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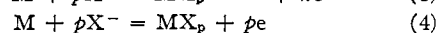
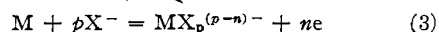
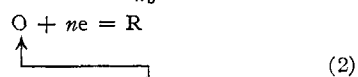
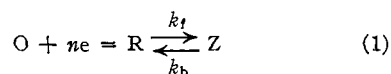
Theory of Voltammetry at Constant Current. IV. Electron Transfer Followed by Chemical Reaction

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In Part I the properties of potential-time curves for electrode processes in which electron transfer is followed by a chemical transformation are established from the rigorous solution of the corresponding boundary value problem. In Part II the transition time for catalytic processes in which the catalytic process is a first-order chemical process is derived, and the validity of this theoretical analysis is verified for the catalytic reduction of Ti(IV) in presence of hydroxylamine. In Part III properties of potential-time curves for the anodic oxidation of a metal with formation of a complex ion are established and verified experimentally for the anodic oxidation of silver in potassium cyanide. In Part IV potential-time curves for the anodic oxidation of a metal with the formation of a precipitate are discussed and studied experimentally in the case of the oxidation of silver in halide solutions. Transition times for spherical diffusion and for linear diffusion with partial mass transfer by migration in an electric field of constant intensity are derived in the Appendix by Gleb Mamantov and one of the authors (P.D.).

Theoretical treatments of various electrode processes in voltammetry at constant current were previously reported.^{1,2} The theory of other processes in which the electron transfer is followed by chemical reaction is reported here. The processes represented by the following symbolic equations will be considered



where O is a reducible substance and R its product of reduction; Z is a substance which is not reduced or oxidized at the potentials at which the reduction of O occurs; M is a metal, and X⁻ is either a complex forming substance or an ion which forms the insoluble substance MX_p. Properties of the potential-time curves corresponding to these processes will be derived for the case in which mass transfer is solely controlled by linear diffusion; migration of the electrolyzed species is made negligible by the addition of a large excess of supporting electrolyte, and convection is minimized by the use of a horizontal working electrode and by limiting the duration of electrolysis to 1-2 minutes.

Electrode processes without any kinetic complication and with mass transfer controlled either by spherical diffusion or by linear diffusion and migration are treated in the appendix.

Part I. Kinetic Processes Represented by Equation 1

The Boundary Value Problem.—The variations of the concentration of substance O during electrolysis are not affected by the kinetics of the chemical reaction R ⇌ Z, and consequently the value of the concentration C_O(0, t) at the electrode

(1) (a) P. Delahay and T. Berzins, *THIS JOURNAL*, **75**, 2486 (1953); (b) T. Berzins and P. Delahay, *ibid.*, **75**, 4205 (1953); (c) P. Delahay and C. C. Mattax, *ibid.*, **76**, 874 (1954); (d) P. Delahay, *Disc. Faraday Soc.*, in press (1954).

(2) For a general discussion and bibliography, see P. Delahay "New Instrumental Methods in Electrochemistry," Interscience Publ. Co., New York, N. Y., 1954, Chapter VIII.

surface, as derived by Sand,³ is still valid. Thus

$$C_O(0, t) = C^0 - \frac{2i_0 t^{1/2}}{\pi^{1/2} n F D_O^{1/2}} \quad (5)$$

where t is the time elapsed since the beginning of electrolysis, C⁰ the bulk concentration of reducible substance, i₀ the current density, F the faraday, and D_O the diffusion coefficient of substance O. The notation C_O(0, t) indicates that the concentration of substance O is taken at x = 0, x being the distance from the electrode. The transition time τ, which is defined by the condition C_O(0, t) = 0, or by the relationship

$$\tau^{1/2} = \frac{\pi^{1/2} n F D_O^{1/2} C^0}{2i_0} \quad (6)$$

does not depend on the kinetics of a reaction in which R might be involved.

