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Application of the Theory of Absolute Reaction Rates to Overvoltage

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It is shown by means of the theory of absolute reaction rates that the current density I at an electrode is related to the overvoltage V by the expression $I = I_0 e^{\alpha VF/RT}$ where I_0 is a constant for a given electrode, representing the current passing in each direction at the reversible potential, and α is the fraction of the added potential V operating between the initial and activated states. Since α is about 0.5 for many electrodes, it appears that the energy barriers at the electrode surface is a symmetrical one. The quantity I_0 is equal to $Be^{-\Delta H_1^\ddagger/RT}$, where ΔH_1^\ddagger is the heat of activation of the rate-determining process responsible for overvoltage, and B is $C_1(kT/h)F/N \cdot e\Delta S_1^\ddagger/R$, where k , h , F , N and R are universal constants, T is the temperature, ΔS_1^\ddagger is the entropy of activation and C_1 is the concentration, per unit area, of the species involved in the slow process. Since ΔH_1^\ddagger and I_0 can be obtained from experimental data, it is possible to evaluate B , which is found to be independent of the nature of the cathode or the hydrogen ion concentration of the solution, and hence it appears that C_1 is almost constant for all electrodes in aqueous solutions. This suggests that the rate-determining step in the discharge of a hydrogen ion involves a water molecule, for only in this way could C_1 remain constant, and the slow process is believed to consist in the transfer of a proton from a molecule of water attached to the solution to an-

other water molecule attached to the electrode surface. The suggested prototropic mechanism permits of an approximate estimate of ΔS_1^\ddagger , and taking C_1 as 10^{15} molecules of water per sq. cm, the value of B calculated is in satisfactory agreement with experiment. The mechanism suggested immediately leads to the expectation of a symmetrical barrier at the electrode surface and so accounts for the value of 0.5 for α . The linear rate of attainment of overvoltage and the effect of changes in zeta-potential are readily explained, and it is shown that metals which form strong M-H bonds should have low overvoltages, as found in practice. The hydrogen-deuterium electrolytic separation factor is considered from the standpoint of the prototropic theory of overvoltage, and an explanation is proposed for the influence of the cathode material and of temperature. Oxygen overvoltage is attributed to a proton transfer in the opposite direction, i.e., from a water molecule on the electrode to one in a layer associated with the solvent, and so the striking similarities between cathodic and anodic phenomena can be readily understood. The high overvoltage accompanying the discharge of H_3O^+ and OH^- but not other ions is attributed to the fact that these ions are comfortably built into the structure of the solvent water.

INTRODUCTION

WHEN an electrode, immersed in a solution of its own ions (or of the ions of a gas with which it is saturated), is at its reversible potential the rate of deposition of ions on to the electrode is equal to the rate of re-ionization of the deposited substance: under these conditions there is no net flow of current and the resultant rate of deposition is zero. If material is to be deposited at an appreciable rate or, in other words, in order that an appreciable current may flow from electrode to solution, or vice versa, it is necessary to impose an additional electrical potential on the system; the magnitude of this excess potential determines the net rate of deposition, i.e., the current strength. The difference between the actual potential required to permit current to flow at a particular current density and the reversible value for the electrode

in the given solution is called the "overvoltage" or "overpotential"¹ at that current density. In assessing the reversible potential it is the general practice to suppose that the substances deposited are in their standard states; a gas, e.g., hydrogen or oxygen, is supposed to be at 1 atmos. pressure if this is the external pressure at which electrolysis occurs. The overvoltage obtained in this manner is, of course, important from the practical point of view, but for theoretical treatment it is preferable to define the overvoltage as the potential in excess of the reversible potential of the electrode *under the experimental conditions*. In this way polarization phenomena resulting from changes in concentration of the electrolyte or from the fact that the solution may be super-saturated with gas, since this may be necessary

¹ For recent reviews, see S. Glasstone, *The Electrochemistry of Solutions* (Van Nostrand, Second edition, 1937), Chap. XVII; Ann. Reports Chem. Soc. **34**, 107 (1937); F. P. Bowden and J. N. Agar, *ibid.* **35**, 90 (1938); K. Wirtz, *Zeits. f. Elektrochemie* **44**, 303 (1938).

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before bubbles can form, are excluded from the true overvoltage. As the latter is probably related to the energy of activation of the slowest stage involved in the process of deposition of material on the electrode, it may be called the "activation overvoltage."² The deposition of metals, except those of the iron group, generally requires only a small overvoltage, but appreciable values, rising sometimes to as much as one volt, accompany the liberation of hydrogen and oxygen.

THE RATE-DETERMINING STEP

In the electrolysis of any aqueous solution the over-all reaction is the conversion of water into hydrogen and oxygen, and the various stages involved at the cathode are as follows: (1) the transport of H_3O^+ to the electrode layer; (2) the transfer of the ions, or possibly protons, to the electrode, and their discharge by electrons; (3) the combination of the hydrogen atoms on the electrode surface to form molecular hydrogen; and (4) the evolution of the hydrogen molecules in bubbles of gas. The slowest of these stages determines the overvoltage corresponding to a given current density. That stage (1) is not rate-determining is shown by the fact that the overvoltage depends on the nature of the metal used as cathode and is very small at an electrode of platinized platinum: further, the activation energy for the transport process is less than 3.5 kcal.,³ which is much smaller than that usually associated with overvoltage (see Table I). Although (4) probably plays some part, it is apparently of relatively minor importance in determining overvoltage: the evolution of chlorine gas bubbles, as a result of the electrolysis of chloride solutions, for example, requires only a small overvoltage. The suggestion that stage (3) is the slow process was originally made by Tafel,⁴ but this view leads to expectations in disagreement with the facts. If the electrode surface is sparsely covered with atomic hydrogen, the rate of the reaction $2H \rightarrow H_2$ is given by kn^2 , where k is a constant and n is the number of atoms of adsorbed hydrogen per sq. cm of

electrode surface. If the rate of the reverse process, that is the dissociation of hydrogen molecules into atoms, is negligible in comparison with that of the direct reaction, as it will be at appreciable current densities, the current flowing (I) is proportional to the rate of formation of molecular hydrogen: it is thus possible to write $I = kn^2$. The potential E of any atomic hydrogen electrode may be written in the form*

$$E = (RT/F) \ln n + \text{constant}, \quad (1)$$

where the constant depends on the hydrogen ion concentration of the solution: the potential of the reversible electrode would then be

$$E_0 = (RT/F) \ln n_0 + \text{constant}, \quad (2)$$

n_0 being the number of hydrogen atoms per sq. cm of surface at the reversible potential. The overvoltage V , equal to $E - E_0$, is then given by

$$V = (RT/F) \ln n/n_0. \quad (3)$$

Combination of Eq. (3) with the result $I = kn^2$ then gives

$$I = kn_0^2 e^{2VF/RT}$$

or, more generally,

$$I = I_0 e^{2VF/RT} = I_0 e^{\alpha VF/RT}, \quad (4)$$

where I_0 is a constant, and α is equal to 2. According to Eq. (4) the plot of V against $\ln I$ should be a straight line of slope $RT/2F$, but it has been found experimentally for a number of metals that although the plot is linear, the slope is $2RT/F$, that is, α in Eq. (4) is 0.5 instead of 2. In order to account for this discrepancy Volmer and Erdey-Grúz,⁵ Gurney,⁶ and others⁷ have suggested that part of stage (2), namely the neutralization of the hydrogen ion, is the slow process in the formation of gaseous hydrogen at an electrode, and hence is the fundamental cause of

* Strictly speaking the *activity*, and not the concentration of atomic hydrogen, should be used; under the conditions specified, however, i.e., a sparsely covered surface, n is probably a measure of the activity.

