QUARTERLY REVIEWS

THE MECHANISM OF ELECTRODE PROCESSES IN AQUEOUS SOLUTIONS.

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I. Introduction

THE electrolysis of aqueous solutions may involve a wide range of electrode reactions and consequent variation in the products of electrolysis. Thus at an anode there may occur evolution of oxygen from the discharge of the hydroxyl ion, discharge of other anions to give specific products, dissolution of the anode material to give metallic ions, and electrolytic oxidation of ions or un-ionised substances in the solution. Similarly at a cathode there may occur evolution of hydrogen from the discharge of the hydrogen ion, deposition of metals from the discharge of metallic ions, and electrolytic reduction of ions or un-ionised substances in the solution. A satisfactory general theory of electrolysis should make it possible to predict what will be the nature and current efficiencies of the electrode reactions in any particular set of experimental conditions. So far as any such general theory has yet been approached, it suggests, from simple energy considerations, that the anodic process requiring the least positive potential and the cathodic process requiring the least negative potential will normally take place. Since, however, the potential at which an electrode process occurs may depend very largely on its mechanism and be quite different from the calculated thermodynamic value, a complete understanding of the mechanism of the possible electrode reactions is a necessary preliminary to the application of any such general theory of electrolysis.

In this Review, therefore, attention will be primarily directed to the present state of our knowledge of the mechanism of the reactions occurring at working electrodes,* *i.e.*, electrodes at which current is passing and electrolysis is continuously occurring. In contrast to the behaviour of reversible electrodes in equilibrium with ions in solution, which is relatively simple and amenable to general quantitative treatment by thermodynamic methods, working electrodes exhibit highly complex specific phenomena, and the elucidation of the mechanism of any particular anodic or cathodic process

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* The reactions occurring at the dropping-mercury electrode in polarography constitute a particular specific field and will not be included here.

constitutes a formidable physicochemical problem. The main features which a complete understanding of the mechanism should explain are:

(*a*) The potential at which the process occurs at a given rate and its dependence on experimental conditions; this aspect embraces the whole field of the kinetics of electrode reactions, polarisation, and overpotential.

(*b*) The current efficiency of the process and how it is affected by experimental variables; this is of interest where alternative electrode reactions are possible and is particularly important in technical applications of electrolysis.

(*c*) The specific phenomena associated with the anodic dissolution and cathodic deposition of metals, such as anodic passivity and the physical properties and structure of electrodeposited metals.

Although these aspects of electrode phenomena have been the subject of continual investigation over the past 50 years, since the pioneer work of Le Blanc and Caspari, and a wealth of empirical data has been accumulated, it cannot be claimed that any very satisfactory or complete theoretical interpretation has yet been achieved, and there exists a diversity of ideas which still await a general synthesis.

II. Experimental Methods

Voltammetric Methods.—The classical method of investigating reactions at working electrodes involves the determination of the current density (c.d.)–potential relations under various experimental conditions, and their correlation with the processes taking place as ascertained by chemical analysis. In general, the current passing through the electrolytic cell is raised in stages by the application of an increasing e.m.f., and the potential of the electrode under investigation at each c.d. is measured against a standard reference electrode in the solution. Where a stationary state is rapidly reached at the electrode, the instantaneous c.d.–potential curves are usually reproducible and provide a variety of information. For instance, the potential at which any particular process begins is indicated by a sudden increase in the current passing, and the rates of the reaction per unit area of the electrode surface at different potentials are measured by the corresponding c.d.s; furthermore, if there exists a limiting rate at which the reaction can occur, this is indicated by the presence of a limiting c.d. and a characteristic step in the curve. By making observations at different temperatures, the dependence of the rate of reaction on temperature, as indicated by the variation of c.d. at a fixed potential, can be found and the energy of activation of the reaction deduced. Similarly, the influence of concentration of electrolyte, pH value, solvent, etc., on the rate of the electrode reaction can be investigated. The nature and current efficiency of the process occurring in any particular section of the c.d.–potential graph may be ascertained by carrying out electrolyses at appropriate fixed c.d.s and determining the products formed.

Where a stationary state at the electrode is not rapidly achieved, and the potential of the electrode varies with time at constant c.d., the position is rather more complicated. In this case, starting with the electrode in a reproducible virgin state, it may be polarised at constant c.d. and the variation of potential with time observed ; by carrying out a series of experiments of this type at different c.d.s, a c.d.–potential graph may then be constructed the potentials being taken either when the electrode has reached a steady state on prolonged polarisation or after comparable periods of polarisation. Alternatively, it may often be of interest to study the variation of the rate of an electrode reaction with time by following the variation in c.d. at a fixed potential. The exploration of c.d.–potential relations and the identification of the reactions occurring at particular potentials have been greatly simplified in recent years by the introduction of instruments with the aid of which the potential of a working electrode may be fixed at any arbitrary value, the current being automatically adjusted to maintain this potential. Thus Hickling [1] has described an electronic device of this type, termed a potentiostat, which is suitable for use with small currents and is specially adapted to the rapid determination of c.d.–potential curves and the direct observation of the rate of an electrode reaction at fixed potential under various experimental conditions, and J. J. Lingane and others [2] have described mechanical potentiostats suitable for large currents which are particularly useful in carrying out electrolyses at fixed potentials and determining the products formed.

Rate of Growth of Polarisation Potentials.—The data given by the methods discussed above refer to a working electrode when a steady state has been attained or approached, and it is apparent that valuable additional information should be provided by the study of the variation of potential with the quantity of electricity passed in the earliest stage of polarisation, *i.e.*, immediately following the completion of the electrical circuit and before any products of electrolysis have left the electrode. Two main methods have been developed suitable for high and for low c.d.s, respectively.

In work at high c.d.s, the electrode in a reproducible virgin state is polarised at constant c.d., and the very rapid variation of the potential with time is followed oscillographically. Pioneer experiments in this field, which met with only limited success, were made by Le Blanc and Reichinstein about 1910,[3] but it is only in the last 20 years that valuable results have been achieved. In the early successful experiments [4] of Bowden and Rideal and of Baars, the voltage developed between the working and the reference electrode was applied, preferably after amplification, to some form of string galvanometer, the movement of which was photographed on a film moving at constant speed. After suitable calibration, measurement of the track produced permitted construction of a graph of potential against quantity of electricity passed. Many later workers have used a similar

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[1] *Trans. Faraday Soc.*, 1942, **38**, 27.

[2] *Ind. Eng. Chem. Anal.*, 1945, **17**, 332 ; Faraday Soc. Discussion, 1947, **1**, 203 ; C. W. Caldwell, R. C. Parker, and H. Diehl, *Ind. Eng. Chem. Anal.*, 1944, **16**, 532.

[3] M. Le Blanc, *Abh. Bunsen Ges.*, 1910, No. 3 ; D. Reichinstein, *Z. Elektrochem.*, 1909, **15**, 734, 913 ; 1910, **16**, 916.

[4] F. P. Bowden and E. K. Rideal, *Proc. Roy. Soc.*, 1928, *A*, **120**, 59 ; E. Baars, *Sitzungsber. Ges. Beförd. Naturw. Marburg*, 1928, **63**, 213 ; see also H. D. Holler, *Bur. Stand. Sci. Papers*, 1925, **20**, 153.

technique,[5] but there has been a general tendency in recent years to avoid the difficulties attendant on the inertia of any mechanical oscillograph by using the cathode-ray tube as the indicating instrument.[6] A further development [7] avoids the inherent difficulties of single sweep oscillographic methods, in the observation and recording of high-speed transients, by the use of a repetitive method which gives a stationary picture on the oscillograph screen showing directly the variation of potential with quantity of electricity passed.

At very low c.d.s, the change of potential with time occurs relatively slowly and can be followed over a period of seconds or minutes by taking successive readings from a suitable form of electrometer. This method thus has the advantage of simplicity. It was first used in the investigation of the anodic polarisation of silver,[8] and has subsequently been employed by many workers.[9] The main difficulty encountered arises from the great effect of small amounts of depolarisers in the solution and the danger of loss of electrolytic products from the electrode surface. To minimise this, special types of cell have been devised in which only a very small volume of electrolyte is in contact with the electrode,[10] and in recent work [11] on the cathodic polarisation of mercury at very low c.d.s the interesting device has been used of completely isolating the cathode and catholyte in a sealed glass vessel, contact being made with the anolyte and reference electrode through the glass walls.

These charging-curve methods have so far been mainly employed in the investigation of the processes occuring before the cathodic evolution of hydrogen and the anodic evolution of oxygen. Where a linear relation between potential and quantity of electricity passed is found, the process is generally identified as the charging of a double layer, and from the slope of the graph the capacity can be simply obtained since $C = \delta q/\delta V$, where C is the capacity in microfarads, q the quantity of electricity in microcoulombs, and V the voltage developed in volts. Where discharge of ions occurs to give adsorbed products or compounds with the electrode material, this is indicated by a step in the charging curve from which the potential range over which the reaction takes place and the quantity of electricity

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[5] H. Brandes, *Z. physikal. Chem.*, 1929, **142**, 97 ; T. Erdey-Grúz and M. Volmer, *ibid.*, 1930, **150**, 213 ; T. Erdey-Grúz and G. G. Kromrey, *ibid.*, 1931, **157**, 213 ; W. J. Shutt and V. J. Stirrup, *Trans. Faraday Soc.*, 1930, **26**, 635 ; W. J. Shutt and A. Walton, *ibid.*, 1932, **28**, 740.

[6] J. A. V. Butler and J. D. Pearson, *ibid.*, 1938, **34**, 806, 1163 ; J. A. V. Butler and I. M. Barclay, *ibid.*, 1940, **36**, 128.

[7] A. Hickling, *ibid.*, p. 364 ; 1945, **41**, 333.

[8] R. Luther and F. Pokorny, *Z. anorg. Chem.*, 1908, **57**, 290.

[9] J. A. V. Butler and G. Armstrong, *Proc. Roy. Soc.*, 1932, *A*, **137**, 604 ; G. Armstrong, F. R. Himsworth, and J. A. V. Butler, *ibid.*, 1933, *A*, **143**, 89 ; J. A. V. Butler and G. Drever, *Trans. Faraday Soc.*, 1936, **32**, 427 ; A. Slygin and A. Frumkin, *Acta Physicochim. U.R.S.S.*, 1935, **3**, 791 ; 1936, **4**, 911 ; 1936, **5**, 819 ; B. Ershler and M. Proskurnin, *ibid.*, 1937, **6**, 195 ; B. Ershler, *ibid.*, 1937, **7**, 327 ; B. Ershler and G. Deborin, *ibid.*, 1940, **13**, 347 ; B. Ershler, Faraday Soc. Discussion, 1947, **1**, 269.

[10] B. Ershler, G. Deborin, and A. Frumkin, *Trans. Faraday Soc.*, 1939, **35**, 464.

[11] F. P. Bowden and K. E. W. Grew, Faraday Soc. Discussion, 1947, **1**, 86, 91.

involved in it can be measured. Hence the number of atoms of hydrogen or oxygen participating in the process can be found, and if the number of metal atoms in unit area of the electrode surface is known, the nature and thickness of the film formed can be precisely worked out. The method has already proved very valuable, since the information given is of a very direct and unequivocal nature, and it seems likely to be of wide application to other electrode reactions. The main difficulty in the interpretation of the data provided is at present the determination of the number of metal atoms in unit area of the electrode surface ; this involves a knowledge of the ratio of the real to the apparent area of the electrode surface, about which there is considerable uncertainty. A measure of this ratio can be obtained by Bowden and Rideal's method,[12] in which the cathodic capacity of the electrode in acid solution is measured and compared with that of mercury for which the ratio is taken to be unity, but an alternative method for checking these figures would be very useful.

Rate of Decay of Polarisation Potentials.—The study of the decrease of the potential of a working electrode with time after interruption of the polarising current has attracted considerable attention largely from the point of view of separating the various factors contributing to overpotential. Early workers [13] made use of commutator methods in which the polarising current was mechanically interrupted for varying times, and the potential measured in these intervals. Later workers [14] have generally employed mechanical or cathode-ray oscillographs for following the decay process, the general technique being similar to that involved in the study of charging curves. A method has also been described[15] in which an electronic interrupter is used in combination with a special type of potentiometer ; the polarising current is interrupted for adjustable intervals of time, varying from about 10^{-5} second upwards, and the potential at the end of each interval is measured. The information furnished by the study of decay curves is not so simple or direct as that provided by charging curves. Arrests corresponding to particular depolarisation reactions can sometimes be distinguished, and some indication of double layer capacities obtained, but in general the interpretation of a decay curve involves a knowledge of the mechanism of the polarisation, and hence the method has been mainly used in testing various theories of overpotential.