The equation of the potential-time curve is derived by introducing C_O(0, t) and C_R(0, t) in the equation for the electrode potential. If the electron transfer is totally irreversible, the potential of the working electrode is independent of C_R(0, t), and the potential-time curve is not affected by the transformation R ⇌ Z. If the process is reversible, the potential is given by the Nernst equation, where both C_O(0, t) and C_R(0, t) appear; in that case the potential depends on the kinetics of the reaction R ⇌ Z. The concentration C_R(0, t) can be derived as follows. If the transformation R ⇌ Z is of the first order, substances R and Z obey the following modified forms of Fick's equation

$$\partial C_R(x, t) / \partial t = D_R \partial^2 C(x, t) / \partial x^2 - k_f C_R(x, t) + k_b C_Z(x, t) \quad (7)$$

$$\partial C_Z(x, t) / \partial t = D_Z \partial^2 C(x, t) / \partial x^2 + k_f C_R(x, t) - k_b C_Z(x, t) \quad (8)$$

where the k's are formal rate constants. The first boundary condition is obtained by noting that substance R is produced at the electrode surface at constant flux. Thus

$$D_R [\partial C_R(x, t) / \partial x]_{x=0} = -i_0 / n F \quad (9)$$

The second boundary condition expresses that Z is not reduced or oxidized at the electrode; hence the flux of this substance is equal to zero at x = 0, *i.e.*

$$D_Z [\partial C_Z(x, t) / \partial x]_{x=0} = 0 \quad (10)$$

As initial condition one can prescribe C_R(x, 0) =

(3) H. J. S. Sand, *Phil. Mag.*, **1**, 45 (1901).

$C_Z(x, 0) = 0$. Finally, one has $C_R(x, t) \rightarrow 0$ and $C_Z(x, t) \rightarrow 0$ for $x \rightarrow \infty$.

The solution of this boundary value problem is obtained by the Laplace transformation, and the concentration $C_R(0, t)$ is

$$C_R(0, t) = \frac{i_0}{nFD^{1/2}} \frac{K}{1+K} \left\{ \frac{2t^{1/2}}{\pi^{1/2}K} + \frac{\text{erf}[(k_f + k_b)^{1/2}t^{1/2}]}{(k_f + k_b)^{1/2}} \right\} \quad (11)$$

where K is the equilibrium constant for $R \rightleftharpoons Z$ ($K = k_f/k_b$), and D is the common value of D_R and D_Z which are assumed to be equal.

Potential-Time for Reversible Processes.—By applying the Nernst equation one deduces the electrode potential from 5 and 11. It is useful to introduce the transition time (equation 6) in the equation for the potential, which takes then the form

$$E = E_{1/2} - \frac{RT}{nF} \ln \Xi + \frac{RT}{nF} \ln \frac{\tau^{1/2} - t^{1/2}}{t^{1/2}} \quad (12)$$

with

$$E_{1/2} = E^0 + \frac{RT}{nF} \ln \frac{f_0 D_R^{1/2}}{f_R D_O^{1/2}} \quad (13)$$

and

$$\Xi = \frac{1}{1+K} + \frac{\pi^{1/2}K}{2(1+K)} \frac{\text{erf}[(k_f + k_b)^{1/2}t^{1/2}]}{(k_f + k_b)^{1/2}} \quad (14)$$

In equation 13 E^0 is the standard potential for the couple O-R, and the f 's are the activity coefficients. If one deletes the term in Ξ , equation 12 is identical to the equation derived by Karaoglanoff⁴ for the case of a reversible process without kinetic complication. The influence of the term in Ξ is apparent from Fig. 1, which was constructed for the following data: $E_{1/2} = 0$ volt, $K = 10^3$, $\tau = 0.1$ sec. It is seen that the potential-time curve is

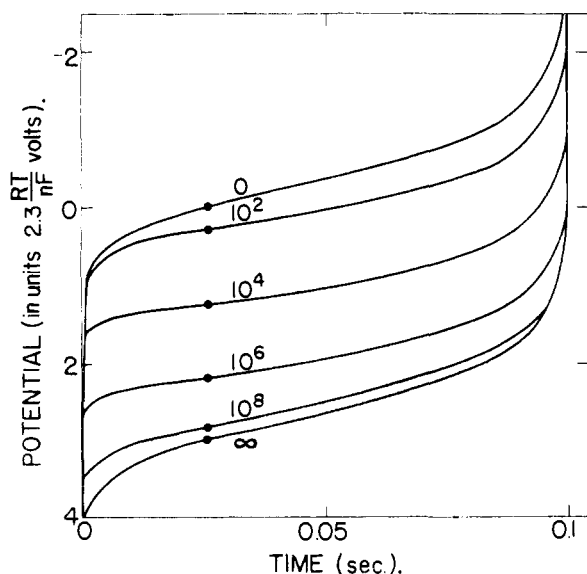


Fig. 1.—Potential-time curves for a kinetic process represented by equation 1. Number of each curve is the value of k_f in sec^{-1} . Solid circle indicates the potential at $\tau/4$.