⁵ T. Erdey-Grúz and M. Volmer, *Zeits. f. physik. Chemie* **150A**, 203 (1930).

⁶ R. W. Gurney, *Proc. Roy. Soc.* **A134**, 137 (1931); see also R. H. Fowler, *Trans. Faraday Soc.* **28**, 368 (1932).

⁷ See, A. Frumkin, *Zeits. f. physik. Chemie* **164A**, 121 (1933); J. A. V. Butler, *Trans. Faraday Soc.* **28**, 379 (1932); *Proc. Roy. Soc.* **A157**, 423 (1936); *Zeits. f. Elektrochemie* **44**, 55 (1938); J. A. V. Butler and G. Armstrong, *Proc. Roy. Soc.* **A137**, 604 (1932).

² F. P. Bowden and J. N. Agar, reference 1, p. 91; *Proc. Roy. Soc.* **A169**, 206 (1938).

³ A. E. Stearn and H. Eyring, *J. Chem. Phys.* **5**, 113 (1937).

⁴ J. Tafel, *Zeits. f. physik. Chemie* **50**, 641 (1905).

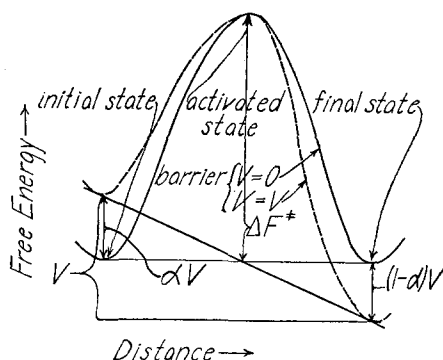


FIG. 1.

overvoltage: it has been shown, on the basis of these views, that α might reasonably have the value 0.5 as found experimentally.

ABSOLUTE REACTION RATE THEORY

Although it appears to be probable that a portion of stage (2) is the rate-determining step at most cathodes, some difficulty has been felt in accepting the suggestion that the addition of an electron to a hydrogen ion, or to a proton, requires an appreciable energy of activation. Since electrolysis may be considered as a rate process, the current strength being a measure of the velocity of reaction at a given overvoltage, it appeared possible that a further insight into the mechanism of electrode processes might be obtained by applying the theory of absolute reaction rates.⁸ According to this theory⁹ the specific rate k' of any reaction is given by the expression, assuming the transmission coefficient equal to unity,

$$k' = (kT/h)e^{-\Delta F^\ddagger/RT} \quad (5)$$

and for a *reversible* electrode the specific rate of the discharge process, i.e., of the direct reaction, may be written

$$k_1' = (kT/h)e^{-\Delta F_1^\ddagger/RT}, \quad (6)$$

while for the reverse reaction

$$k_2' = (kT/h)e^{-\Delta F_2^\ddagger/RT}, \quad (7)$$

where ΔF_1^\ddagger , as usual, is the standard free energy required to form the activated state from the reactants, i.e., the free energy of activation for the direct reaction, whereas ΔF_2^\ddagger is the corresponding free energy of activation for the reverse process. These equations satisfy the thermodynamic requirement that k_1'/k_2' is equal to the equilibrium constant K of the process, since $\Delta F_1^\ddagger - \Delta F_2^\ddagger$ represents the standard free energy increase ΔF of the whole reaction, and K is $e^{-\Delta F/RT}$. At the reversible potential at which (6) and (7) hold good, no current passes, but if an overvoltage V is applied, the rate of the direct reaction exceeds that of the reverse process and current flows at a definite rate. Without making any assumptions as to the mechanism of the discharge process, it may be supposed that the effect of the excess potential is to diminish the free energy increase requisite for the formation of the activated state from reactants, thus assisting the direct process, whereas the reverse process is retarded.¹⁰ If the additional potential V acts across the energy barrier between initial and final states, and α is the fraction of this electrical potential operative between the initial and activated states (Fig. 1), then the potential αV will facilitate the formation of the latter by decreasing the free energy by an amount αVF . At the same time the potential $(1-\alpha)V$ will oppose the reverse reaction, increasing the free energy required by $(1-\alpha)VF$. The specific reaction rates for direct and reverse reactions at the overvoltage V are then

$$k_1' = (kT/h)e^{-\Delta F_1^\ddagger/RT} \cdot e^{\alpha VF/RT}$$

and

$$k_2' = (kT/h)e^{-\Delta F_2^\ddagger/RT} \cdot e^{-(1-\alpha)VF/RT}. \quad (8)$$

$$\therefore k_1' = A_1 e^{\alpha VF/RT}, \quad k_2' = A_2 e^{-(1-\alpha)VF/RT}, \quad (9)$$

where A_1 and A_2 are constants. Since no assumption has been made concerning the nature of the reactants and resultants, their concentrations may be represented by C_1 and C_2 units, i.e., atoms, molecules or ions, per sq. cm, so that the direct and reverse reaction rates, in units per sq. cm, are

$$v_1 = A_1 C_1 e^{\alpha VF/RT} \quad \text{and} \quad v_2 = A_2 C_2 e^{-(1-\alpha)VF/RT}. \quad (10)$$

⁸ For reviews, see H. Eyring, Chem. Rev. 17, 65 (1935); Trans. Faraday Soc. 34, 41 (1938).

⁹ A different application of the theory, based on an assumed mechanism, is given by G. Okamoto, J. Horiuti and K. Hirota, Sci. Papers Inst. Phys. Chem. Res. Tokyo 29, 223 (1936).

¹⁰ F. P. Bowden, Proc. Roy. Soc. A126, 107 (1929); T. Erdey-Grúz and M. Volmer, reference 5; R. W. Gurney, reference 6; J. Horiuti and M. Polanyi, Acta Physicochim. U. R. S. S. 2, 505 (1935).