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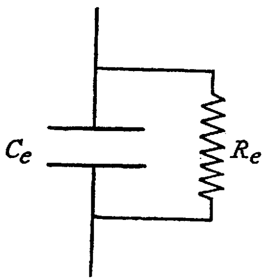
[12] *Proc. Roy. Soc.*, 1928, *A*, **120**, 80.

[13] E. Newbery, *J.*, 1914, **105**, 2419 ; 1916, **109**, 1051, 1066 ; 1922, **121**, 7 ; 1924, **125**, 511 ; S. Glasstone, *J.*, 1923, **123**, 2926 ; 1924, **125**, 250 ; 1925, **127**, 1824 ; M. Knobel, *J. Amer. Chem. Soc.*, 1924, **46**, 2613 ; H. J. S. Sand, J. Grant, and W. V. Lloyd, *J.*, 1927, 378 ; A. L. Ferguson and G. Van Zyl, *Trans. Electrochem. Soc.*, 1925, **47**, 227 ; A. L. Ferguson and G. M. Chen, *J. Physical Chem.*, 1932, **36**, 1156 ; A. L. Ferguson, *Trans. Electrochem. Soc.*, 1939, **76**, 113.

[14] F. P. Bowden and E. K. Rideal ; E. Baars, *locc. cit.*, ref. (4) ; A. L. Ferguson and G. M. Chen, *J. Physical Chem.*, 1934, **38**, 1117 ; A. L. Ferguson and S. Kleinheksel, *ibid.*, 1938, **42**, 171 ; A. L. Ferguson, *Trans. Electrochem. Soc.*, 1939, **76**, 113 ; Faraday Soc. Discussion, 1947, **1**, 50 ; E. Newbery, *Proc. Roy. Soc.*, 1925, *A*, **107**, 486 ; *Trans. Electrochem. Soc.*, 1930, **58**, 187 ; *Trans. Faraday Soc.*, 1947, **43**, 127.

[15] A. Hickling, *Trans. Faraday Soc.*, 1937, **33**, 1540 ; A. Hickling and F. W. Salt, *ibid.*, 1941, **37**, 450 ; F. W. Salt, Faraday Soc. Discussion, 1947, **1**, 169.

Alternating-current Methods.—In recent years the use of variable-frequency alternating current of small voltage amplitude superimposed upon the direct polarising current at a working electrode has provided a new experimental approach. In general, a working electrode may be regarded as comprising capacity and resistance components, and under suitable experimental conditions the simple network shown in the figure is an adequate representation in many cases; C_e is the apparent electrical capacity as defined by $C_e = \partial q/\partial V$, and R_e is the effective electrical resistance, governed by the rate of the electrode process, and defined by $R_e = \partial V/\partial i$. The behaviour of the electrode, considered in this way, may be investigated by combining it with a large unpolarisable electrode and measuring its impedance by A.C. bridge methods,[16] or the current–voltage amplitude and phase relations may be studied by oscillographic methods.[17] At potentials such that no actual discharge of ions takes place, R_e is infinite and C_e becomes identical with the capacity of the double layer at the electrode; this provides a very convenient method for the measurement of double-layer capacities.[18] Where discharge of ions can occur and diffusion is the only slow stage in the electrode reaction, then the concentration of the ions concerned at the interface oscillates about a mean value with the same frequency as the current but different phase, and [19]



$$R_e = \frac{RT}{zF^2c_0}\sqrt{\frac{2}{D\omega}} \quad \text{and} \quad C_e = \frac{z^2F^2c_0}{RT}\sqrt{\frac{D}{2\omega}} + C'$$

where D is the diffusion coefficient of the potential-determining ion, z its valency, c_0 the concentration in moles per c.c., ω the frequency of the alternating current, C' the capacity of the double layer, and $\boldsymbol{R}$, T, and $\boldsymbol{F}$ have their usual significance. Where the discharge of the ion is itself slow, these expressions have to be modified and an additional resistance term introduced, which, by making certain assumptions, can be correlated with the reaction rate. Thus P. Dolin and B. Ershler [20] have deduced that the measured total resistance should decrease with increasing frequency and approach a residual value at high frequencies equal to $\boldsymbol{R}T/z\boldsymbol{F}J_0$, where J_0 is the c.d. at which the reaction can occur at the mean potential under

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[16] G. Jones and S. M. Christian, *J. Amer. Chem. Soc.*, 1935, **57**, 272; P. Dolin and B. Ershler, *Acta Physicochim. U.R.S.S.*, 1940, **13**, 747; D. C. Grahame, *J. Amer. Chem. Soc.*, 1941, **63**, 1207; see also B. Breyer and F. Gutmann, *Trans. Faraday Soc.*, 1946, **42**, 650; 1947, **43**, 785.

[17] T. Borissova and M. Proskurnin, *Acta Physicochim. U.R.S.S.*, 1936, **4**, 819; 1940, **12**, 371; J. E. B. Randles, Faraday Soc. Discussion, 1947, **1**, 11.

[18] Cf. A. Frumkin and M. Proskurnin, *Trans. Faraday Soc.*, 1935, **31**, 110; M. Proskurnin and M. Vorsina, *Compt. rend. Acad. Sci. U.R.S.S.*, 1939, **24**, 915; D. C. Grahame, *loc. cit.*, ref. (16).

[19] F. Krüger, *Z. physikal. Chem.*, 1903, **45**, 1; T. R. Rosebrugh and W. Lash Miller, *J. Physical Chem.*, 1910, **14**, 816.

[20] *Loc. cit.*, ref. (16); B. Ershler, Faraday Soc. Discussion, 1947, **1**, 269.

equilibrium conditions (exchange current). J. E. B. Randles[21] has considered the particular case of the discharge of metallic ions at amalgam electrodes in a similar way and has shown how the rate constants for the discharge reactions can be derived from the measured capacities and resistances. Although the results so far obtained in this way should be interpreted with caution since the correlation of reaction rate with observed resistance involves a number of assumptions, the method seems likely to be of great value in the study of the kinetics of electrode reactions.

III. Electrode Kinetics and Polarisation Phenomena

When ions are discharged at an electrode at an appreciable rate, the electrode potential may be displaced from the reversible value. The electrode is then said to be polarised and to exhibit an overpotential or overvoltage which is defined as the potential difference between such a working electrode and a similar reversible electrode in the same solution. Two main factors may contribute to this overpotential:

(*a*) Changes in concentration of the ions near the electrode as a result of electrolysis may set up a potential difference; this is usually referred to as concentration polarisation or concentration overpotential.

(*b*) Thermodynamic irreversibility in the electrode reaction may necessitate an increased potential; this is the factor generally implied when the term overpotential is used without qualification and it is sometimes distinguished as activation overpotential.[22]

In addition, if there is any appreciable resistance between the working and the reference electrode, the measured potential difference may include an ohmic fall of potential equal to the product of the resistance and current strength. This has sometimes been termed resistance overpotential,[22] but since it is not characteristic of the particular system being studied, but depends largely on the particular experimental arrangement adopted, and since experimental technique is generally directed to eliminating or minimising this component, it is perhaps better regarded as an undesirable resistance error.[23]

Concentration Polarisation.—As a result of electrolysis, the concentration of the ions taking part in the reaction at a working electrode usually tends to diminish at the electrode surface. This tendency is opposed by the bringing up of ions to the electrode by diffusion, convection, and migration, and a steady state is eventually reached when a concentration gradient has been established and the ionic concentration at the electrode surface has a value (c_e) less than the value (c) in the bulk of the electrolyte. Hence, by the Nernst equation, the reversible potential of the working electrode is changed by an amount

$$\eta_c = \frac{RT}{zF} \log_e \frac{c}{c_e} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

As the reference electrode is usually outside the region of these concentration

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[21] *Loc. cit.*, ref. (17).

[22] F. P. Bowden and J. N. Agar, *Ann. Reports*, 1938, **35**, 90.

[23] A. Hickling, *loc. cit.*, ref. (15).

changes, η_c is included in the measured total potential difference and constitutes the concentration overpotential.

Concentration polarisation is liable to occur with all electrode processes, and its magnitude and dependence upon experimental conditions are best considered [24] by reference to the empirical concept of the diffusion layer.[25] It is supposed that a working electrode is covered by a thin layer of solution, within which convection is negligible, and across which the ions pass by diffusion and migration. If it is assumed as a first approximation that the concentration gradient across the layer is linear, then application of Fick's law to the diffusion of the relevant ionic species of diffusion coefficient D (cm.^{2} sec.$^{-1}$) gives

$$\text{Rate of diffusion, g.-ion/sec.} = AD(c - c_e)/\delta \quad . \quad . \quad (2)$$

where δ is the thickness of the layer, A its area (equal to the area of the electrode), and c and c_e are the boundary concentrations in g.-ion/c.c. In the presence of excess of indifferent electrolyte, so that migration of the ions in carrying the current is negligibly small, this can be equated to the current passing, and hence

$$AD(c - c_e)/\delta = IA/zF \quad . \quad . \quad . \quad . \quad (3)$$

where I is the c.d. in amp./sq. cm. Hence on rearrangement

$$c_e = c - I\delta/DzF \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and substituting in equation (1)

$$\eta_c = \frac{RT}{zF}\log_e\frac{1}{(1 - I\delta/cDzF)} \quad . \quad . \quad . \quad . \quad (5)$$

From this relation it is seen that concentration overpotential will be minimised by high diffusion coefficient, concentration, and valency of the relevant ion, while it will be increased by high c.d. and conditions which favour a thick diffusion layer. In unstirred aqueous solutions at room temperature, δ has a fairly constant value of about 0·03 cm.; [26] it is appreciably decreased by rise of temperature and very considerably by agitation, and both these factors therefore tend to reduce concentration overpotential. It is apparent from equation (5) that for a given set of conditions there will exist a limiting value of I at which the concentration overpotential may become infinitely large when the second term in the bracket approaches unity. This is termed the limiting diffusion c.d. for the process under consideration, and corresponds to a state of affairs in which c_e approaches zero; further increase of c.d. will then cause the potential to change to such a value that another

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[24] Cf. J. N. Agar and F. P. Bowden, *Proc. Roy. Soc.*, 1938, *A*, **169**, 206.

[25] A. A. Noyes and W. R. Whitney, *Z. physikal. Chem.*, 1897, **23**, 689; W. Nernst, *ibid.*, 1904, **47**, 52; W. Nernst and E. S. Merriam, *ibid.*, 1905, **53**, 235; E. Brunner, *ibid.*, 1904, **47**, 56; 1906, **58**, 1; F. Weigert, *ibid.*, 1907, **60**, 513; T. R. Rosebrugh and W. Lash Miller, *loc. cit.*, ref. (19); R. E. Wilson and M. A. Youtz, *Ind. Eng. Chem.*, 1923, **15**, 603; S. Glasstone, *Trans. Electrochem. Soc.*, 1931, **59**, 277.

[26] Early work suggested a value of 0·05 cm. (see S. Glasstone and A. Hickling, "Electrolytic Oxidation and Reduction", 1935, Chap. 3, for review). More recent studies have given appreciably lower values (cf. I. M. Kolthoff and J. J. Lingane, "Polarography", 1941, Chap. 32; *J. Physical Chem.*, 1941, **45**, 1062; *J. Amer. Chem. Soc.*, 1939, **61**, 3344; A. Hickling and W. H. Wilson, *Nature*, 1948, **162**, 489).

electrode process can occur. From equation (5) it is apparent that the limiting diffusion c.d. (I_d) is given by

$$I_d = cDzF/\delta \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Equation (5) can therefore be rewritten

$$\eta_c = \frac{RT}{zF} \log_e \frac{I_d}{I_d - I} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Limiting c.d.s are readily measured experimentally from observations on c.d.–potential curves, and hence the accuracy of the relation expressed in the form of equation (7) can easily be tested ; it appears to hold satisfactorily.[27] In the above deduction it has been assumed that the migration of the ions to the electrode is negligibly small ; where this is not so, the contribution made to the c.d. by transport can be allowed for, and equation (5) then becomes

$$\eta_c = \frac{RT}{zF} \log_e \frac{1}{(1 - I\delta n/cDzF)} . \quad . \quad . \quad . \quad (8)$$

where n is the sum of the transport numbers of all the ions in the diffusion layer other than the species being discharged. It is thus apparent that the migration of the ions will tend to reduce concentration polarisation and increase the limiting c.d.