(4) Z. Karaoglanoff, *Z. Elektrochem.*, **12**, 5 (1906). The Nernst equation can be applied although a current flows through the cell and thermodynamic equilibrium is not achieved. It can be shown that kinetic equations reduce to the Nernst equation when the rate constant for electron transfer at the standard potential is sufficiently large.

shifted toward more anodic potentials as the transformation R to Z becomes more rapid. This is to be expected since the concentration of R at the electrode surface decreases when k_f increases (K being constant). Note also that potential-time curves for values of k_f comprised between 0 and ∞ are somewhat distorted.

Influence of Current Density.—It is convenient to characterize the position of the potential-time curve by the potential $E_{\tau/4}$ at one-fourth of the transition time. This potential is equal to the sum of the first two terms on the right-hand side in 12. The variations of $E_{\tau/4}$ with current density are determined by the dependence of Ξ on current density. Two extreme cases will be first considered according to whether the current density is very low or very high.

When the current density is sufficiently low, the argument of the error function for $t = \tau/4$ in (14) is larger than 2. The second term on the right-hand of (14) virtually vanishes for sufficiently large values of $(k_f + k_b)^{1/2}(\tau/4)^{1/2}$, and $E_{\tau/4}$ is practically equal ($K \gg 1$) to $E_{1/2} + (RT/nF) \ln K$; equilibrium for the reaction $R \rightleftharpoons Z$ is then established. When the current density is sufficiently large, the argument of the error function is smaller than 0.1. The error function can then be expanded (for small arguments), and Ξ approaches the value $1 + 1/(1+K)$ as i_0 increases; $E_{\tau/4}$ is simply equal to $E_{1/2}$ ($K \gg 1$). The transition time is then so short that the transformation $R \rightarrow Z$ does not take place to any appreciable extent.

There is an intermediate range of current densities in which Ξ is proportional to current density. Thus, if one has $(k_f + k_b)^{1/2}(\tau/4)^{1/2} > 2$ and $K \gg 1$, Ξ is inversely proportional to $(\tau/4)^{1/2}$; since $(\tau/4)^{1/2}$ is inversely proportional to current density (see equation 6), it follows from equations 12 and 14 that E is a linear function of $\ln i_0$. The rate constant k_f can be obtained from the slope of this line (equation 14, $k_f \gg k_b$).

Only a few kinetic processes represented by equation 1 have been reported thus far.⁵ The occurrence of a kinetic process was deduced by polarography in these cases. No rigorous treatment of polarographic waves corresponding to process (1) has been reported so far, but Kern⁶ gave an approximate treatment and Kivalo⁷ has announced the development of such a treatment.⁸ It is quite likely that such kinetic processes are not rare in organic chemistry, and voltammetry at constant current might be a suitable tool for studying them.

Part II. Catalytic Processes Represented by Equation 2

The Boundary Value Problem.—Because of the occurrence of the reaction $R + Z = O$, kinetic terms must be added to Fick's equation. Modified equations will be written for the case in which there is a large excess of Z; C_Z is then equal to C_Z^0 for any value of x and t . The condition under which this hypothesis is valid will be derived below. It will also be assumed that the backward chemical reaction can be neglected. Thus

$$\frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C(x,t)}{\partial x^2} + k_f C_Z^0 C_R(x,t) \quad (15)$$

$$\frac{\partial C_R(x,t)}{\partial t} = D_R \frac{\partial^2 C(x,t)}{\partial x^2} - k_f C_Z^0 C_R(x,t) \quad (16)$$

where k_f is a formal rate constant.

The boundary conditions

$$D_O \left[\frac{\partial C_O(x,t)}{\partial x} \right]_{x=0} + D_R \left[\frac{\partial C_R(x,t)}{\partial x} \right]_{x=0} = 0 \quad (17)$$

$$D_O \left[\frac{\partial C_O(x,t)}{\partial x} \right]_{x=\infty} = i_0/nF \quad (18)$$

express that the sum of the fluxes of O and R at $x = 0$ are equal and that the flux of O at the electrode

(5) (a) L. I. Smith, I. M. Kolthoff, S. Wawzonek and P. M. Ruoff, *THIS JOURNAL*, **63**, 1018 (1941); (b) Z. Vavrin, *Collection Czech. Chem. Commun.*, **14**, 367 (1949); (c) F. Santavy, *ibid.*, **15**, 112 (1950); (d) R. Brdicka and P. Zuman, *ibid.*, **15**, 766 (1950).