The current passing is determined by the difference between these rates, and if each reacting unit may be regarded as carrying the equivalent of a single charge, the current density I , in amp. per sq. cm, is given by

$$I = (v_1 - v_2)F/N \quad (11)$$

$$= (C_1A_1e^{\alpha VF/RT} - C_2A_2e^{-(1-\alpha)VF/RT})F/N, \quad (12)$$

where F is the faraday, i.e., 96,500 coulombs, and N is the Avogadro number. If V is small, that is for very low overvoltages, the exponentials may be expanded and all terms other than the linear one neglected: thus

$$I = [C_1A_1(1 + \alpha VF/RT) - C_2A_2\{1 - (1 - \alpha)VF/RT\}]F/N. \quad (13)$$

It will be seen from Eq. (10) that at the reversible potential, when V is zero, C_1A_1 is equal to C_2A_2 , and if this equality may be assumed to hold also for small values of V ,* then Eq. (13) becomes

$$I = (C_1A_1 \cdot VF/RT)F/N. \quad (14)$$

At low overvoltages, therefore, there should be a linear relationship between current and overvoltage: this has been found for the evolution of hydrogen and the deposition of metals.¹¹ For higher values of V , the rate of the reverse reaction becomes negligibly small in comparison with that of the discharge process, so that it is possible to write

$$I = (C_1A_1e^{\alpha VF/RT})F/N = I_0e^{\alpha VF/RT}. \quad (15)$$

I_0 , whose significance will be seen shortly, is equal to $C_1A_1 \cdot F/N$. This is identical with Eq. (4), and, as already seen, it applies at many cathodes, α having the value of 0.5. Since α is the fraction of the overvoltage effective between initial and activated states of the discharge process, it follows (see Fig. 1) that the fall of potential between the initial and activated states must be, at least approximately, one-half that across the

* According to the theory developed below C_1A_1 and C_2A_2 should be equal, irrespective of the magnitude of the overvoltage, for both hydrogen and oxygen evolution.

¹¹ J. A. V. Butler, *Trans. Faraday Soc.* **28**, 379 (1932); J. A. V. Butler and G. Armstrong, *J. Chem. Soc.* 743 (1934); M. Volmer and T. Erdey-Grúz, *Zeits. f. physik. Chemie* **159A**, 165 (1921); M. Volmer and H. Wick, *ibid.* **172A**, 429 (1935).

whole energy barrier;¹² in other words, the energy barrier at the electrode surface is almost symmetrical. This conclusion is of fundamental importance in deciding the nature of the essential electrode reaction.

NATURE OF REACTING SPECIES

The next matter to consider is the species involved in the electrode process, and some information on this point may be obtained by calculating the value of C_1 , the concentration of this substance. According to Eq. (12) the magnitude of the current passing in the forward direction, i.e., corresponding to the direct process, is

$$I(\text{forward}) = (C_1A_1e^{\alpha VF/RT})F/N \quad (16)$$

and at the reversible potential, when $V=0$, this becomes

$$I_0 = C_1A_1 \cdot F/N \quad (17)$$

$$= C_1(kT/h)e^{-\Delta F_1^\ddagger/RT} \cdot F/N. \quad (18)$$

Since ΔF^\ddagger may be replaced by $\Delta H^\ddagger - T\Delta S^\ddagger$, it follows that

$$I_0 = C_1(kT/h)F/N \cdot e^{\Delta S_1^\ddagger/R}e^{-\Delta H_1^\ddagger/RT} \quad (19)$$

$$= B \cdot e^{-\Delta H_1^\ddagger/RT}, \quad (20)$$

where B is equal to $C_1(kT/h)F/N \cdot e^{\Delta S_1^\ddagger/R}$: the quantities ΔS_1^\ddagger and ΔH_1^\ddagger are the entropy and heat of activation, respectively, of the direct electrode process. The value of I_0 may be determined by plotting $\ln I$, or $\log I$, against V , obtained experimentally for relatively high overvoltages and then extrapolating to $V=0$. The heat of activation ΔH_1^\ddagger can be derived from the temperature coefficient of overvoltage at constant current density, or from the temperature coefficient of current density at constant overvoltage, provided it is assumed that C_1 and ΔS_1^\ddagger are independent of temperature. From a knowledge of I_0 and ΔH_1^\ddagger it is possible to calculate B , by means of Eq. (20), and the results obtained from the available experimental data¹³ are recorded in Table I. Except for the results with platinum in sodium hydroxide, which are

¹² T. Erdey-Grúz and H. Wick, *Zeits. f. physik. Chemie* **162A**, 53 (1932).

¹³ F. P. Bowden and J. N. Agar, reference 1, p. 99.

TABLE I. *Hydrogen overvoltage at 25°.*

ELECTRODE	ELECTROLYTE	12 + LOG I_0	ΔH_1^\ddagger KCAL.	LOG B
Mercury	0.2N H_2SO_4	0.8	18.0	2.0
Mercury	0.2N NaOH	3.8	8.7	2.2
Gallium	0.2N H_2SO_4	5.2	15.2	2.5 (87°C)
Wood's alloy	0.2N H_2SO_4	4.0	16.4	2.0 (87°C)
Bright platinum	0.2N H_2SO_4	6.2	11.5	2.6
Bright platinum	0.2N H_2SO_4	6.8	9.5	1.7
Bright platinum	0.2N NaOH	5.0	7.0	2.1
Bright platinum	0.2N NaOH	6.3	6.0	2.7
Palladium	0.2N H_2SO_4	7.3	9.0	1.9
Palladium	0.2N NaOH	7.0	10.0	2.3

stated to be very dependent on the condition of the surface, and with mercury in the same electrolyte, where the low value of α , *viz.*, 0.24,¹³ indicates the presence of complicating factors, e.g., the discharge of sodium ions to form a dilute amalgam, the figures in the last column are virtually constant, and B , which involves C_1 and ΔS_1^\ddagger , is apparently independent of the nature of the electrode and electrolyte. This result suggests that the species whose concentration is represented by C_1 is *the same in all aqueous solutions and at all electrodes*, and the obvious conclusion to draw is that the substance is *water*. The provisional inference is, therefore, that the rate-determining step in the discharge of hydrogen ions involves a molecule of water. As a first approximation it may be assumed that a water molecule occupies 10^{-15} sq. cm: this is roughly the mean area of cross section of a single water molecule in pure water or of a metal atom of diameter 3A. The quantity C_1 would thus be about 10^{15} molecules per sq. cm, and since kT/h at 25° is about 6×10^{12} , F is 96,500 and N is 6×10^{23} , it follows that

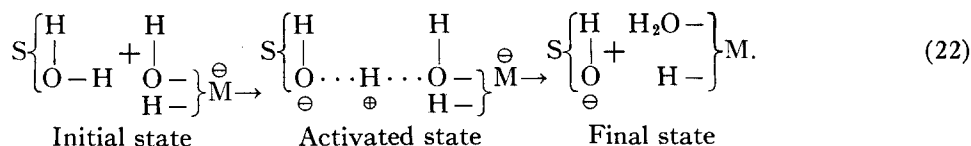
$$B = 9.6 \times 10^8 \cdot e^{\Delta S_1^\ddagger/R}. \quad (21)$$