With concentrated well-stirred solutions of simple salts, concentration polarisation is usually very small except at extremely high c.d.s, and from equation (7) it is seen that in general the working c.d. must exceed about one-tenth of the limiting value before the overpotential can become substantial ; thereafter it increases very rapidly with rise of c.d. If, however, the substance to be liberated at the electrode is present in the solution as a complex ion in equilibrium with a very small concentration of simple ion, the latter being discharged, the position is rather different. Here the limiting c.d. is controlled by diffusion of the complex ion and may be quite high, but the potential is governed by the minute concentration of simple ion and this may be markedly affected by electrolysis even at very low c.d.s ; hence considerable overpotential may develop under these conditions. Abnormal concentration polarisation of this kind is frequently observed in the electro-deposition of metals from cyanide solutions.[28]

The above discussion of concentration overpotential has been based on the empirical concept of the diffusion layer, since this provides a simple and direct approach. Attempts to treat the problem more fundamentally have until recently been unsuccessful. If the transfer of ions from an unstirred solution to a plane electrode is treated by ordinary diffusion theory, then no indication is obtained that a stationary state should be set up in a short time and a diffusion layer of definite thickness established. Since these are characteristic features of the behaviour of a working electrode,

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[27] I. M. Kolthoff and J. J. Lingane, *op. cit.*, ref. (26), Chap. 9 ; I. M. Kolthoff and H. A. Laitinen, *J. Physical Chem.*, 1941, **45**, 1062.

[28] Cf. F. Foerster, *Z. Elektrochem.*, 1907, **13**, 561 ; S. Glasstone, *J.*, 1929, 690, 702 ; O. A. Essin and E. Alfimova, *J. Physical Chem. Russia,* 1936, **8**, 137 ; O. A. Essin and T. Beklemysheva, *J. Gen. Chem, Russia,* 1936, **6**, 1602.

it is apparent that some further factor must enter into the transfer process, and this is provided by convection, due to density differences, which serves to keep the concentration of the solution uniform at a small distance from the electrode. B. Levich [29] has recently succeeded in developing a fundamental theory of convective diffusion, which leads to the conclusion that a diffusion layer will in general be set up and permits the calculation of its thickness in some special cases, and J. N. Agar [30] has used the method of dimensional analysis combined with data obtained from the analogous problem of heat transfer and arrives at similar results.

The problem of the variation of concentration overpotential with time at constant c.d. has received some attention. H. J. S. Sand [31] considered the case of an electrode in an unstirred solution, and, utilising Fick's diffusion equations, deduced that the time necessary for the concentration of ions at the electrode surface to be reduced to zero (transition time τ) should be given by

$$\tau = k(c/I)^2 \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where k is a constant, c the bulk concentration, and I the c.d. This relation has been verified under special conditions such that convection is small.[32] Where no special precautions are taken to avoid convection it would not be expected that the equation should hold accurately since at all c.d.s below the limiting value the transition time will be infinite; Z. Karaoglanoff,[33] however, showed that it applied fairly well to the oxidation of ferrous and reduction of ferric ions in these circumstances provided the c.d. used was appreciably higher than the limiting value. J. A. V. Butler and G. Armstrong [34] have investigated a number of cathodic reduction processes, and find that in general for short transition times the results can be represented by the relation

$$(I - I_d)\sqrt{\tau} \propto c \quad . \quad . \quad . \quad . \quad . \quad (10)$$

which approximates to equation (9) when the c.d. used is much higher than the limiting value; for long transition times, however, it appeared that the data were more in accordance with a relation of the form

$$(I - I_d)\tau \propto c \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Activation Overpotential.—If any stage in the overall electrode reaction in between the arrival of the ions at the surface of the electrode and the ultimate formation of the stable electrolytic product is slow and limits the rate at which the electrode reaction can occur, then the electrode will exhibit

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[29] *Acta Physicochim. U.R.S.S.*, 1942, **17**, 257; 1943, **19**, 117, 133; Faraday Soc. Discussion, 1947, **1**, 37; see also A. Eucken, *Z. Elektrochem.*, 1932, **38**, 341.

[30] Faraday Soc. Discussion, 1947, **1**, 26.

[31] *Phil. Mag.*, 1901, **1**, 45; *Z. physikal. Chem.*, 1900, **35**, 461; *Trans. Faraday Soc.*, 1905, **1**, 1; see also T. R. Rosebrugh and W. Lash Miller, *loc. cit.*, ref. (19); J. N. Agar and F. P. Bowden, *loc. cit.*, ref. (24).

[32] H. J. S. Sand, *loc. cit.*, ref. (31); T. G. Cottrell, *Z. physikal. Chem.*, 1903, **42**, 385; I. M. Kolthoff and H. A. Laitinen, *J. Amer. Chem. Soc.*, 1939, **61**, 3344.

[33] *Z. Elektrochem.*, 1906, **12**, 5.

[34] *Proc. Roy. Soc.*, 1933, *A*, **139**, 406; 1933, **143**, 89; *Trans. Faraday Soc.*, 1936, **32**, 989; 1934, **30**, 1173.

activation overpotential. In general, two main theoretical methods have been used in considering and treating this type of overpotential. The modern view, which has been developed in various ways [35] in recent years, has focussed attention particularly on ion-discharge as the likely rate-determining process, and regards the electrode potential as directly affecting its speed. Thus, if it is supposed that there is an energy barrier to be surmounted such that an energy of activation W is required at the reversible potential, then this energy may be regarded as dependent upon the electrode potential. If a cathodic reaction is under consideration, the energy of activation will be decreased by making the electrode more negative, and for a displacement of potential η, equal to the activation overpotential, the new energy of activation will be $W - \alpha\eta\boldsymbol{F}$, where α is a coefficient the value of which must lie between zero and unity. Thus at the reversible potential the rate of ion-discharge will be proportional to $k_1 a_+ \mathrm{e}^{-W/\boldsymbol{RT}}$ where a_+ is the activity of the cation at the surface of the electrode and k_1 is a constant, and since no net current is here flowing this must also be the rate of the reverse ionisation process. For the polarised cathode, the rate of the forward reaction will be increased and will be given by $k_1 a_+ \mathrm{e}^{-(W-\alpha\eta\boldsymbol{F})/\boldsymbol{RT}}$, it being assumed for simplicity that the activity of the cation is not changed, and the rate of the reverse reaction will be decreased and will be given by $k_2 a' \mathrm{e}^{-[W'+(1-\alpha)\eta\boldsymbol{F}]/\boldsymbol{RT}}$, where a' is the activity of the discharged ions and W' is the activation energy of the ionisation reaction. Hence for a univalent cation, the current I flowing per unit area at a working cathode will be given by

$$I = \boldsymbol{F}k_1 a_+ \mathrm{e}^{-(W-\alpha\eta\boldsymbol{F})/\boldsymbol{RT}} - \boldsymbol{F}k_2 a' \mathrm{e}^{-[W+(1-\alpha)\eta\boldsymbol{F}]/\boldsymbol{RT}} \quad . \quad . \quad . \quad (12)$$

For appreciable displacements from the reversible potential the rate of the ionisation reaction is very small and hence

$$I \triangleq \boldsymbol{F}k_1 a_+ \mathrm{e}^{-(W'-\alpha\eta\boldsymbol{F})/\boldsymbol{RT}} \quad . \quad . \quad . \quad . \quad . \quad (13)$$

which reduces to

$$\eta = a + (\boldsymbol{RT}/\alpha\boldsymbol{F}) \log_e I \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where a is a constant including the activation energy W. Alternatively equation (13) may be written

$$\eta = (\boldsymbol{RT}/\alpha\boldsymbol{F}) \log_e I/I_0 \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where I_0 is the c.d. corresponding to the rate of the electrode reaction at the reversible potential. From equation (14) it is seen that the plot of η against $\log_{10} I$ should be a straight line of slope $2{\cdot}303\boldsymbol{RT}/\alpha\boldsymbol{F}$, and this type of relation is often found to hold experimentally. The variation of overpotential with temperature at constant c.d. is then given by

$$\left(\frac{\partial\eta}{\partial T}\right)_I = -\frac{(W - \alpha\eta\boldsymbol{F})}{\alpha\boldsymbol{F}T} \quad . \quad . \quad . \quad . \quad . \quad (16)$$

and of c.d. with temperature at constant overpotential by

$$\left(\frac{\partial \log_e I}{\partial T}\right)_\eta = \frac{W - \alpha\eta\boldsymbol{F}}{\boldsymbol{R}T^2} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

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[35] See, *e.g.*, F. P. Bowden and J. N. Agar, *loc. cit.*, ref. (22) ; J. A. V. Butler, " Electrocapillarity ", 1940, Chap. 6 ; S. Glasstone, K. J. Laidler, and H. Eyring, " The Theory of Rate Processes ", 1941, Chap. 10.

from which expressions, given suitable experimental data, W can be found. For small polarisations, where the electrode potential is close to the reversible value, the rate of the ionisation process cannot be neglected. Simplifying equation (12) and expanding the exponential terms, this reduces to

$$\eta \propto (RT/F)I \qquad . \quad . \quad . \quad . \quad . \quad (18)$$

i.e., in these circumstances the overpotential is directly proportional to the c.d.

This approach to the problem of activation overpotential is very attractive in its simplicity and directness, and it provides a useful basis for the interpretation of experimental data. It is important to recognise, however, that it can only be applied if the slow stage responsible for activation overpotential concerns the discharge of ions. Although the nature of the energy of activation is not specified, and might be involved either in the neutralisation of an ion or in its dehydration, the fundamental postulate is that it will be affected by the electrode potential. If, however, the slow stage in the electrode reaction occurs after the ions are discharged, and does not involve charged particles, it is not clear why the electrode potential should exercise any direct effect on the rate of the electrode reaction. In this case the older approach to the problem of overpotential seems more useful. This postulated that, owing to the slowness of the electrode reaction, some unstable intermediate electrolytic substance, regarded as more electromotively active than the ultimate product, would tend to accumulate at the electrode surface, and under a given set of experimental conditions would attain a stationary concentration and set up its own electrode potential. Where adequate thermodynamic data exist, the potential of the intermediate in a standard state can be calculated, and if the activity of the substance at the electrode surface can be inferred from the postulated mechanism of the electrode reaction, the potential it should set up can be calculated from the Nernst equation, and its dependence upon c.d., temperature, and other experimental variables can be deduced. This quasi-thermodynamic method has been used by a number of authors,[36] particularly in connection with the problem of hydrogen overpotential, and often leads to an equation for the dependence of overpotential upon c.d. of a form similar to equation (14).

These two theoretical approaches to activation overpotential do not seem to be in any way necessarily opposed; each would appear to be of value in its own field. Where the process of ion-discharge is slow, the second method obviously breaks down, since it assumes a thermodynamic equilibrium between some chemical product and its ions to be instantaneously set up. Similarly, where ion-discharge is not the slow process in an electrode reaction, the first method seems equally inapplicable, since it is difficult here to see how the electrode potential can then directly affect the kinetics of the electrode process. The methods are, therefore, rather complementary, and in any particular case it is the agreement of the inferences which result from the two treatments with experimental observations which must decide which is the more useful method and simultaneously will throw

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[36] See, *e.g.*, A. Hickling and F. W. Salt, *Trans. Faraday Soc.*, 1942, **38**, 474.

light on the probable location of the rate-determining stage in the electrode reaction.

The main electrode processes in which activation overpotential is conspicuously shown are the cathodic liberation of hydrogen, the anodic evolution of oxygen, and the electrodeposition of nickel, iron, and cobalt, and these are discussed in subsequent sections. There has recently been a tendency [37] to cite as examples of activation overpotential any reactions in which the working potentials differ from the values calculated from free-energy data, and processes such as the anodic evolution of nitrogen in the electrolysis of azide solutions and the Kolbe and the Hofer–Moest reactions have been quoted. Although such reactions are indubitably irreversible in the thermodynamic sense, it may perhaps be doubted whether this extension of the idea of overpotential is a useful one. The commonly accepted definition of overpotential contains the implication that a reversible electrode for the system under consideration can be experimentally realised or approached under special conditions, and this is certainly not the case with the reactions mentioned. Furthermore, it is quite possible that in many electrolytic oxidation and reduction processes, which would be included in the extended concept, the products formed do not arise by direct discharge of ions but by the action of chemical oxidising and reducing agents first produced at the electrodes.