(6) D. M. H. Kern, *THIS JOURNAL*, **75**, 2473 (1953).

(7) P. Kivalo, *ibid.*, **75**, 3286 (1953).

(8) After completion of this manuscript a rigorous treatment for linear diffusion by D. M. H. Kern appeared in *ibid.*, **76**, 1011 (1954).

surface is constant, respectively. As initial condition one prescribes $C_O(x, 0) = C^0$ and $C_R(x, 0) = 0$. Furthermore, the functions $C_O(x, t)$ and $C_R(x, t)$ are bounded for $x \rightarrow \infty$: $C_O(x, t) \rightarrow C^0$ and $C_R(x, t) \rightarrow 0$ for $x \rightarrow \infty$.

The function $C_O(0, t)$ is derived by using the Laplace transformation, and the following result is obtained on the assumption that D_O and D_R are equal

$$C_O(0, t) = C^0 - \frac{i_0 \operatorname{erf}[(k_f C_Z^0 t)^{1/2}]}{n F D^{1/2} (k_f C_Z^0)^{1/2}} \quad (19)$$

where D represents the common value of D_O and D_R .

Transition Time.—The transition time τ_c is obtained from (19) by prescribing the condition $C_O(0, \tau_c) = 0$. The resulting equation can be modified by introducing the transition time τ_d which would be obtained in the absence of any catalytic effect; the time τ_d is given by equation 6. After a simple transformation one derives

$$\left(\frac{\tau_c}{\tau_d}\right)^{1/2} = \frac{2\gamma}{\pi^{1/2} \operatorname{erf}(\gamma)} \quad (20)$$

where

$$\gamma = (k_f C_Z^0 \tau_c)^{1/2} \quad (21)$$

Values of the function on the right-hand side of (20) are plotted against γ in Fig. 2. Equation 20 can be applied to the determination of the rate constant k_f if τ_c and τ_d are known. The value of the function in the right-hand member in (20) is then known, and the argument can be read in a table of this function.⁹

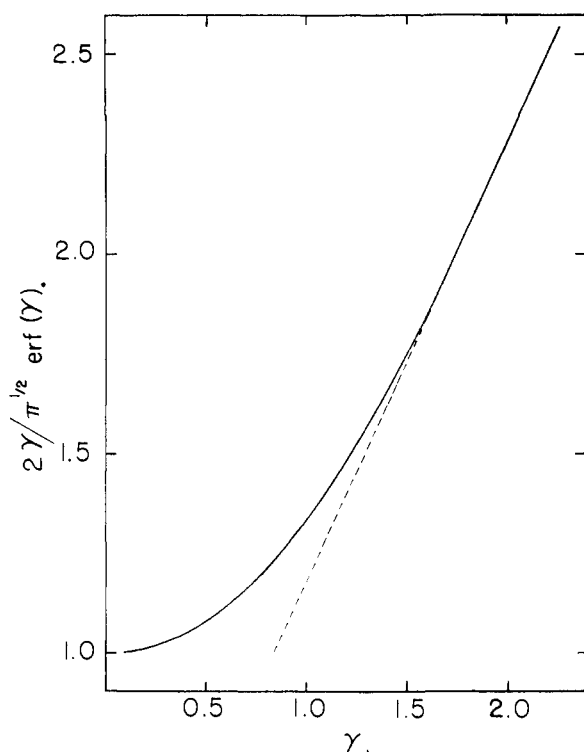


Fig. 2.—Variations of the function $2\gamma/[\pi^{1/2} \operatorname{erf}(\gamma)]$ with γ . Dotted line is asymptote.

It was assumed in the above derivation that $C_Z(x, t) = C_Z^0$. The condition under which this

(9) A detailed table is given in the doctoral thesis of C. C. Mattax (June, 1954).

assumption is valid can be established readily by considering the fictitious transition time τ_Z which should be observed if substance Z were directly reduced. The time τ_Z is given by equation 6 in which C^0 is made equal to C_Z^0 . Concentration polarization for Z is negligible if $\tau_Z \gg \tau_c$, or in view of (6) and (20), when the following condition is fulfilled.

$$C_Z^0 \gg C^0 (\tau_c / \tau_d)^{1/2} \quad (22)$$

Influence of Current Density.—The function of γ in equation 20 is equal to unity for $\gamma = 0$ as one can ascertain by expanding the error function for small arguments. Hence, the ratio $(\tau_c / \tau_d)^{1/2}$ approaches unity as $k_f C_Z^0$ or τ_c decreases. Since τ_c decreases when the current density is increased, $(\tau_c / \tau_d)^{1/2}$ approaches unity for sufficiently high current densities. Conversely, one has $(\tau_c / \tau_d)^{1/2} \rightarrow \infty$ for $i_0 \rightarrow 0$.