MECHANISM OF CATHODE PROCESS

To determine whether the assumption that a molecule of water is involved in the rate-determining stage is in harmony with the experimental value of B it is necessary to assess ΔS_1^\ddagger , at least roughly, and this can only be done

if something is known of the nature of the initial and activated states. The next step, therefore, is to postulate a more detailed mechanism for the slow reaction at the cathode. It is suggested that in the absence of strongly adsorbed substances an electrode in aqueous solution becomes covered to a considerable extent by a unimolecular layer of water molecules, probably in the form of H and OH attached to atoms of the metal, which are at the same thermodynamic potential as and hence in equilibrium with the electrode itself. Adjacent to this layer there is another layer of water molecules attached to and at the same thermodynamic potential as the bulk of the electrolyte, and the excess potential V at the electrode may be regarded, as explained below, as operating entirely across these two layers of water molecules.* The slow stage in the discharge of a hydrogen ion is then believed to be the transfer of a proton from a molecule of water on the solution side to one attached to the electrode. The rate-determining step is thus a kind of prototropic change, and such processes are known to be associated with heats of activation of about 10 to 20 kcal.,¹⁴ and hence are of the same order as those found for the cathodic liberation of hydrogen. Even when the proton has to move through a distance of the order of a molecular diameter, or less, as would be the case in the suggested cathode process, the heat of activation is of a similar magnitude: this is proved by the stability at ordinary temperatures of the keto- and enol-forms of tautomeric compounds such as acetoacetic ester. It will be noted that according to the above postulate the overvoltage acts across two layers of water molecules and since it is probable that the activated state lies midway between them, the requirement that half the excess potential V operates between the initial and activated states is satisfied.

The slow prototropic process, which is the essential cause of overvoltage, may then be represented as follows:



* The layer attached to the solution may be somewhat diffuse, but for present purposes it can be regarded as being sharply defined without introducing any serious error.

¹⁴ See, for example, G. F. Smith, J. Chem. Soc., 1744 (1934); 1824 (1936); 1413 (1937).

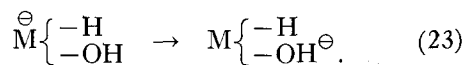
The symbol S refers to the solution and M to the electrode surface, the \ominus sign on M being used to indicate an electron which is believed to be available at the cathode.¹⁵ It is evident that the activated state consists virtually of H_3O^+ and OH^- , and so it appears that the entropy of activation ΔS_1^\ddagger will be very close to that accompanying the transfer of a proton from one water molecule to another, i.e., $\text{H}_2\text{O} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{OH}^-$, which represents the ionization of water in any aqueous solution. Taking $a_{\text{H}_3\text{O}^+} \cdot a_{\text{OH}^-}$ as 10^{-14} at 25° and $a_{\text{H}_2\text{O}}$ as 55 moles per liter, the equilibrium constant is found to be 3.3×10^{-18} ; since ΔH for the ionization of water is 13.6 kcal., it follows that $e^{\Delta S_1^\ddagger/R}$ is 3.3×10^{-8} . According to the above arguments, therefore, $e^{\Delta S_1^\ddagger/R}$, required for the calculation of B by Eq. (21) should have the same value, and hence $\log B$ is approximately 1.5, in satisfactory agreement with that found from overvoltage measurements (Table I). The suggestion that the slow process at a cathode involves the transfer of a proton from one molecule of water to another is thus consistent with the experimental facts.

In the derivation of Eq. (21) it has been assumed that the concentration of water molecules is 10^{15} per sq. cm; strictly speaking this applies to the layer attached to the solution, but the concentration on the electrode surface will probably be much the same. In other words the electrode is supposed to be completely covered with water molecules. If strictly true this conclusion would be contrary to the observations made by various authors¹⁶ on the quantity of electricity required to change a hydrogen electrode to an oxygen electrode, and vice versa: from these measurements it appears that the former is covered with a layer of hydrogen and the latter with a layer of oxygen atoms. It must be remembered that neither the calculations on

which this conclusion is based nor those in the present paper are accurate within a factor of at least two and it is not impossible that the electrode surface is covered to the extent of one-half, or of that order, by water molecules and the remainder by hydrogen or oxygen atoms.

RATE OF ATTAINMENT OF OVERVOLTAGE

The increase of cathode potential, from the reversible to the overvoltage value, at a constant current is a linear function of the quantity of electricity passed;¹⁷ this result implies that the attainment of overvoltage is equivalent to the charging of a condenser and is accompanied by the building up of an electrical double layer. The rate of the prototropic process at the cathode, which is $I_0 e^{\alpha \pi F/RT}$, can only approach that required by the current strength when the potential π is close to the overvoltage value V for the given current: if the potential is below this point another process must be responsible for the removal of electrons brought up to the cathode. It is suggested, therefore, that while the overvoltage is building up the cathodic reaction is exclusively



A water molecule exists on the surface as H and OH and the latter unites with an electron to form an OH^- ion on the electrode surface. Since (23) is the only cathodic process the number of these ions will be directly proportional to the quantity of electricity passed. If the OH^- ions in the electrode layer are balanced by an equal number of H_3O^+ ions in the solution layer, the double layer potential will increase with time in a linear manner, as found in practice. It is only when the potential approaches the overvoltage value that the velocity of process (22) becomes appreciable: the rate of growth of the potential due to (23) then falls off, and finally becomes zero at the steady overvoltage state when the prototropic process keeps pace with the current.*

¹⁷ F. P. Bowden and E. K. Rideal, *Proc. Roy. Soc.* **A120**, 59 (1928); E. Baars, *Sitzungsber. Ges. Beförd. Naturwiss., Marburg* **63**, 213 (1928); T. Erdey-Grúz and M. Volmer, reference 5; A. Hickling, private communication.

* It should be emphasized that the scheme proposed for the establishment of the double layer potential measured as overvoltage does not involve any assumptions or implications as to the origin of the reversible electrode potential.

¹⁵ The so-called "electrochemical mechanism" described by J. Horiuti and G. Okamoto (*Sci. Papers Inst. Phys. Chem. Res. Tokyo* **28**, 231 (1936); K. Hirota and J. Horiuti, *Bull. Chem. Soc. Japan* **13**, 228 (1938) has some features in common with the above scheme: the theory which attributes overvoltage to the slow rate of neutralization of H_2^+ cannot, however, be regarded as satisfactory.

¹⁶ F. P. Bowden, *Proc. Roy. Soc.* **A125**, 446 (1929); J. A. V. Butler and G. Armstrong, *ibid.* **A137**, 604 (1932); G. Armstrong, F. R. Himsworth and J. A. V. Butler, *ibid.* **A143**, 89 (1933); A. Frumkin and A. Šlygin, *Acta Physicochim. U. R. S. S.* **5**, 819 (1936); B. Ershler, *ibid.* **7**, 327 (1937).