IV. The Cathodic Evolution of Hydrogen

The formation of gaseous hydrogen from the discharge of hydrogen ions is, under most conditions, a highly irreversible process characterised by a marked activation overpotential, and it is one of the most thoroughly investigated of electrode reactions. In early work, great difficulty was encountered in obtaining reproducible values of hydrogen overpotential at most cathodes, and although considerable improvement has resulted from modern techniques in which the greatest possible care is taken to eliminate impurities from electrode and electrolyte, and to allow for the influence of time of polarisation, published values still have a relative rather than an absolute significance. It has, however, been possible to establish the influence of most experimental factors.

The most striking feature of hydrogen overpotential is its marked dependence upon the nature of the cathode material. This is illustrated by the values summarised in Table I, which are the measured overpotentials at various cathodes in N-hydrochloric acid at a c.d. of 1 ma./sq. cm.[38] In general, as was pointed out by W. R. Mott,[39] metals of low melting point have high overpotentials and *vice versa*, although the correlation is by no means exact; as would be expected from this, overpotential, like melting point, seems to be a periodic function of atomic number.[40] From some

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[37] Cf. J. N. Agar, *Ann. Reports*, 1947, **44**, 5; H. P. Stout, *Trans. Faraday Soc.*, 1945, **41**, 64.

[38] Selected values taken from the work of A. Hickling and F. W. Salt, *ibid.*, 1940, **36**, 1226, and J. O'M. Bockris, *ibid.*, 1947, **43**, 417, carried out under similar conditions.

[39] *Trans. Electrochem. Soc.*, 1909, **15**, 569.

[40] A. J. Allmand and H. J. T. Ellingham, *Trans. Faraday Soc.*, 1924, **19**, 748.

theories of hydrogen overpotential it might be expected that there should be a parallelism between overpotential and the thermionic work function of the electrode material; this has recently been investigated by J. O'M. Bockris,[41] who has reached the interesting conclusion that the relation is of an inverse type, an increase in work function from one metal to another leading to a decrease of overpotential.

TABLE I

Hydrogen overpotentials (volts) in acid solution

Tl . . .	1·05	In . . .	0·80	Cu . . .	0·54	Mo . . .	0·30
Hg . . .	1·04	Bi . . .	0·69	Ag . . .	0·46	W . . .	0·27
Cd . . .	0·99	Nb . . .	0·65	Ta . . .	0·41	Pt . . .	0·25
Pb . . .	0·88	Be . . .	0·63	Fe . . .	0·40	Au . . .	0·17
Sn . . .	0·85	Al . . .	0·58	Ni . . .	0·33	Platinised Pt	0·01

Hydrogen overpotential increases slowly with rise of c.d., and over a considerable range the relation is a logarithmic one and, as first noted by J. Tafel,[42] can be expressed by the equation $\eta = a + b \log_{10} I$, where a and b are constants depending upon the nature of the cathode material and temperature. This relation has been the subject of much study and certainly holds with considerable accuracy over the c.d. range 10^{-6} to 10^{-3} amp./sq. cm. for most cathodes. Since b varies with temperature and nearly all theories of hydrogen overpotential lead to its expression as a factor embodying $\boldsymbol{RT}/\boldsymbol{F}$, the equation is now frequently written in the form

$$\eta = a + (2{\cdot}303\boldsymbol{RT}/\alpha\boldsymbol{F}) \log_{10} I$$

(cf. equation 14) and particular attention has been directed to the value of α. According to those theories of hydrogen overpotential which regard the ion discharge step as the slow stage in the electrode reaction, it seems probable that α should be 0·5, which would give b a value of 0·116 at 17°. For mercury cathodes in carefully purified acid solutions, values very close to this have been observed, and for many metals b is in the vicinity of 0·1; wide variations are, however, also encountered, and values as high as 0·3 for lead and as low as 0·02 for platinised platinum have been reported.[43] There has been a marked tendency in recent years to suggest [22] that b always has the theoretical value (corresponding to $\alpha = 0{\cdot}5$) for pure metals and that discrepancies are due to contamination of the surfaces studied, and in agreement with this it is found that traces of catalytic poisons tend to increase b. This view would not, however, account for the values of b lower than 0·116, which are often found, and furthermore the high values, even if due to contamination, remain experimental facts which require explanation. The investigation of hydrogen overpotential at c.d.s below 10^{-6} amp./sq. cm. is difficult owing to the great effect of minute amounts of depolarisers, but

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[41] *Loc. cit.*, ref. (38).

[42] *Z. physikal. Chem.*, 1905, **50**, 641.

[43] For lists of values of b, see F. P. Bowden and J. N. Agar, *loc. cit.*, ref. (22); A. Hickling and F. W. Salt; J. O'M. Bockris, *locc. cit.*, ref. (38).

it has been shown [44] that Tafel's equation holds for a mercury cathode down to 10^{-9} amp./sq. cm., while for catalytically active metals such as platinum there is some evidence that η is proportional to I at very low c.d.s.[45] The study of hydrogen overpotential at high c.d.s, above 10^{-3} amp./sq. cm., involves experimental difficulties due to the magnitude of the resistance error which may be included in the measured potential differences. B. Kabanov,[46] using the direct method of measurement and attempting to correct for resistance error, claimed that Tafel's equation applied accurately at silver, amalgamated silver, and platinum cathodes up to c.d.s greater than 10 amp./sq. cm. On the other hand, Hickling and Salt,[38] working in the c.d. range 10^{-3} to 1 amp./sq. cm., found that for some metals there were negative deviations from Tafel's equation and there was frequently a tendency for the overpotential to approach a specific limiting value ; they used an electronic interrupter method in which the potential was measured after interruption of the polarising current for varying periods, and the values extrapolated to zero time of interruption. These results have been criticised by A. Frumkin [47] on the ground that the graphical extrapolations are unreliable, but it may be noted that Bockris,[38] using the direct method of measurement under conditions such that resistance error is minimised, has observed similar tendencies with some metals.

Tafel [42] noted that hydrogen overpotential at most cathodes tended to rise with time of polarisation, and this has been confirmed by many subsequent workers. Mercury, tungsten, and platinised platinum give overpotentials which reach constant values within a very short period of polarisation, and most common metals attain a stationary state within about one hour, but with some electrodes, notably platinum and palladium, the potentials may increase over a prolonged period ; with electrodeposited metals these times are usually reduced. In some cases the deposition of impurities from the electrolyte upon the cathode may contribute to this time variation, but in general there appears little doubt that the phenomenon is a characteristic feature of hydrogen overpotential. Its importance in determining the conditions necessary for obtaining reproducible measurements of hydrogen overpotential has been stressed in recent papers.[38] On very prolonged electrolysis, roughening of the cathode surface may sometimes cause a decrease of overpotential.

A large number of investigations of the influence of hydrogen-ion concentration on hydrogen overpotential have been made,[48] and although the results are not completely satisfactory, the bulk of the evidence seems to

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[44] F. P. Bowden and K. E. W. Grew, Faraday Soc. Discussion, 1947, **1,** 86.

[45] J. A. V. Butler and G. Armstrong, *Trans. Faraday Soc.*, 1932, **28,** 380 ; M. Volmer and H. Wick, *Z. physikal. Chem.*, 1935, **172,** 429.

[46] *Acta Physicochim. U.R.S.S.*, 1936, **5,** 193.

[47] *Ibid.*, 1943, **18,** 23.

[48] See, *e.g.*, J. Tafel, *loc. cit.*, ref. (42) ; S. Glasstone, *J.*, 1924, **125,** 2646 ; F. P. Bowden, *Trans. Faraday Soc.*, 1928, **24,** 473 ; *Proc. Roy. Soc.*, 1929, *A*, **126,** 107 ; S. Lewina and V. Sarinsky, *Acta Physicochim. U.R.S.S.*, 1937, **6,** 491 ; 1937, **7,** 485 ; S. Jofa and B. Kabanov, *ibid.*, 1939, **10,** 616 ; A. Hickling and F. W. Salt, *Trans. Faraday Soc.*, 1941, **37,** 333.

indicate that in dilute solutions of pure acids the overpotential is practically independent of pH. In concentrated acid solutions it has been reported that the overpotential decreases with increasing concentration.[49] According to some theories, the overpotential might be expected to increase with decreasing hydrogen-ion concentration in acid solutions containing an excess of added salts, and this variation has been observed by some workers, although the change is small.[50] At high c.d.s in dilute acid solutions concentration overpotential may occur and has recently been investigated ; [51] where the electrolyte contained excess of neutral salt, the polarisation was in general that to be expected from the change in hydrogen-ion concentration at the cathode surface, but in dilute acid solutions not containing any added electrolyte very high overpotentials exhibiting many peculiar features were observed. Few measurements have been made [52] in alkaline solution, and these generally at a mercury cathode where amalgam formation may cause complication, but it appears that Tafel's equation is approximately obeyed, b having, however, a value considerably greater than in acid solution. Variation of the nature of the solvent might be expected to have a considerable effect on hydrogen overpotential if the hydrogen ion is involved in the rate-determining step. Measurements have been made [53] in methyl and ethyl alcohol, acetic and formic acid, ether, ethylene glycol, dioxan, *cyclo*hexanol, and liquid ammonia. So far as the results can be readily summarised, it would appear that some lowering of high overpotentials takes place in the anhydrous solutions, although with low overpotential cathodes the influence is much smaller ; the solvent effect is, however, very complex, and in mixed aqueous–non-aqueous solutions maxima are frequently observed at intermediate compositions.

Investigation of the rate of decay of hydrogen overpotential on interruption of the polarising current suggests that two depolarisation processes are involved.[54] One, which becomes apparent only at high c.d.s, greater than 10^{-3} amp./sq. cm., leads to a rapid drop of potential in the first thousandth of a second and seems to depend primarily on the polarising

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[49] S. Jofa, *Acta Physicochim. U.R.S.S.*, 1939, **10,** 903 ; A. J. de Bethune and G. E. Kimball, *J. Chem. Physics*, 1945, **13,** 53 ; A. Rius and J. Llopis, *Anal. Fís. Quím.*, 1946, **42,** 897.

[50] S. Lewina and V. Sarinsky, *loc. cit.*, ref. (48) ; C. Wagner and W. Traud, *Z. Elektrochem.*, 1938, **44,** 391 ; S. Jofa and A. Frumkin, *Acta Physicochim. U.R.S.S.*, 1943, **18,** 183.

[51] G. E. Coates, *J.*, 1945, 484 ; P. M. Bryant and G. E. Coates, Faraday Soc. Discussion, 1947, **1,** 115.

[52] F. P. Bowden and H. F. Kenyon, *Nature*, 1935, **135,** 105.

[53] G. Carrara, *Z. physikal. Chem.*, 1909, **69,** 75 ; S. Swann and E. O. Edelmann, *Trans. Electrochem. Soc.*, 1930, **58,** 75 ; S. Lewina and M. Silberfarb, *Acta Physicochim. U.R.S.S.*, 1936, **4,** 275 ; I. S. Novoselski, *J. Physical Chem. U.S.S.R.*, 1938, **11,** 369 ; V. Pleskov, *Acta Physicochim. U.R.S.S.*, 1939, **11,** 305 ; A. Hickling and F. W. Salt, *Trans. Faraday Soc.*, 1941, **37,** 224 ; J. O'M. Bockris, Faraday Soc. Discussion, 1947, **1,** 95 ; J. O'M. Bockris and S. Ignatowicz, *Trans. Faraday Soc.*, 1948, **44,** 519 ; J. O'M. Bockris and R. Parsons, *ibid.*, p. 860.

