We have also found that a similar relation holds for the discharge of other ions, etc., at the cathode, *e.g.*, in the reduction of ferric salts, of methylene blue, and of quinone, in solutions containing also the reduced substance, for small currents the displacement of the potential difference from the reversible value is approximately proportional to the current density. In these cases a much larger current can be passed before the linearity ceases to hold.

Further, T. Erdey-Grúz and M. Volmer in a recent paper ⁴ have studied the overvoltages required for the deposition of the metals Zn, Cd, Ni, Pb, Bi, Cu and Ag, and find in most cases that the displacement

⁴ *Z. physikal. Chem.*, **157**, 165, 1931.

of the potential difference from the reversible value varies linearly with the current for very small values, and with the logarithm of the current at higher values, as is required by (6). This equation may therefore prove to be general for electrolytic processes.

The reverse term may also be of importance in determining the decay of the overvoltage. According to the measurements of Bowden and Rideal,⁵ the quantity of electricity required to increase the hydrogen overvoltage by 1 volt is about 10^{-5} coulombs/cm.² If we represent this quantity by B , $-B dV/dt$ must be equal to the rate at which electrons are lost by the electrode at open circuit. If the latter quantity is represented by (2) we have

$$-B dV/dt = kT e^{E_0 - E_1 + FV/2RT} \quad (10)$$

The constants in this expression can be evaluated given a knowledge of the $V - \log i$ curve, and using these values (10) can be integrated. The following table gives the variation of V (measured against the mercurous sulphate electrode) with time, when its initial value is 1.8 volts, as calculated in this way.

V .	t (secs.).	V .	t (secs.).
1.8	0	1.30	4
1.66	0.004	1.18	40
1.54	0.04	1.06	400
1.42	0.4	0.94	4000

Mr. G. Armstrong and I have made a number of experiments on the rate of decay of the hydrogen overvoltage at mercury in sulphuric acid solutions. In one experiment the value $V = 1.42$ was reached in 4 secs., and the value 1.30 in about 400 secs., a much slower decay than that calculated. Bowden has suggested that the persistence of the hydrogen overvoltage is due to the deposition and solution in the mercury of small quantities of the alkali metals present as impurities. In these experiments we had an auxiliary mercury cathode by which the solution was electrolysed for about 30 hours previous to the measurement of the decay at the other electrode, and during part of this time the solution was vigorously stirred. While we have not definitely excluded the possibility of this behaviour being due to traces of alkali metals, we have thus shown that it remains after a fairly drastic treatment to remove such traces.

A slower rate of decay would be given by using (6). Then we should have

$$-B dV/dt = K[H^+] e^{FV/2RT} - K'[H] e^{-FV/2RT} \quad (11)$$

We have seen that during the passage of a large steady current, the second term on the right of this equation is small in comparison with the first. But if the rate of loss of hydrogen atoms at the electrode surface is comparatively slow, the second term will become of importance when V has reached a lower value (V decreases by about 0.4 volts in less than half a second). Thereafter the decay of the overvoltage will be mainly determined by the rate of loss of hydrogen atoms from the electrode.

⁵ Bowden and Rideal, *loc. cit.*

It seems, probably, that this occurs mainly by their combination to form hydrogen molecules. A study of the decay of the hydrogen overvoltage, when effects due to impurities are definitely excluded, would thus throw light on the formation of hydrogen molecules from atoms at the electrode surface. We are at present engaged on experiments of this kind.

*King's Buildings,
West Mains Road,
Edinburgh.*