The foregoing considerations are essentially borne out experimentally in the catalytic reduction of Ti(IV) in presence of hydroxylamine. The kinetics of this reaction was studied by Blazek and Koryta¹⁰ by polarography. Hydroxylamine is reduced in a one-electron rate determining step provided that the NH_2 radicals formed are removed by a substance (oxalic acid) present in large excess.¹¹ Experimental results are summarized in Fig. 3 in which $(\tau_c / \tau_d)^{1/2}$ is plotted against current density (see also "Experimental"). Line 1 represents the average relative value of $i_0^{1/2}$ in the absence of hydroxylamine. This line is horizontal as one would expect from equation 6 for a process in which there is no chemical reaction. Curves 2 and 3 represent the variations of $(\tau_c / \tau_d)^{1/2}$ with current density as calculated for $k_f = 30$ l. mole⁻¹ sec.⁻¹. The agreement is fairly good if one takes into account that rather poorly defined transition times were obtained. The above value of k_f for 30° is somewhat lower than the datum $k_f = 42$ l. mole⁻¹ sec.⁻¹ reported by Blazek and Koryta.¹⁰ We repeated the polarographic determinations of these authors and confirmed their results. The discrepancy between the two results probably can be ascribed to the poor definition of potential-time curves and the resulting error on transition times.

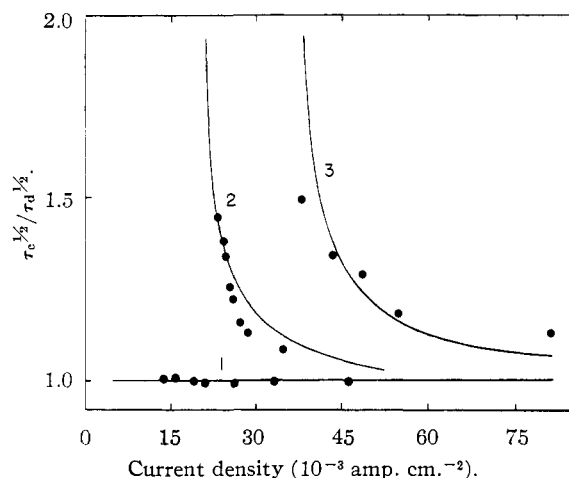


Fig. 3.—Variations of $(\tau_c / \tau_d)^{1/2}$ with current density for the catalytic reduction of Ti(IV) in presence of hydroxylamine: curve 1, no hydroxylamine (see explanation in text); curve 2, 0.49 *M* hydroxylamine; curve 3, 1.46 *M*.

Catalytic processes represented by equation 2 can also be studied by polarography and various treatments, among which the one of Koutecky¹² is the most rigorous, have been advanced. The only real advantage of voltammetry at

(10) A. Blazek and J. Koryta, *Collection Czechoslov. Chem. Commun.*, **18**, 326 (1953).

(11) P. Davis, M. G. Evans and W. C. E. Higginson, *J. Chem. Soc.*, 2563 (1951).

(12) J. Koutecky, *Collection Czechoslov. Chem. Commun.*, **18**, 311 (1953).

constant current over polarography is that catalytic processes, which cannot be studied with a mercury electrode, can be investigated.

Part III. Anodic Oxidation of a Metal with Formation of a Complex (Equation 3)