[54] See, *e.g.*, E. Baars, *loc. cit.*, ref. (4) ; G. Armstrong and J. A. V. Butler, *Trans. Faraday Soc.*, 1933, **29,** 1261 ; A. L. Ferguson, *Trans. Electrochem. Soc.*, 1939, **76,** 113 ; A. Hickling and F. W. Salt, *loc. cit.*, ref. (15).

c.d. used ; the second, which is observed at all c.d.s, leads to a slower decay and follows a course such that the overpotential ultimately becomes proportional to the logarithm of the time, and the rate of decay is then primarily dependent upon the nature of the cathode material. The rate of build-up of hydrogen overpotential has been studied by charging-curve methods. At a mercury cathode, which has been very fully investigated,[55] the potential varies linearly with the quantity of electricity passed until it is close to the hydrogen evolution value, and the process appears to correspond simply to the formation of an ionic double layer having a capacity of about 20 μF./sq. cm. in pure acid solutions. At platinum cathodes the formation of an approximately monatomic layer of adsorbed hydrogen atoms can be detected.

Hydrogen overpotential is lowered by increase of temperature, and for high-overpotential metals the temperature coefficient is some $-$ 0·002 to $-$ 0·003 v./degree, whereas for low overpotential metals it is very much smaller.[56] Heats of activation, calculated by equations (16) and (17) from the rather limited experimental data available, range from about 6 to 20 kg.-cals. for different cathodes.[22] Early experiments on the effect of pressure on hydrogen overpotential led to uncertain results, but more recent investigations indicate that η is slightly decreased by rise of pressure.[57]

The addition of catalytic poisons such as arsenious oxide, mercuric chloride, and carbon disulphide markedly increases hydrogen overpotential at catalytically active cathodes,[58] and similar effects have been reported [59] for colloidal substances such as gelatin and gum arabic which are often used as addition agents in electroplating ; alkaloids of the quinoline group have been observed [60] to bring about a lowering of overpotential at mercury cathodes, although they raise the overpotential at platinised platinum electrodes. Capillary-active substances usually have some influence on hydrogen overpotential, but any general relation is so far obscure.[61]

The overpotential of deuterium is definitely higher than that of hydrogen

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[55] F. P. Bowden and E. K. Rideal ; E. Baars, *locc. cit.*, ref. (4) ; H. Brandes, T. Erdey-Grúz *et al.*, *locc. cit.*, ref. (5) ; A. Hickling, *loc. cit.*, ref. (7) ; F. P. Bowden and K. E. W. Grew, *loc. cit.*, ref. (11).

[56] E. K. Rideal, *J. Amer. Chem. Soc.*, 1920, **42,** 94 ; M. Knobel and D. B. Joy, *Trans. Electrochem. Soc.*, 1923, **44,** 443 ; G. M. Westrip, *J.*, 1924, **125,** 1112 ; S. Glasstone, *ibid.*, p. 2651 ; W. D. Harkins and H. S. Adams, *J. Physical Chem.*, 1925, **29,** 205 ; F. P. Bowden, *Proc. Roy. Soc.*, 1929, *A*, **126,** 107 ; N. Kobosew and N. I. Nekrassow, *Z. Elektrochem.*, 1930, **36,** 529 ; A. Hickling and F. W. Salt, *loc. cit.*, ref. (48).

[57] See, *e.g.*, S. J. Bircher and W. D. Harkins, *J. Amer. Chem. Soc.*, 1923, **45,** 2890 ; H. M. Cassel and E. Krumbein, *Z. physikal. Chem.*, 1934, **171,** 70 ; V. Schischkin *et al.*, *Z. Elektrochem.*, 1934, **40,** 713, 724 ; 1936, **42,** 631, 693 ; G. Schmid and E. K. Stoll, *ibid.*, 1941, **47,** 360.

[58] M. Volmer and H. Wick, *loc. cit.*, ref. (45) ; von Naray-Szabo, *Naturwiss.*, 1937, **25,** 12 ; A. Hickling and F. W. Salt, *loc. cit.*, ref. (48).

[59] C. Marie, *Compt. rend.*, 1908, **147,** 1400 ; J. N. Pring and U. C. Tainton, *J.*, 1914, **105,** 710 ; N. Isgarischew and S. Berkmann, *Z. Elektrochem.*, 1922, **28,** 47 ; G. M. Westrip, *loc. cit.*, ref. (56).

[60] J. O'M. Bockris and B. E. Conway, *Nature*, 1947, **159,** 711.

[61] See, *e.g.*, A. Thiel and E. Breuning, *Z. anorg. Chem.*, 1913, **83,** 329 ; S. Glasstone, *Trans. Faraday Soc.*, 1925, **21,** 36 ; T. Onoda, *Z. anorg. Chem.*, 1927, **165,** 93.

under comparable conditions,[62] implying that the speed of the rate-determining reaction is less, and this factor must therefore be operative in the separation of the isotopes by electrolysis. Cathodes appear to fall into two groups [63] as regards the separation factor ; for platinum, nickel, gold, silver, and copper the factor has values ranging from 5 to 7, while for tin, mercury, and lead it has a value of about 3. A satisfactory theory of hydrogen overpotential might therefore be expected to throw light upon these differences and upon the dependence of the separation factor on experimental conditions.

Theories of Hydrogen Overpotential.—Few problems have attracted as much theoretical speculation as that of the mechanism of hydrogen overpotential, and the literature offers a bewildering complexity of alternative views. A very thorough and detailed account of current theories has recently been given by J. O'M. Bockris.[64] It is proposed here to summarise the present position in general terms.

It is now widely agreed that three main reactions may be involved in passing from the hydrated hydrogen ion to hydrogen gas and may be intimately concerned in the development of hydrogen overpotential. There is first the discharge of the hydrogen ion, involving its dehydration, to give hydrogen atoms which, in most cases, will be adsorbed upon the metal cathode surface, *viz.*,

$$H_3O^+ + Me + e \longrightarrow H_2O + MeH \quad . \quad . \quad . \quad (I)$$

This may be followed by the combination of hydrogen atoms in pairs according to the Tafel [42] catalytic mechanism, thus :

$$2MeH \longrightarrow 2Me + H_2 \quad . \quad . \quad . \quad . \quad (II)$$

or by discharge of a further hydrogen ion upon an adsorbed hydrogen atom according to the electrochemical mechanism first suggested by Heyrovsky, thus :

$$H_3O^+ + MeH + e \longrightarrow H_2O + Me + H_2 \quad . \quad . \quad . \quad (III)$$

Any one of these stages may be the rate-determining step responsible for the observed overpotential.

The idea that the discharge of the hydrogen ion might be a slow process (reaction I) first attracted favourable attention when developed mathematically from different standpoints by Erdey-Grúz and Volmer [5] and R. W. Gurney,[65] and it has been adopted in various forms by many subsequent workers ; [66] its later development is particularly due to A. Frumkin.[67] In its extended form, in which allowance is made for the activity of the hydrogen

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[62] F. P. Bowden and H. F. Kenyon, *loc. cit.*, ref. (52) ; J. Heyrovsky and O. H. Muller, *Coll. Czech. Chem. Comm.*, 1935, **7**, 281.

[63] J. Horiuti and G. Okamoto, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **28**, 231 ; H. F. Walton and J. H. Wolfenden, *Trans. Faraday Soc.*, 1938, **34**, 436.

[64] *Chem. Reviews*, 1948, **43**, 525.

[65] *Proc. Roy. Soc.*, 1931, *A*, **134**, 137.

[66] See, *e.g.*, R. H. Fowler, *Trans. Faraday Soc.*, 1932, **28**, 368 ; J. A. V. Butler, *ibid.*, p. 379 ; *Proc. Roy. Soc.*, 1936, *A*, **157**, 423 ; J. Horiuti and M. Polanyi, *Acta Physicochim. U.R.S.S.*, 1935, **2**, 505.

[67] *Ibid.*, 1937, **7**, 475 ; 1943, **18**, 23 ; Faraday Soc. Discussion, 1947, **1**, 57.

ions in the double layer adjacent to the cathode, if the coefficient α is given the probable value of 0·5, it leads to an equation for the overpotential of the form

$$\eta = \text{const.} + \frac{2RT}{F} \log_e I - \frac{RT}{F} \log_e [\text{H}^+] - \psi \quad . \quad . \quad (19)$$

where ψ is related to the electrokinetic potential. In pure acid solutions, this reduces to

$$\eta = \text{const.} + \frac{2RT}{F} \log_e I \quad . \quad . \quad . \quad . \quad (20)$$

which is an equation of the Tafel type, b being 0·116 at 17°, in close agreement with the value found for a mercury cathode. Addition of neutral salts to the electrolyte would be expected to decrease ψ and hence increase the overpotential, while if ψ is kept constant and the pH value varied, η should increase with decreasing hydrogen-ion concentration in agreement with some reported observations. Furthermore, the theory would predict that in the initial growth of hydrogen overpotential, the rate-determining process should be the building-up of an ionic double layer, and hence the potential should be directly proportional to the quantity of electricity passed, which again is found experimentally for a mercury cathode. The slow-discharge theories therefore account satisfactorily for some aspects of hydrogen overpotential, particularly at high overpotential cathodes, but they seem defective in many other respects. For instance, they have provided no real explanation of the marked dependence of overpotential on cathode material ; in a qualitative manner it can be seen that where a metal is a good adsorbent for hydrogen atoms with a high heat of adsorption, the energy of activation of the neutralisation process may be reduced and hence the overpotential lowered, but no detailed treatment has yet been worked out. Furthermore, they give no explanation of such characteristic features of hydrogen overpotential as the variation with time, the influence of catalytic poisons, and the solvent effect. The initial postulate of the slow-discharge theories, *viz.*, that the neutralisation of the hydrogen ion is slow, is a concept which is not altogether easy to accept, and H. Eyring, S. Glasstone, and K. J. Laidler [68] have put forward a new theory of overpotential in which it is supposed that the rate-determining stage is the transfer of a proton from a water molecule in the solution to an adsorbed water molecule on the cathode. By application of the theory of absolute reaction rates to this process the usual equation for the dependence of overpotential upon c.d. can be deduced, with the coefficient α having the value of 0·5 ; the variation of overpotential with electrode material can also be qualitatively accounted for in terms of the strength of the Me–H bonds formed. The theory is also considered to be applicable to the explanation of oxygen overpotential, the rate-determining stage here being the reverse of that at a cathode, *i.e.*, the transfer of a proton from a molecule of adsorbed water on the anode to one in the solution, and this is supposed

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[68] *J. Chem. Physics*, 1939, **7**, 1053 ; *Trans. Electrochem. Soc.*, 1939, **76**, 145 ; G. E. Kimball, S. Glasstone, and A. Glassner, *J. Chem. Physics*, 1941, **9**, 91.

to account for certain apparent similarities between hydrogen and oxygen overpotentials. Several workers have criticised the theory adversely on various grounds,[69] and from the experimental standpoint it might be expected that, according to it, change of solvent would have a much larger effect on hydrogen overpotential than is in fact found.

The view that hydrogen overpotential is due to the accumulation of atomic hydrogen at the cathode appears to have originated with Tafel.[42] In its simplest form it supposes that the rate of combination of hydrogen atoms (reaction II) is slow, and that therefore at any appreciable rate of electrolysis there will exist a small concentration of atomic hydrogen at the electrode, and this, as may readily be shown thermodynamically, will give rise to a potential substantially more negative than the reversible hydrogen potential. Those metals which are good catalysts for the combination of hydrogen atoms might then be expected to give low overpotentials, while those with little catalytic power would have high overpotentials, and K. F. Bonhoeffer [70] has shown that this correlation does hold experimentally. Other evidence, such as the ready diffusion of cathodic hydrogen through metals,[71] the action of catalytic poisons,[58] the marked reducing power of high overpotential cathodes,[72] and the transference of overpotential from the polarised to the unpolarised side of iron and palladium diaphragms separating two electrolytes,[73] lends further qualitative support to the general theory. If, however, the kinetics of the process are considered, and it is assumed that the potential is proportional to the logarithm of the adsorbed hydrogen atom concentration, the dependence of overpotential upon c.d. is given by the equation

$$\eta = \text{const.} + (RT/2F) \log_e I \quad . \quad . \quad . \quad . \quad (21)$$

This is of the correct form but with the coefficient $\alpha = 2$, giving b a value of 0·029 at 17°; this is very much lower than is observed experimentally, except for very active electrodes such as platinised platinum. It has, however, been pointed out [36] that there is no theoretical basis for considering the potential as directly dependent upon the logarithm of the adsorbed hydrogen concentration, but rather the pressure of free atomic hydrogen in equilibrium with it should be considered. If this is done, then for poor adsorbents or for surfaces approaching saturation much larger values of b are obtained.[74] The possibility of the electrochemical mechanism (reaction III) being involved in the determination of the rate of the overall electrode

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[69] A. Frumkin, *Acta Physicochim. U.R.S.S.*, 1940, **12**, 243; J. A. V. Butler, *J. Chem. Physics*, 1941, **9**, 279.