INFLUENCE OF ELECTROLYTE

Unless the electrolyte is more alkaline than pH 12, the cathodic overvoltage is independent of the hydrogen ion concentration:¹⁸ this result is in agreement with the theory developed above. The number of water molecules per sq. cm of electrode surface will not differ appreciably in acid, neutral or alkaline media, and if ΔF_1^\ddagger for the activation process also remains unchanged, as is very probable, then it follows from Eq. (15) that the overvoltage, at constant current density, will not be dependent on the pH of the solution. This conclusion, however, may require some modification in certain circumstances, as will be seen below.

The effect of added electrolytes on overvoltage is not known with certainty, but it appears that when the zeta-potential at the interface between mercury and dilute sulfuric acid is made more positive, as a result of the adsorption of positive ions, the overvoltage is increased, whereas when the zeta-potential becomes more negative, that is when anions are taken up preferentially by the metal, the overvoltage is decreased.¹⁹ These facts can be readily explained if the change in the zeta-potential resulting from the addition of a salt can be attributed to the preferential adsorption of one ion in the layer attached to the electrode and the other by the layer associated with the solution. For example, if the positive ions are in excess in the electrode layer, the zeta-potential will become more positive: the presence of these excess positive charges will tend to oppose the passage of protons over the energy barrier and hence the activation energy will be in excess of the normal value. If it is supposed that the fraction β of the increase $\Delta\zeta$ of the zeta-potential operates between the initial and activated states, then Eq. (15) becomes

$$I = I_0 e^{(\alpha V_1 - \beta \Delta\zeta)F/RT}, \quad (24)$$

where V_1 is the new overvoltage. It follows,

therefore, that for the same current density

$$V_1 = V + (\beta/\alpha)\Delta\zeta, \quad (25)$$

where V is the overvoltage in the absence of the added salts. According to recent investigations¹⁹ β/α is 0.5 to 0.7 for a mercury cathode, assuming $\Delta\zeta$ to be equal to the change in the potential at the mercury-solution interface at the electrocapillary maximum. If the ions causing the zeta-potential are adsorbed in the two water layers, as has been suggested, then this potential should operate over the same region as the overvoltage, and β/α should be unity. In view of the assumptions made in assessing $\Delta\zeta$, the agreement is as good as could be expected.

The lowering of overvoltage sometimes observed²⁰ when the pH of the electrolyte exceeds 12 is probably to be attributed to an effect similar to that just described. The adsorption of the negatively charged hydroxyl ions into the water layer near the electrode will facilitate the passage of protons over the energy barrier and so the overvoltage is diminished.²¹ At a mercury cathode the overvoltage is apparently independent of the pH even in alkaline solutions:²² if this is the case then it must be assumed that there is no preferential adsorption of hydroxyl ions on mercury.

If the electrolyte contains substances which are strongly adsorbed on the electrode surface, e.g., catalytic poisons, such as arsenic compounds, or long chain acids and alcohols, the area available for the adsorption of water molecules will be greatly decreased. The points available for the acceptance of protons is thus less than would be the case if the solution did not contain adsorbable compounds, and hence it is probable that a higher overvoltage would be required for the same apparent current density. Materials which are adsorbed to a small extent only, e.g., ethyl alcohol, acetone and acetic acid, sometimes lower overvoltage²³ because of other factors mentioned below.

¹⁸ J. Tafel, reference (4); S. Glasstone, J. Chem. Soc. 125, 2414, 2646 (1924); F. P. Bowden, Trans. Faraday Soc. 24, 473 (1928); Proc. Roy. Soc. A126, 107 (1929); S. Lewina and V. Sarinsky, Acta Physicochim. U. R. S. S. 6, 491 (1937); 7, 485 (1937); C. Wagner and W. Traud, Zeits. f. Elektrochemie 44, 391 (1938).

¹⁹ S. Jofa *et al.* Acta Physicochim. U. R. S. S. 10, 317 (1939).

²⁰ S. Glasstone, reference 16, p. 2414.

²¹ The work of A. Frumkin *et al.*, Acta Physicochim. U. R. S. S. 3, 791 (1935); 4, 911 (1936) suggests that the adsorptive properties of a platinum-electrode surface are different in acid and alkaline solutions.

²² S. Glasstone, reference 16, p. 2646.

²³ S. Glasstone, Trans. Faraday Soc. 21, 36 (1925).

INFLUENCE OF ELECTRODE MATERIAL

If the value of I_0 given by Eq. (19) is introduced into (15) it is seen that

$$I = C_1(kT/h)F/N \cdot e^{\Delta S_1^\ddagger/R} e^{-\Delta H_1^\ddagger/RT} e^{\alpha VF/RT}. \quad (26)$$

In the absence of strongly adsorbed substances, it appears that the different overvoltages of various metals must be attributed to differences in ΔH_1^\ddagger , the heat of activation of the rate-determining process: the higher the value of ΔH_1^\ddagger the greater the overvoltage. If the metal is one that adsorbs hydrogen readily, that is it forms strong $M-H$ bonds, then the oxygen atom of a water molecule held on such a surface will have increased affinity for the formation of a bond with hydrogen: the attachment of a proton to such an oxygen atom will, therefore, be facilitated and the heat of activation of the prototropic change responsible for overvoltage will be relatively low. This conclusion will be apparent from a consideration of the potential energy curves for the initial and final states of the rate-determining process (Fig. 2).²⁴ If the metal attracts the water molecule by forming strong $M-H$ bonds, thus increasing the attraction of the proton, curve *A* will be less steep and ΔH_1^\ddagger will be diminished. Further, if the electrode material adsorbs atomic hydrogen readily, the position of curve *B* will be lowered, and this will also have the effect of decreasing ΔH_1^\ddagger and hence the overvoltage. Metals, such as platinum, palladium, copper, nickel, iron and silver, which adsorb hydrogen strongly should thus have low overvoltages, in agreement with experiment: these substances are as may be expected, good catalysts for the $2H \rightarrow H_2$ reaction,²⁵ but this is not to be taken as evidence for the view that atomic hydrogen is responsible for overvoltage, as was at one time suggested. The elements mercury, lead, zinc, tin and cadmium form only feeble $M-H$ bonds, and hence these metals have high overvoltages. They should be poor catalysts for the recombination of atomic hydrogen and this has been verified for lead.²⁵

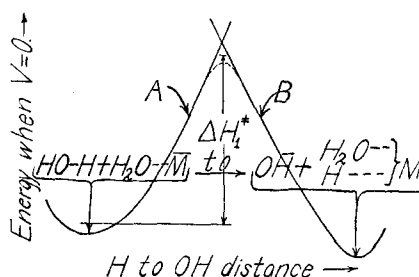


FIG. 2.