[70] *Z. physikal. Chem.*, 1924, **113**, 199.

[71] See C. J. Smithells, " Gases and Metals ", 1938, p. 77, for a full account of this phenomenon.

[72] See S. Glasstone and A. Hickling, *op. cit.*, ref. (26), Chap. 5.

[73] H. H. Uhlig, N. E. Carr, and P. H. Schneider, *Trans. Electrochem. Soc.*, 1941, **79**, 111; A. Frumkin and N. Aladjalova, *Acta Physicochim. U.R.S.S.*, 1943, **19**, 1; see also H. P. Stout, Faraday Soc. Discussion, 1947, **1**, 107.

[74] A. Hickling and F. W. Salt, *loc. cit.*, ref. (36); J. Horiuti, G. Okamoto, and K. Hirota, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1936, **29**, 223.

reaction has been particularly studied by Horiuti and his co-workers;[75] results in moderate quantitative agreement with experimental observations have been obtained on this basis. If, on the other hand, III is assumed to be a fast reaction and to become of importance at surfaces largely covered with adsorbed hydrogen atoms,[76] then by making fairly plausible assumptions as to the relative participation of reactions II and III in the removal of adsorbed hydrogen, it has been found possible to account for negative deviations from the Tafel equation at high c.d.s and the approach to constant values of overpotential, for the general form of hydrogen overpotential decay, and for the observed separation coefficients of hydrogen and deuterium.[36]

It is, of course, entirely possible that the mechanism of hydrogen overpotential may be different at different metals, a point of view which has been emphasised by a number of authors.[77] So far as the present position can be summarised, it would appear that there is a fair general measure of agreement among workers in this field that at low overpotential cathodes the rate-determining stage responsible for overpotential is the formation of molecular hydrogen from adsorbed hydrogen atoms (reaction II and/or III). At high overpotential cathodes, such as mercury, there is little evidence of the presence of adsorbed hydrogen, and a considerable body of opinion holds that the slow-discharge mechanism (reaction I) is in closest agreement with the experimental observations. This dual view, which is in many ways very attractive, meets, however, with a fundamental difficulty which has not so far been resolved. If the formation of molecular hydrogen is accepted as the rate-determining step at low overpotential cathodes which are known to be good catalysts for the combination of hydrogen atoms, it is not easy to see why it should not also apply to high overpotential metals which are known to be poor catalysts for the reaction.

V. The Anodic Evolution of Oxygen

It has generally been considered that an oxygen electrode consisting of oxygen gas at a passive electrode in contact with an aqueous solution should give rise to a potential corresponding to the equilibrium

$$O_2 + 2H_2O + 4e \rightleftharpoons 4OH^-$$

and the potential of such an oxygen electrode against a hydrogen electrode (both at 1 atm. pressure) in the same solution can be calculated from thermodynamic data in a number of ways[78] and is found to be 1·23 v. at 17°; this leads to a value of + 0·40 v. for the standard potential of oxygen.

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[75] *Idem, ibid.*; J. Horiuti, *ibid.*, 1940, **37**, 274; G. Okamoto, *J. Fac. Sci. Hokkaido Imp. Univ.*, 1937, **2**, 115; see also A. Frumkin, *loc. cit.*, ref. (67); P. Lukowtsew, S. Lewina, and A. Frumkin, *Acta Physicochim. U.R.S.S.*, 1939, **11**, 21; A. Legran and S. Lewina, *ibid.*, 1940, **12**, 243; P. Dolin and B. Ershler, *ibid.*, 1940, **13**, 747; K. Rosenthal, P. Dolin, and B. Ershler, *ibid.*, 1946, **21**, 213.

[76] N. Kobosew and N. I. Nekrassow, *loc. cit.*, ref. (56).

[77] L. P. Hammett, *Trans. Faraday Soc.*, 1933, **29**, 770; F. P. Bowden and J. N. Agar, *loc. cit.*, ref. (22); J. A. V. Butler, *loc. cit.*, ref. (35).

[78] See S. Glasstone, " The Electrochemistry of Solutions ", 1945, p. 334.

Attempts to realise such a reversible oxygen electrode experimentally at room temperature have been unsuccessful;[79] in practice, the potential reached is always lower than the theoretical value and drifts with time, and it does not vary with alteration of pressure of oxygen gas in the way to be expected from the Nernst equation. The potentials at which oxygen is formed at a working anode have, therefore, usually been measured relatively to a hydrogen electrode in the same solution, and the calculated value for the reversible oxygen electrode has been used in assessing the oxygen overpotential.

TABLE II

Oxygen overpotentials (volts) in alkaline solution

c.d. (amp./sq. cm.) =	10^{-4}.	10^{-1}.	c.d. (amp./sq. cm.) =	10^{-4}.	10^{-1}.
Au	0·93	1·53	Ni	0·45	0·91
Pt	0·80	1·50	C (graphite)	0·37	1·12
Cd	0·67	1·21	Fe	0·37	0·56
Cu	0·49	0·73	Platinised Pt	0·32	0·89
Pd	0·48	1·12	Co	0·32	0·54
Ag	0·45	0·94			

Early measurements[80] indicated that oxygen overpotentials were substantial and varied considerably with the nature of the anode material. It was also found[81] that the overpotential varied very markedly with time of polarisation, and this factor, which has been ignored by many later workers, contributes to the great difficulty which has been met in obtaining reproducible values of oxygen overpotential. It has recently been shown,[82] however, that, starting with a clean metal anode and polarising at constant c.d. until the potential is steady, oxygen overpotentials reproducible to about ± 0·02 v. can be obtained, and in Table II are given the values obtained by this procedure at a number of anodes in N-potassium hydroxide at 20°;[82] the dependence of overpotential on c.d. varies considerably with different electrode materials, so that it is impossible to arrange them in

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[79] See F. Foerster, " Elektrochemie wässeriger Lösungen ", 1922, p. 200, for account of early work; N. H. Furman, *J. Amer. Chem. Soc.*, 1922, **44**, 2685; G. Tammann and F. Runge, *Z. anorg. Chem.*, 1926, **156**, 85; W. T. Richards, *J. Physical Chem.*, 1928, **32**, 990; H. V. Tartar and V. E. Wellman, *ibid.*, p. 1171; T. P. Hoar, *Proc. Roy. Soc.*, 1933, *A*, **142**, 628; H. G. Bain, *Trans. Electrochem. Soc.*, 1940, **78**, 173.

[80] See, *e.g.*, A. Coehn and Y. Osaka, *Z. anorg. Chem.*, 1903, **34**, 86; F. Foerster and A. Piguet, *Z. Elektrochem.*, 1904, **10**, 714; J. B. Westhaver, *Z. physikal. Chem.*, 1905, **51**, 65; E. Müller and F. Spitzer, *Z. anorg. Chem.*, 1906, **50**, 321.

[81] F. Foerster, *loc. cit.*, ref. (80); *Z. physikal. Chem.*, 1909, **69**, 236.

[82] A. Hickling and S. Hill, Faraday Soc. Discussion, 1947, **1**, 236. For other measurements on the influence of electrode material, see T. Onoda, *J. Chem. Soc. Japan*, 1922, **43**, 782; *Z. anorg. Chem.*, 1927, **165**, 79; M. Knobel, P. Caplan, and M. Eiseman, *Trans. Electrochem. Soc.*, 1923, **43**, 55; M. Knobel, *ibid.*, 1925, **47**, 131; M. de K. Thompson and A. L. Kaye, *ibid.*, 1931, **60**, 229; A. D. Garrison and J. F. Lilly, *ibid.*, 1934, **65**, 275; H. Hunt, J. F. Chittum, and H. W. Ritchey, *ibid.*, 1938, **73**, 299; G. Grube and W. Gaupp, *Z. Elektrochem.*, 1939, **45**, 290; M. de K. Thompson and G. H. Sistare, *Trans. Electrochem. Soc.*, 1940, **78**, 259.

any order of decreasing overpotential which will be generally valid, and hence two sets of values are given for moderate and for high c.d.s respectively.

It may be noted that oxygen overpotentials tend to be even higher than those observed with hydrogen ; gold and platinum anodes show the highest values, while those at cobalt and iron are relatively low, and there appears to be no relation whatever to the corresponding hydrogen overpotentials.

Oxygen overpotential increases with rise of c.d., and in acid solutions the dependence seems to follow a Tafel equation, b for platinum having a value in the vicinity of 0·12.[83] On this slender basis it has been supposed [22] that there is a fundamental similarity between the kinetics of oxygen and of hydrogen evolution, but it is very doubtful whether this claim can be substantiated. Thus, in alkaline solution it has been shown [82] that, although over limited ranges of c.d. the η–log I graphs for cobalt, iron, nickel, platinum, platinised platinum, palladium, silver, and copper all show agreement with an equation of the Tafel type, b varying, however, between 0·07 and 0·30, yet when the graphs are considered in their entirety a number of discrepancies are apparent. The most striking feature is that at a number of anodes, notably gold, palladium, and graphite, the graphs have a step-like character, the overpotential changing abruptly in certain specific c.d. regions ; furthermore at low c.d.s there appears to be a general tendency for the overpotentials to approach constant minimum values.

The influence of pH value and nature of electrolyte on oxygen overpotential has not been very fully investigated, and the results reported are not in agreement. Hoar [79] studied a platinum anode in sulphuric acid, neutral phosphate buffer, and dilute sodium hydroxide solution over the c.d. range 10^{-7} to 10^{-5} amp./sq. cm., and found that a Tafel relation was followed in each case, the overpotentials being nearly the same in acid and in alkali but somewhat higher in phosphate buffer. F. P. Bowden and H. W. Keenan [84] found that in alkaline solutions the overpotential decreased as the hydroxyl-ion concentration increased, while in sulphuric acid it was independent of pH value. More recently, A. Hickling and S. Hill,[85] working with fully polarised platinum, gold, and palladium anodes in N-potassium hydroxide, neutral phosphate buffer, and N-sulphuric acid over the c.d. range 10^{-5} to 1 amp./sq. cm., have found that at low c.d.s the overpotential is almost independent of pH value, but at high c.d.s increases considerably with increasing pH ; this is attended by an increase in the slopes of the η–log I graphs, and at gold and palladium with the appearance of the step-like dependence which is largely absent in acid solution. J. O'M Bockris [86] has compared oxygen overpotentials in M-sulphuric acid solutions in water, and in acetic acid–water and dioxan–water mixtures ; he finds that addition of either non-aqueous component causes an increase of overpotential, rapidly

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[83] Cf. F. P. Bowden, *Proc. Roy. Soc.*, 1929, *A*, **126**, 107 ; T. P. Hoar, *loc. cit.*, ref. (79).

[84] Quoted in ref. (22).

[85] Unpublished work ; see S. Hill, Thesis, Liverpool, 1948.

[86] Faraday Soc. Discussion, 1947, **1**, 229.

at first and then more slowly, the slopes of the Tafel lines also being increased. E. Muller [87] found that addition of sodium fluoride to an acid electrolyte considerably increased the oxygen overpotential at a platinum anode, the effect increasing with increasing fluoride concentration. This has been confirmed by more recent work; [85] the effect occurs in both acid and alkaline electrolytes, but is only apparent at relatively high c.d.s, and appears to be specific to platinum, no influence being apparent at gold, cobalt, or palladium anodes.

A number of observations of the influence of temperature on oxygen overpotential have been made.[88] In general, the overpotential is decreased by rise of temperature, and temperature coefficients of — 0·003 and — 0·002 v./degree at platinum in acid and in alkaline electrolytes have been reported.[89] Calculation of the corresponding energies of activation in the conventional way gives values of 18·7 and 25·3 kg.-cals., respectively,[89] although in view of the different slopes of the Tafel lines reported by various workers, it is doubtful how reliable these values are. Limited observations on the decay of oxygen overpotential, mainly at platinum anodes, have been made,[90] and it appears that in the long-term decay η becomes proportional to log t, as for hydrogen overpotential. It has been variously reported that oxygen overpotential is diminished by the superimposition of an alternating current,[91] and by light and X-rays,[92] but fuller investigation seems to be required before the exact significance of these results can be assessed.