The constancy of the quantity *B* in Table I, and the prototropic theory of overvoltage, imply that the concentration of water molecules per *apparent* sq. cm of electrode surface is approximately constant: this can only be true if the surface is relatively smooth and the apparent and real areas are not very different. If the electrode surface is roughened, however, the quantity C_1 will be increased and as a consequence the overvoltage at an *apparent* constant current density will decrease. It is well known that roughening an electrode surface decreases the overvoltage, but it is possible that other factors besides mere increase of surface are responsible. The number of active adsorption centers probably increases more rapidly than does the actual surface area and, further, specially active centers may be developed: this is probably true for platinized platinum electrodes.

ALTERNATIVE ELECTRODE PROCESSES

The model proposed here does not, of course, exclude the possibility that in certain circumstances other steps in the discharge process may become rate-determining: for example, on some electrodes the combination of atomic hydrogen to form molecules may be the slowest process. Since α is very close to 0.5 at electrodes of mercury, gallium, silver, nickel, etc., it is unlikely that the recombination reaction is the cause of overvoltage in these cases, but when α is large, for example at platinum, copper and palladium,²⁶ under certain conditions, where values of 0.8 and more have been observed, it is possible that this process is of importance in determining the

²⁴ Cf. J. Horiuti and M. Polanyi, *Acta Physicochim. U. R. S. S.* **2**, 505 (1935); J. Horiuti and G. Okamoto, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, **28**, 231 (1936); J. A. V. Butler, *Proc. Roy. Soc. A157*, 423 (1936); *Zeits. f. Elektrochemie* **44**, 55 (1938).

²⁵ K. F. Bonhoeffer, *Zeits. f. physik. Chemie* **113**, 199 (1924).

²⁶ C. A. Knorr and E. Schwartz, *Zeits. f. Elektrochemie* **40**, 38 (1934); *Zeits. f. physik. Chemie* **176A**, 161 (1936); M. Volmer and H. Wick, *ibid.* **172A**, 429 (1935); K. Wirtz, *ibid.* **36B**, 435 (1937).

current strength at a given overvoltage. When the electrode forms very strong $M-H$ bonds the heat of activation of the prototropic process may become so low that the reaction $2H \rightarrow H_2$ becomes the rate-determining step. According to Tafel's calculations (p. 1054) α should then become equal to 2, and values of α between 2 and 0.5 are presumably due to the fact that the combination of atoms and the prototropic change have velocities of the same order, and hence both are effective in determining the rate of discharge of hydrogen ions. As the overvoltage is raised the rate of atom combination increases as the exponential of twice the overvoltage, and that of the prototropic reaction as the exponential of half the overvoltage; the former process will thus become very rapid as compared with the latter. It is evident, therefore, that the combination of atomic hydrogen can only be rate-determining, and hence the ultimate cause of overvoltage, when the latter is small.²⁷

In the derivation of Eq. (4), with $\alpha=2$, it was assumed that the electrode surface was sparsely covered with atomic hydrogen so that the combination process is kinetically of the second order; if the surface becomes completely covered the reaction should become of zero order, and α should, apparently, decrease from 2 to 0.²⁸ This would only be true, however, if the concentration of atomic hydrogen was always a measure of its activity (see note, p. 1054), but this is certainly not the case. It is probable that as the surface becomes more fully covered and the apparent order of the combination of atomic hydrogen decreases, the activity coefficient increases, with the result that α would not diminish to zero. There is in fact reason for believing that α could not fall below 2 if the process $2H \rightarrow H_2$ were wholly responsible for overvoltage: from the viewpoint of energy barriers, the factor $e^{2VF/RT}$ in Eq. (4) arises because each of the two hydrogen atoms acquires additional energy $e^{VF/RT}$ when the ion becomes discharged by passing over the barrier across which the overvoltage V operates. If this is the case it is evident that provided H_2 molecules are formed, α should be 2, and it should not fall below this value unless some

reaction other than $2H \rightarrow H_2$ is responsible for the overvoltage.

It may be remarked that according to the prototropic mechanism of overvoltage α is only 0.5 if the energy barrier is approximately symmetrical and the potential fall is uniform.¹² If for any reason there is distortion, then α may fall to zero if the activated state is pushed out towards the solution, or increase to unity if it approaches the electrode more closely.

MINIMUM OVERVOLTAGE, SURFACE TENSION EFFECTS, ETC.

Various workers have found a connection between overvoltage and bubble formation: MacInnes and Adler,²⁹ for example, showed that the potential at a platinized platinum cathode fluctuated during the formation and liberation of a bubble of gas. These phenomena, as the aforementioned authors suggested, are undoubtedly due to supersaturation effects, and probably do not represent true, i.e., activation, overvoltage changes because the reversible potential of the hydrogen alters in a corresponding manner. Such changes of the reversible electrode potential are readily understandable but are outside the scope of the treatment by the theory of absolute reaction rates and are excluded from the present discussion by the definition of overvoltage given on p. 1053. It may be observed that the so-called "minimum overvoltage," which is the difference between the reversible potential for gas at 1 atmos. pressure and the measured cathode potential when hydrogen bubbles commence to be evolved, may not be a true overvoltage, since the concentration of gas in the vicinity of the cathode under these conditions probably exceeds the normal saturation value. Nevertheless, provided the surface forces at the electrode are not changed appreciably the extent of supersaturation requisite for steady bubble formation represents a fairly definite condition, irrespective of external influences, and so the measured minimum overvoltage is a constant for a given electrode under a variety of conditions.³⁰ Alterations in the electrode or electrolyte which influence the degree of

²⁷ L. P. Hammett, *Trans. Faraday Soc.* **29**, 770 (1933).

²⁸ Cf. G. Okamoto, J. Horiuti and K. Hirota, *Sci. Papers Inst. Phys. Chem. Res. Tokyo* **29**, 223 (1936); see also F. P. Bowden and J. N. Agar, reference 1, p. 104.

²⁹ D. A. MacInnes and L. Adler, *J. Am. Chem. Soc.* **41**, 194 (1919).

³⁰ See S. Glasstone and G. D. Reynolds, *Trans. Faraday Soc.* **28**, 582 (1932).

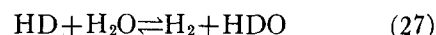
supersaturation, e.g., the presence of substances which influence interfacial tensions, will alter the observed "minimum overvoltage" to some extent, but the true overvoltage may remain unchanged unless, as is not improbable, there are corresponding appreciable changes in the quantities C_1 , ΔH_1^\ddagger or ζ . There does not appear to be any means, however, of distinguishing between true and apparent overvoltage changes under these conditions.

SEPARATION OF HYDROGEN AND DEUTERIUM

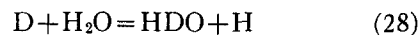
The electrolytic separation of hydrogen and deuterium is attributed to the difference in overvoltage for the deposition of the two isotopic forms, and the expected larger value for deuterium has been confirmed experimentally. It is necessary to demonstrate, therefore, that the higher overvoltage for deuterium is consistent with the theory developed above. The free energy of ionization of deuterium oxide, i.e., $D_2O + D_2O = D_3O^+ + OD^-$, calculated from the known ionic product, is about 1000 cal. greater than for ordinary water, and hence it may be supposed that the free activation energies for the transfer of a deuteron and a proton at a cathode differ by a similar amount. Utilizing the method described on p. 1058, and making the same assumptions it is found that ΔS_1^\ddagger is almost identical for proton and deuteron transfer, and hence it follows that the heat of activation for the deuterotropic change must be approximately 1000 cal. greater than for the cathodic prototropic change. Assuming the difference to be actually 1200 cal., it can be readily calculated that the specific rate of the discharge process involving hydrogen is 7.4 times as great as that for deuterium: this is of the correct order to account for the observed separation coefficients. From the limited data available it appears that ΔH_1^\ddagger for hydrogen evolution from 0.2 *N*-sulfuric acid at a mercury cathode is 18.0 kcal., whereas for deuterium discharge it is 20.9 kcal.¹³ If ΔS_1^\ddagger for the cathodic process is the same for the transfer of a proton and a deuteron, as the approximate calculations suggest, then the difference is larger than expected. From the value of ΔH_1^\ddagger for deuterium $\log B$ is found to be 3.24, which is higher than those in Table I: if the heat of activation for deuterium evolution is

assumed to be 19.2 kcal., however, i.e., 1200 cal. larger than for hydrogen, $\log B$ is calculated as almost exactly 2.0. A difference of 1200 cal., rather than 2900 cal., in the heats of activation would thus be consistent with the mechanism of hydrogen discharge proposed in this paper and the subject merits further experimental investigation. If the zero-point energies of the activated states do not differ greatly, the difference in the heats of activation for deuterotropic and prototropic reactions should be equal to the difference in the zero-point energies of the D—O and H—O bonds, i.e., about 1400 cal.: This is also in harmony with the arguments given above.

It is of interest that the hydrogen-deuterium separation factors obtained with different metals fall roughly into the same two groups as do overvoltages themselves: at low overvoltage metals, e.g., platinum, nickel and silver, the separation coefficient is about 6, whereas at high overvoltage electrodes, e.g., lead (in acid solution), mercury and tin, the value is in the vicinity of 3.³¹ The latter figure is very close to that expected if the equilibrium



were established at the cathode,³² and this is presumably what happens on high overvoltage metals. It has been seen that elements of this type form only weak M—H bonds, so that the hydrogen and deuterium atoms on the surface, liberated by electrolysis, have a high energy content and hence are reactive.* It is probable, therefore, that the surface reaction



requiring a heat of activation of about 12 kcal.,³³ which will lead to the establishment of equilibrium conditions, takes place rapidly on a high overvoltage electrode. In order that complete equilibrium may be established it is necessary that the HDO molecule, which is presumably

³¹ B. Topley and H. Eyring, *J. Chem. Phys.* **2**, 217 (1934); J. Horiuti and G. Okamoto, reference 24; H. F. Walton and J. H. Wolfenden, *Trans. Faraday Soc.* **34**, 436 (1938).

³² See A. Farkas and L. Farkas, *J. Chem. Phys.* **2**, 468 (1934); *Proc. Roy. Soc. A* **146**, 623 (1934).

* The marked reduction efficiencies, e.g., of organic compounds, observed at high overvoltage cathodes can be accounted for in this manner.

³³ See K. H. Geib, *Zeits. f. Elektrochemie* **44**, 83 (1938) for summary of data.

attached to the electrode as OH and D (or OD and H), should be able to leave the surface readily and exchange with H₂O molecules: this will occur if the bonds holding the OH (or OD) and D (or H) to the surface are weak in comparison with the O—D (or O—H) bond. It is just at high overvoltage electrodes, where the strength of the M—H bond is small, that this condition is satisfied. At low overvoltage cathodes the activity of the hydrogen will be small and there will be little tendency for the equilibrium (27) to be attained.

Increase of temperature will not only increase the specific rate of reaction (28) but it will also speed up the recombination of hydrogen atoms on the surface and hence decrease their concentration. If the heats of activation of the two processes are such that the first reaction is favored more than the second when the temperature is raised, then there will be a closer approach to equilibrium and the separation factor will decrease: this is the case at platinum, nickel and silver cathodes. On the other hand, if increase of temperature favors the atom recombination process, so that there is a marked decrease in the concentration of atomic deuterium on the surface, the equilibrium state will be less readily attained and the separation factor may rise: a result of this type has been observed with a tin cathode.³⁴

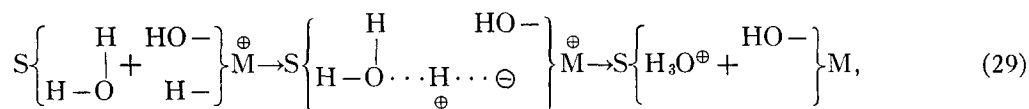
At a platinized platinum cathode the separation factor is about 3, in spite of the low overvoltage: at this electrode, however, departure from equilibrium can never be very appreciable, for on a platinized surface water reacts relatively rapidly even with molecular deuterium, or HD,³⁵ and so the separation factor is never likely to

differ to any great extent from the theoretical value.

Although the hydrogen-deuterium separation coefficient is generally independent of the hydrogen ion concentration of the electrolyte, at a lead electrode it is as high as 6 in an alkaline solution as compared with 3 in acid solution: it may be significant that the overvoltage of lead is definitely less in media of high pH than in acid solution,¹⁹ and cathodic reduction is generally more efficient in an acid electrolyte. The presence of excess of hydroxyl ions, however, also produces other changes in the conditions at an electrode surface.³⁶

OXYGEN OVERTVOLTAGE

Interaction between the evolved oxygen and the electrode material leads to complications in the study of anodic phenomena, but in spite of the difficulties it has become evident that there is a fundamental similarity between the processes occurring at anode and cathode. The kinetics of the deposition of oxygen bears a marked resemblance to that for hydrogen evolution,³⁷ and both in acid and dilute alkaline solutions the variation of oxygen overvoltage with current density at a platinum anode is given by Eq. (15), with α having a value of approximately 0.5, as for hydrogen ion discharge.^{37, 38} These results are in agreement with the suggestion that the rate-determining process for oxygen evolution is a prototropic change, similar to that postulated for hydrogen evolution but in the opposite direction. A proton from a water molecule attached to the surface is transferred to one in the layer associated with the electrolyte: thus



the sign \oplus on M representing the deficit of an electron. The hydroxyl radicals formed on the surface react in pairs with the ultimate formation of molecular oxygen, the intermediate stage, or

stages, being relatively rapid. The connection between oxygen and hydrogen overvoltage is at once evident, and the fact that α in Eq. (15) is

³⁴ H. F. Walton and J. H. Wolfenden, reference 31.