Theories of Oxygen Overpotential.—From the preceding account it is apparent that speculation as to the mechanism of oxygen overpotential must be deemed premature until fuller and more reliable experimental observations are available; in particular, it is very desirable that in future experimental work due allowance should be made for the great influence of time of polarisation, and that observations should be made over extensive ranges of c.d. Such suggestions as to the origin of oxygen overpotential which have been made have been put forward largely by analogy with the more thoroughly investigated case of hydrogen overpotential; thus it has been suggested that the rate-determining stage is the neutralisation of the hydroxyl ion,[93] the heterogeneous combination of oxygen atoms to give

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[87] *Z. Elektrochem.*, 1904, **10**, 776; E. Müller and A. Scheller, *Z. anorg. Chem.*, 1905, **48**, 112; see also N. A. Isgarischev and D. V. Stepanov, *Z. Elektrochem.*, 1924, **30**, 138.

[88] F. Foerster, *loc. cit.*, ref. (81); T. Onoda, *loc. cit.*, ref. (82); F. P. Bowden, *loc. cit.*, ref. (83); V. A. Roiter and R. B. Yampolskaya, *Z. physikal. Chem.*, 1937, **9**, 763; H. P. Stout, Faraday Soc. Discussion, 1947, **1**, 246.

[89] F. P. Bowden and H. P. Stout, *locc. cit.*, ref. (88).

[90] E. Newbery, *Proc. Roy. Soc.*, 1927, *A*, **114**, 103; V. V. Picheta, *J. Gen. Chem. Russia*, 1931, **1**, 377; J. A. V. Butler and G. Armstrong, *Trans. Faraday Soc.*, 1933, **29**, 1261; A. L. Ferguson and H. Bandes, *Trans. Electrochem. Soc.*, 1942, **81**, preprint 11.

[91] See, *e.g.*, G. Grube and B. Dulk, *Z. Elektrochem.*, 1918, **24**, 237; S. Glasstone, *J. Amer. Chem. Soc.*, 1925, **47**, 940.

[92] G. Grube and J. Baumeister, *Z. Elektrochem.*, 1924, **30**, 322; F. P. Bowden, *Trans. Faraday Soc.*, 1931, **27**, 505; J. P. E. Duclaux, *Compt. rend.*, 1935, **200**, 1838.

[93] R. W. Gurney, *loc. cit.*, ref. (65); see also R. Audubert and E. T. Verdier, *Compt. rend.*, 1941, **213**, 870; R. Audubert, Faraday Soc. Discussion, 1947, **1**, 72.

gaseous oxygen,[94] the evaporation of oxygen dipoles from the anode surface,[95] and the transfer of a proton from a water molecule on the anode surface to one in the electrolyte.[68] Until further experimental data are available any detailed treatment of mechanism would seem futile, but some general points appear worthy of consideration.

Thermodynamic data now available from spectroscopic studies permit the ready calculation of the standard potentials of the hydroxyl radical and of atomic oxygen, which may be intermediates in the anodic reaction, and for these species at 1 atm. pressure the values found are + 2·01 and + 1·60 v., respectively, on the hydrogen scale in the vicinity of room temperature.[85] The maximum overpotentials to which these species could give rise at the anode would, therefore, be about 1·6 and 1·2 v., respectively. The former value is adequate to cover the range of overpotentials experimentally observed, but the latter would not account for the very high overpotentials at gold and platinum at high c.d.s. Hence it would appear that if the slow stage in the anode reaction is the combination of hydroxyl radicals, the magnitude of the observed overpotentials could be explained. The obvious way in which it might be supposed that such radicals react at the anode is

$$\left.\begin{array}{lcl} 2OH & \rightarrow & H_2O + O \\ 2O & \rightarrow & O_2 \end{array}\right\} \quad \text{followed by} \qquad (I)$$

Experimental observations on the disappearance of hydroxyl radicals in dissociated water vapour suggest, however, that this does not take place to any appreciable extent in the gaseous state, since attempts to detect atomic oxygen have been unsuccessful,[96] and it seems likely, therefore, that it would not occur at an anode. In this connection the work of W. G. Berl [97] is of great importance. He has shown that a completely satisfactory reversible oxygen electrode can be set up experimentally by bubbling oxygen through a porous carbon electrode immersed in alkaline solutions of hydrogen peroxide. The potential corresponds to the equilibrium

$$O_2 + H_2O + 2e \rightleftharpoons OH^- + HO_2^-$$

and the electrode satisfies all the criteria of reversibility ; for instance, the potential varies with the activities of the reacting species in accordance with a Nernst equation, passage of quite large currents does not displace the potential and the electrode reaction is in accordance with the postulated equation, and the standard potential of — 0·04 v. is in fair agreement with that calculated from free energy data. Since Berl's oxygen electrode involves in one direction the formation of hydroxyl ions from oxygen and water and in the other direction the discharge of hydroxyl ions, and since it is completely reversible, it suggests that there is no intrinsic slowness in the neutralisation or formation of the hydroxyl ion. It may well be, therefore, that at an anode it is the difficulty of formation of the HO_2 radical,

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[94] See F. Foerster, *op. cit.*, ref. (79), p. 335. [95] F. P. Bowden, *loc. cit.*, ref. (83).

[96] Cf. W. H. Rodebush *et al.*, *J. Chem. Physics*, 1933, **1**, 696 ; 1936, **4**, 293 ; *J. Amer. Chem. Soc.*, 1937, **59**, 1924 ; O. Oldenberg, *J. Chem. Physics*, 1935, **3**, 266.

[97] *Trans. Electrochem. Soc.*, 1943, **83**, 253.

with which the hydroxyl radical can react, which is the cause of overpotential, and it has been found experimentally [85] that the addition of small amounts of hydrogen peroxide to the electrolyte causes an immediate drop in oxygen overpotential. Two ways in which hydroxyl radicals might interact at an anode are

$$\left.\begin{array}{lcl} OH + OH & \rightarrow & H_2O_2 \\ OH + H_2O_2 & \rightarrow & H_2O + HO_2 \\ OH + HO_2 & \rightarrow & H_2O + O_2 \end{array}\right\} \quad . \quad . \quad . \quad (II)$$

or reaction might take place between a free hydroxyl radical and one adsorbed upon the oxidised metal surface, thus

$$\left.\begin{array}{rcl} MeO + OH & \rightarrow & MeO\cdots OH \\ MeO\cdots OH + OH & \rightarrow & Me + H_2O + O_2 \end{array}\right\} \quad . \quad . \quad . \quad (III)$$

followed by re-oxidation of the metal, but these mechanisms must at present be regarded as entirely speculative.

VI. Electrolytic Oxidation and Reduction Processes

Anodic oxidation and cathodic reduction reactions are very numerous and varied in character, and it is possible here only to indicate some of their outstanding features.[98] They may be divided into two classes involving reactions which are thermodynamically reversible and irreversible, respectively. In the first category the process takes place at a definite potential almost the same as the reversible oxidation–reduction potential of the system, and provided this is not close to the oxygen or hydrogen evolution potential and that the c.d. is below the limiting value as determined by diffusion of the depolariser to the electrode, the current efficiency is largely independent of experimental variables such as the nature of the electrode material, temperature, and the addition of foreign substances to the electrolyte. Most oxidations and reductions of inorganic ions, involving a simple one- or two-electron transfer, fall into this category, as illustrated by the Fe^{++}/Fe^{+++}, $Fe(CN)_6^{----}/Fe(CN)_6^{---}$, and Tl^{+}/Tl^{+++} systems, and the working electrodes may here be conveniently regarded as merely removing or supplying electrons respectively. When, however, the electrode reaction is thermodynamically irreversible, as seems to be the case with some inorganic and organic ions and most undissociated organic substances, the position is very different. In this case the potential of the working electrode may not be dependent in any simple way upon the depolariser which is being oxidised or reduced, and the current efficiency of the process may vary in a very complex manner with alteration of experimental factors ; in many of these reactions it seems very probable that some chemical oxidising or reducing agent primarily formed at the electrodes brings about the process observed.

A particular type of anodic oxidation which has attracted much attention in recent years is that which involves the polymerisation of anions.

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[98] See S. Glasstone and A. Hickling, *op. cit.*, ref. (26), for full account and complete references up to 1935.

Examples of this kind of reaction are the formation of tetrathionate from thiosulphate ions

$$2S_2O_3^{--} \quad - \quad 2e \quad \rightarrow \quad S_4O_6^{--}$$

of persulphate from sulphate ions

$$2SO_4^{--} \quad - \quad 2e \quad \rightarrow \quad S_2O_8^{--}$$

of ethane and carbon dioxide from acetate ions (Kolbe reaction)

$$2CH_3{\cdot}CO{\cdot}O^- \quad - \quad 2e \quad \rightarrow \quad C_2H_6 + 2CO_2$$

and of diethyl succinate and carbon dioxide from ethyl malonate ions (Crum Brown–Walker synthesis)

$$2C_2H_5{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}COO^- - 2e \quad \rightarrow \quad C_2H_5{\cdot}O{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}OC_2H_5 + 2CO_2$$

Such reactions can be formulated electronically as above, and at first sight it seems reasonable to suppose that they take place by complete or partial neutralisation of the ions at the anode, followed by interaction of the radicals produced. Where the anodic oxidations can be brought about in non-aqueous solutions [99] the phenomena observed are in reasonable agreement with this view, although the anodic potentials are much higher than those calculated from free-energy data, implying that some stage in the reactions is slow. In aqueous solution, however, a very different state of affairs is manifest ; here the current efficiency is very markedly dependent upon the nature of the anode material and upon temperature, and can be greatly affected by the addition of foreign substances to the electrolyte ; furthermore, side reactions leading to different products frequently occur. S. Glasstone and A. Hickling [100] studied the thiosulphate oxidation, and found that small amounts of substances sharing the common property of being catalysts for hydrogen peroxide decomposition, if added to the electrolyte, brought about a very great diminution in the efficiency of tetrathionate formation, in some cases reducing it to zero, and in general there appeared to be a close correlation between the current efficiency and the likely stability of hydrogen peroxide under the experimental conditions. Mainly on this basis, they put forward a theory of electrolytic oxidation which has been applied to a large number of anodic oxidations.[101] According to this view, in aqueous solution hydroxyl ions are considered to discharge at low potentials to form hydroxyl radicals which combine irreversibly to give hydrogen peroxide. This may then react with a depolariser, if present, bringing about its own characteristic oxidation, or it may decompose to give oxygen and water, thus :

$$\begin{tikzcd} & & & \text{Oxidation of depolariser} \\ 2OH^- - 2e \arrow[r] & 2OH \arrow[r] & H_2O_2 \arrow[ur] \arrow[dr] & \\ & & & H_2O + \tfrac{1}{2}O_2 \end{tikzcd}$$

Different types of oxidation may be brought about by products arising from the decomposition of hydrogen peroxide, such as oxygen or metallic oxides

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[99] Cf. S. Glasstone and A. Hickling, *J.*, 1936, 820 ; A. Hickling and J. V. Westwood, *J.*, 1939, 1109 ; S. Glasstone, V. V. Barr, and B. O. Heston, *Trans. Electrochem. Soc.*, 1943, **84**, preprint 10.

[100] *J.*, 1932, 2345, 2800.

[101] See S. Glasstone and A. Hickling, *Chem. Reviews*, 1939, **25**, 407, for general account ; also, *Trans. Electrochem. Soc.*, 1939, **75**, 333 ; A. Hickling and S. H. Richards, *J.*, 1940, 256 ; A. Hickling and F. Rodwell, *J.*, 1943, 90.

formed with the anode material. The anode potentials, which often display peculiar features,[102] are considered to be set up indirectly by the accumulation of oxygen at the anode, or, in some cases by the formation of electromotively active radicals in the oxidation reaction. This hydrogen peroxide theory has been very successful in giving a detailed interpretation of the features of a large number of electrolytic oxidations, but it meets with a number of general difficulties and has been adversely criticised by several authors.[103] For instance, it is not always possible to imitate the results of electrolytic oxidation by chemical oxidation with hydrogen peroxide, and hydrogen peroxide itself tends to be destroyed at an anode; furthermore, it is not clear how the theory in its original form can be connected with the mechanism of oxygen overpotential. Other suggestions which have been made are that the effective oxidising agent at an anode is the hydroxyl radical,[104] or atomic oxygen,[105] but little attempt has yet been made to apply these ideas to the detailed explanation of electrolytic oxidation.

Irreversible electrolytic reduction processes mainly involve undissociated organic substances, although some inorganic reactions, such as the reduction of nitric acid and nitrates to hydroxylamine and ammonia, and of sulphites to hyposulphites (dithionites), are probably irreversible. In general, it is found that the most important factor in determining the course of a cathodic reduction is the cathode potential,[106] and usually reduction occurs most readily and is most intense at cathodes of high overpotential such as mercury and lead, and is least at cathodes of low overpotential such as platinum and nickel, although this is the reverse of the catalytic influence of these metals in chemical hydrogenation processes. It has also been shown that poisoning of low-overpotential cathodes will sometimes improve their efficiencies as reducing agents.[107]

The mechanism of irreversible electrolytic reduction has generally been regarded as involving the formation of atomic hydrogen which reacts chemically with the depolariser, and this simple view seems to be in good agreement with experimental observations in most cases. Thus if the substance to be reduced is represented as RO, and the reduction consists in the removal of oxygen, the possible cathodic reactions would be

$$2\mathrm{H}^+ + 2e \longrightarrow 2\mathrm{H} \begin{array}{l} \nearrow \mathrm{H}_2 \\ \overset{\mathrm{RO}}{\searrow} \mathrm{R} + \mathrm{H}_2\mathrm{O} \end{array}$$

Hence the current efficiency of the reduction process would be determined

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[102] Cf. A. Hickling, Faraday Soc. Discussion, 1947, **1**, 227.

[103] O. J. Walker and J. Weiss, *Trans. Faraday Soc.*, 1935, **31**, 1011; J. A. V. Butler and W. M. Leslie, *ibid.*, 1936, **32**, 435; W. D. Bancroft, *Trans. Electrochem. Soc.*, 1937, **71**, 195; M. Haissinsky, Faraday Soc. Discussion, 1947, **1**, 254.

[104] Cf. A. Klemenc, *Z. physikal. Chem.*, 1939, **185**, 1; S. Glasstone, *Trans. Electrochem. Soc.*, 1943, **84**, preprint 10.

[105] Cf. F. Fichter, *J. Soc. Chem. Ind.*, 1929, **48**, 325T, 341T, 347T.

[106] See, *e.g.*, F. Haber, *Z. Elektrochem.*, 1898, **4**, 506; F. Haber and K. Schmidt, *Z. physikal. Chem.*, 1900, **32**, 271; N. Kobosew and N. I. Nekrassow, *loc. cit.*, ref. (56).

[107] W. M. Monblanova, N. Kobosew, and P. S. Phillippovich, *Acta Physicochim. U.R.S.S.*, 1939, **11**, 317.

by the competition between the latter and hydrogen evolution, and any factor tending to raise the hydrogen overpotential would favour the reduction reaction. Thus at high overpotential cathodes the concentration of atomic hydrogen is high, according to this view, and the combination of hydrogen atoms is slow, and hence reduction tends to be more efficient and intense. Most of the phenomena of cathodic reduction can be qualitatively explained on this theory. This mechanism, however, presupposes that it is the combination of hydrogen atoms which is the slow stage responsible for hydrogen overpotential. If the rate-determining stage is that involving the discharge of a hydrogen ion or the transfer of a proton to the cathode surface, it is by no means clear why high overpotential cathodes should be such good reducing agents. The reduction processes can, of course, be formally represented without involving atomic hydrogen, as

$$RO + 2H^+ + 2e \longrightarrow R + H_2O$$

and it might be suggested that the depolariser is adsorbed on the cathode surface and becomes negatively charged and then reacts directly with hydrogen ions, thus :

$$RO^{--} + 2H^+ \longrightarrow R + H_2O$$

The competing processes might then be the transfer of a proton to the metal cathode leading to hydrogen evolution, and the transfer to an adsorbed molecule of depolariser resulting in reduction. Although there is nothing intrinsically improbable in such a mechanism, it can only be regarded at present as highly speculative, and the atomic hydrogen view undoubtedly affords the more generally useful practical theory.

VII. Cathodic Deposition and Anodic Dissolution of Metals

It is possible here only to touch very briefly upon certain limited aspects of metal deposition and dissolution.

The mechanism of metal deposition has generally been considered [108] as consisting of two main stages : (*a*) the discharge of the metal ions, and (*b*) their incorporation in the metal lattice, although some authors [109] have regarded these processes as occurring simultaneously, the ions being discharged at favourable points on the cathode surface requiring the least discharge potential. If either of the processes (*a*) or (*b*) is slow, then overpotential might be expected to occur. In practice it is found that, when concentration polarisation is allowed for, the cathodic deposition of a metal usually takes place very close to the reversible potential, implying that all stages in the process are rapid and occur without difficulty. An exception to this is afforded by the transition elements iron, cobalt, and nickel, where appreciable overpotentials are observed even at very low c.d.s.[110] This is

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[108] For useful reviews of the mechanism of metal deposition, see L. B. Hunt, *J. Physical Chem.*, 1932, **36**, 1006, 2259 ; F. Müller, *Z. Elektrochem.*, 1937, **43**, 812 ; J. A. V. Butler, *op. cit.*, ref. (35), p. 166 ; G. E. Gardam, Faraday Soc. Discussion, 1947, **1**, 182.

[109] Cf. W. Blum and H. S. Rawdon, *Trans. Electrochem. Soc.*, 1923, **44**, 397 ; K. Frölich and G. L. Clark, *Z. Elektrochem.*, 1925, **31**, 649.

[110] A. Schweitzer, *ibid.*, 1909, **15**, 602 ; R. Schildbach, *ibid.*, 1910, **16**, 967 ; F. Foerster, *Abh. Bunsen Ges.*, 1909, No. 2 ; S. Glasstone, *J.*, 1926, 2887 ; F. Foerster

shown by the figures in Table III for the deposition overpotentials from N-solutions of the metal sulphates at various temperatures.[111]

TABLE III

Metal deposition overpotentials (volts)

	15°.	55°.	95°.
Fe	0·22	0·03	0·00
Co	0·28	0·18	0·08
Ni	0·34	0·20	0·06

The overpotentials are very markedly reduced by rise of temperature, but do not appear to vary very much with c.d. Various suggestions have been made as to the nature of the slow stage responsible for these overpotentials. For instance it has been suggested that it may be the initial discharge of the ions,[112] the conversion of an unstable form of the metal initially deposited into the stable form,[113] and the incorporation of the metal ions after discharge into the crystal lattice,[114] and many of the theories regard the hydrogen which accompanies the deposition of these metals as having an important retarding influence. In the present state of the subject it does not appear possible to arrive at any final conclusion.

Very small overpotentials have been reported [115] in the deposition of metals such as silver, copper, lead, cadmium, and zinc from their salt solutions, and in general it has been found that the overpotential is proportional to the c.d. while this is low; with higher c.d.s the overpotential increases less readily and may tend to a logarithmic dependence upon c.d. Attempts have been made to correlate the dependence with particular slow stages in the electrode reaction, but it appears difficult to arrive at a definite conclusion.[116] Where the cathodic deposition of a metal takes place on an electrode of a different kind, initially a substantial overpotential may be necessary,[117] but this usually decreases greatly as soon as a thin film of the electrodeposited metal is formed.

When a metal is made anodic in a suitable aqueous solution, dissolution

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and K. Georgi, *Z. physikal. Chem.*, Bodenstein Festband, 1931, 453; N. Thon, *Compt. rend.*, 1932, **197,** 1312; V. Roiter and V. Jusa, *Acta Physicochim. U.R.S.S.*, 1936, **4,** 135; V. Roiter, V. Jusa, and E. S. Poluyan, *ibid.*, 1939, **10,** 389.

[111] S. Glasstone, *loc. cit.*, ref. (110).

[112] See, *e.g.*, F. Foerster, *Z. Elektrochem.*, 1916, **22,** 85; N. Thon, *loc. cit.*, ref. (110).

[113] See, *e.g.*, V. Kohlschütter, *Trans. Electrochem. Soc.*, 1924, **45,** 229; S. Glasstone *loc. cit.*, ref. (110).

[114] T. Erdey-Grúz and M. Volmer, *Z. physikal. Chem.*, 1931, **157,** 165; see also L. B. Hunt, *Trans. Electrochem. Soc.*, 1934, **65,** 413.

[115] T. Erdey-Grúz and M. Volmer, *loc. cit.*, ref. (114); T. Erdey-Grúz, *Z. physikal. Chem.*, 1935, **172,** 157; T. Erdey-Grúz and E. Frankl, *ibid.*, 1936, **178,** 266; T. Erdey-Gruz and R. Kardos, *ibid.*, p. 255; O. A. Essin and A. Levin, *J. Gen. Chem. Russia*, 1936, **6,** 1539; O. A. Essin, L. Antropov, and A. Levin, *Acta Physicochim. U.R.S.S.*, 1937, **6,** 447.

[116] Cf. J. A. V. Butler, *loc. cit.*, ref. (108).

[117] T. Erdey-Grúz and M. Volmer, *Z. physikal. Chem.*, 1931, **157,** 182; T. Erdey-Gruz and H. Wick, *ibid.*, 1932, **162,** 63.

usually takes place at potentials only slightly more positive than the reversible value when concentration polarisation is avoided, and the reaction can be regarded simply as the passage of metallic ions from the electrode to the solution ; iron, cobalt, and nickel anodes are again exceptional in showing appreciable irreversibility in the ionisation process.[110] Under appropriate conditions, however, most metallic anodes may become passive, and metal dissolution may be largely replaced by some other process, usually oxygen evolution. The conditions governing the onset of passivity have been largely clarified by the systematic investigations of W. J. Müller and his co-workers, and of Hedges.[118] In general it appears that in the initial stages of passivity the corrosion product, usually a metallic normal or basic salt, tends to accumulate in the vicinity of the anode, and eventually may separate out upon the electrode surface ; when this happens the covered portions of the anode are shielded and the effective c.d. at the exposed parts is raised with corresponding increase of potential until hydroxyl-ion discharge can occur. This may lead to the production of a thin invisible oxide film, if the metallic oxide is a protective one and the film impermeable to metallic ions, which grows under the previously formed salt film, the latter stripping off when oxygen evolution commences, leaving the anode in a clean but passive state. The presence of an oxide film upon passive anodes has been confirmed in more recent work using charging-curve methods under conditions such that passivity sets in almost at once. Thus with platinum and gold anodes,[119] which appear inactive in most solutions, it has been shown that oxide formation begins at the reversible Pt/PtO and Au/Au_2O_3 potentials, and oxygen evolution only commences when an approximately unimolecular film of oxide has been formed ; with gold anodes in chloride solutions, the onset of oxide formation is apparently dependent upon the depletion of chloride ions in the vicinity of the anode.[120] With anodes of nickel, silver, copper, and iron in alkaline solution, again the passivity seems to be accompanied by the formation of an oxide film, the initial thickness when oxygen evolution first begins varying with the metal and with experimental conditions.[121] An interesting anodic phenomenon which has attracted much attention is that of electrolytic polishing. This can be brought about at many anodes in the unstable potential region immediately before oxygen evolution ; it is apparently a differential dissolution effect, projecting points upon the metal surface undergoing particularly rapid corrosion, but in spite of much investigation its precise mechanism is still obscure.[122]

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[118] For reviews and references, see W. J. Müller, *Trans. Faraday Soc.*, 1931, **27**, 736 ; E. S. Hedges, " Protective Films on Metals ", 1932, Chap. 6 ; U. R. Evans, " Metallic Corrosion Passivity and Protection ", 1946, Chap. 1.

[119] Cf. A. Hickling, *Trans. Faraday Soc.*, 1945, **41**, 333 ; 1946, **42**, 518.

[120] Cf. J. A. V. Butler and J. D. Pearson, *ibid.*, 1938, **34**, 806.

[121] See, *e.g.*, A. Hickling and J. E. Spice, *ibid.*, 1947, **43**, 762 ; A. Hickling and D. Taylor, *ibid.*, 1948, **44**, 262 ; Faraday Soc. Discussion, 1947, **1**, 277 ; B. Kabanov, R. Burstein, and A. Frumkin, *ibid.*, p. 259.

[122] For full reviews with references to the extensive literature, see P. A. Jacquet, Proc. 3rd Int. Electrodep. Conference, 1947, 3 ; R. E. Halut, *ibid.*, p. 15.