³⁵ J. Horiuti and M. Polanyi, *Nature* **132**, 819 (1933); **133**, 142 (1934); K. F. Bonhoeffer and K. W. Rummel, *Naturwiss.* **22**, 45 (1934); A. Farkas and L. Farkas, *Trans. Faraday Soc.* **33**, 678 (1937).

³⁶ Cf. A. Šlygin and A. Frumkin, *Acta Physicochim. U. R. S. S.* **3**, 791 (1935); A. Šlygin, A. Frumkin and W. Medwedowsky, *ibid.* **4**, 911 (1936).

³⁷ F. P. Bowden, *Proc. Roy. Soc. A* **126**, 107 (1929).

³⁸ F. P. Bowden and H. W. Keenan, see F. P. Bowden and J. N. Agar, reference 1, p. 102.

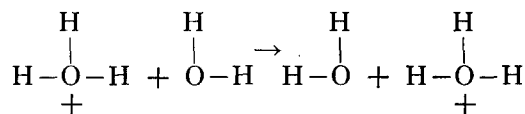
about 0.5 in both cases is readily understood. If this mechanism for the slow process in oxygen evolution is correct, the value of $\log B$ should not be of a very different order from those in Table I. The only experimental data which permit the calculation to be made are those for a platinum anode in dilute sulfuric acid solution;³⁷ $12 + \log I_0$ is 1.57, and ΔH_1^\ddagger is 18.7 kcal. at 14°C, and so $\log B$ is 3.83. This value is somewhat larger than for hydrogen evolution, but in view of the uncertainties associated with the nature of the anode, the agreement is reasonably good.

If there were no formation of surface oxides it would be expected that metals forming strong M-H bonds should have high overvoltages, since the attraction would tend to hinder the removal of a proton from the surface. It is true that smooth platinum, palladium and gold, which have the lowest hydrogen overvoltages, have the highest overvoltages for oxygen evolution,³⁹ but the parallelism does not always hold. Nickel and cobalt, for example, have low overvoltages both at the anode and the cathode: the oxidation of the surface is undoubtedly a complicating factor.

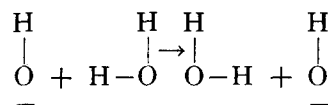
GENERAL REMARKS.—INFLUENCE OF MEDIUM

One of the difficulties of the older theories of overvoltage is that they fail to explain why appreciable overvoltages are only observed when hydrogen and oxygen are evolved in electrolysis, whereas very little overvoltage accompanies the evolution of chlorine gas.⁴⁰ It appears, therefore, that a chlorine ion requires only a small heat of activation in order to pass through the two layers of water molecules at the surface of the anode. The question arises, at this point, why the discharge of hydrogen and hydroxyl ions requires a high energy of activation whereas that for chlorine, or other halogen or metal, ion discharge is small. The answer suggested is that as a consequence of the continuous interchange of protons in aqueous solution the hydrogen and hydroxyl ions are not individual entities which remain unchanged once they are formed by the addition of acid or alkali to the water. Inter-

changes of the type



and



are taking place continuously in all directions, with the result that the H_3O^+ and OH^- ions must be regarded as part of the structure of the solvent water. Since the ions are so comfortably built into the structure of the bulk of the solution, it is evident that the direct passage of either an H_3O^+ or OH^- ion through the terminal layer of water molecules is likely to require a considerable rise in free energy, i.e., a higher free energy of activation is necessary. The transfer of a proton from one water molecule to another, as described in this paper, presumably requires a smaller heat of activation and so provides an alternative mechanism for bringing hydrogen or hydroxyl ions to the appropriate electrode for discharge.

The discharge of hydrogen ions in a non-aqueous solution will presumably depend on a prototropic change analogous to that suggested for aqueous solutions, but there are many factors which make it difficult to predict the relative overvoltages in different media. In alcoholic solutions both the molecule $\text{R}\cdot\text{OH}$ and the ion $\text{R}\cdot\text{OH}_2^+$ are less firmly bound to the bulk of solvent than are H_2O and H_3O^+ , respectively, in water, because the replacement of H by R serves partially to break up the continuous structure. It is to be expected, therefore, that the transfer of a proton from a molecule of alcohol on the layer attached to the solvent to one on the electrode will require a smaller energy of activation than the corresponding process involving water molecules: further, there is a possibility, which apparently does not arise in aqueous solution, that a proton may be transferred from a $\text{R}\cdot\text{OH}_2^+$ ion on the solution side to an alcohol molecule on the cathode. In any case it would appear that the activation energy, and hence presumably the overvoltage, may be expected to be lower in alcoholic media than in

³⁹ A. Coehn and Y. Osaka, *Zeits. f. anorg. Chemie* **34**, 86 (1903).

⁴⁰ F. Chang and H. Wick, *Zeits. f. physik. Chemie* **A172**, 448 (1935).

aqueous electrolytes: this is so at various cathodes in methyl and ethyl alcohols.⁴¹ It would appear, at first sight, that overvoltage should be low when acetic acid is the solvent, for the ion $\text{CH}_3\cdot\text{COOH}_2^+$ would not be part of the structure of the medium: The situation is here complicated by the fact that most of the acetic acid exists in the associated form $(\text{CH}_3\cdot\text{COOH})_2$, and if single molecules only can take part in the prototropic change, overvoltages will be high. The very limited data suggest that the values are higher in acetic acid than in water.⁴²

The addition of moderate amounts of methyl or ethyl alcohols, acetic acid or acetone to an aqueous solution lowers the overvoltage.²³ These substances have a depolymerizing effect on the

solvent, tending to break up the continuous structure of the water,⁴³ and so the prototropic change at the boundary may well require a smaller energy of activation than in pure water. Small amounts of long chain alcohols and acids lower the overvoltage at a lead cathode, probably for the same reason, but larger amounts raise the value because of preferential adsorption on the surface.²³ It is probable that the addition of various organic compounds to an aqueous solution alters the zeta-potential: this, as already seen, might be expected to affect the overvoltage. Further, changes in the interfacial tensions may result in changes in the apparent overvoltage, as previously described.

The authors wish to express their thanks to Professor Hugh S. Taylor for helpful discussions.

⁴¹ G. Carrara, *Zeits. f. physik. Chemie* **69**, 75 (1909); S. Lewina and M. Silberfarb, *Acta Physicochim. U. R. S. S.* **4**, 275 (1936).

⁴² S. Swann and E. O. Edelman, *Trans. Electrochem. Soc.* **58**, 179 (1930).

⁴³ See D. G. Beech and S. Glasstone, *J. Chem. Soc.* **67** (1938).