Consider the anodic oxidation of a metal M with the formation of a complex $MX_p^{(p-n)-}$. The concentration of ion X^- at the electrode surface is given by equation 5 in which n is replaced by n/p . This result can also be written

$$(C_{X^-}) = C_{X^-}^0 [1 - (t/\tau)^{1/2}] \quad (23)$$

where τ is defined by the condition $(C_{X^-})_{x=0} = 0$. Likewise one has the relationship

$$(C_{MX_p^{(p-n)-}})_{x=0} = \frac{C_{X^-}^0}{p} \left(\frac{t}{\tau}\right)^{1/2} \quad (24)$$

which is written on the assumption that the diffusion coefficients of the ion X^- and the complex are equal. The concentration of ion M at the electrode surface can be calculated from 23 and 24 and from the instability constant K of the complex. By introducing the resulting value of $(C_{M^{n+}})_{x=0}$ in the Nernst equation one obtains

$$E = E^0 + \frac{RT}{nF} \ln \frac{Kf_{MX_p^{(p-n)-}}}{p(C_{X^-})^{p-n}f_{X^-}} + \frac{RT}{nF} \ln \frac{(t/\tau)^{1/2}}{[1 - (t/\tau)^{1/2}]^p} \quad (25)$$

for the potential-time curve for reversible electrode processes.

It follows from (25) that E is equal to the first two terms on the right-hand of (25) when the argument of the second logarithmic term is equal to unity. This is the case for example for $t = 0.146\tau$ when $p = 2$. A plot of $\log \{(t/\tau)^{1/2}/[1 - (t/\tau)^{1/2}]^p\}$ against E should yield a straight line whose reciprocal slope is $2.3RT/nF$. This conclusion was verified experimentally in the anodic oxidation of silver in potassium cyanide at 30° (Fig. 4); the experimental reciprocal slope of 0.064 is in good agreement with the theoretical value of 0.060. Likewise the experimental potential -0.53 volt (vs. S.C.E.), at which the logarithmic term vanishes, is in fair agreement with the value -0.46 volt (vs. S.C.E.) one calculates from (25) on the basis of the values $E^0 = 0.800$ volt (vs. N.H.E.) and $K =$

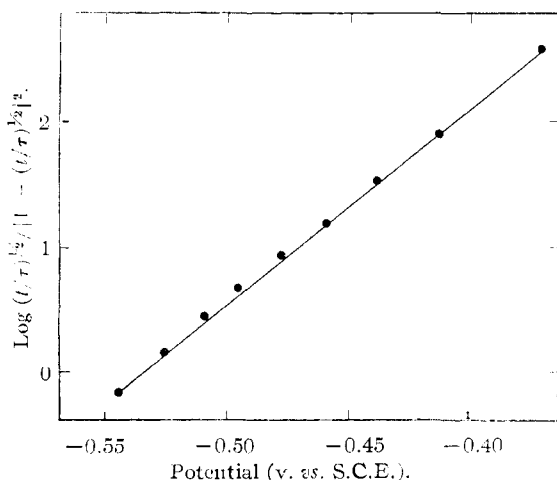


Fig. 4.—Logarithmic plot for the anodic oxidation of silver in 5 mM potassium cyanide.

1.8×10^{-19} , it being assumed that the activity coefficients in (25) are equal to unity.

It should be emphasized that the foregoing treatment is valid provided that *only one complex is formed and that equilibrium for complex formation is achieved*. If this is not the case one must take into account the kinetics of reaction 3. The resulting system of differential equations is non-linear, and the problem becomes arduous.

Part IV. Anodic Oxidation of a Metal with Formation of an Insoluble Substance (Equation 4)

It is difficult to develop a quantitative interpretation of the anodic oxidation of metals with formation of a film of insoluble substance. However, a simple interpretation can be developed if one neglects the diffusion process in the film. This simplified approach is valid when the film is so thin that it does not offer virtually any barrier to diffusion from and to the electrode. Processes leading to the formation of an insoluble precipitate MX_p can then be treated by calculating $(C_{X^-})_{x=0}$ on the basis of equation 5 in which n/p is substituted for n . By introducing the value of $(C_{X^-})_{x=0}$ in the solubility product S , solving for $C_{M^{n+}}$, and introducing the resulting value in the Nernst equation, one obtains

$$E = E^0 + \frac{RT}{nF} \ln \frac{S}{(C_{X^-})^p} - \frac{pRT}{nF} \ln [1 - (t/\tau)^{1/2}] \quad (26)$$

At time $t = 0$ the potential E has the value represented by the first two terms on the right-hand side of (26). Furthermore, a plot of $\log [1 - (t/\tau)^{1/2}]$ against E should yield a straight line whose slope is $-2.3pRT/nF$. This is essentially the case in the anodic oxidation of silver in chloride and bromide solutions at 30° (Fig. 5); the experimental reciprocal slopes in Fig. 5 are -0.067 and -0.061 while the theoretical value is 0.060. The potentials E at time $t = 0$ in Fig. 5 yield $S_{AgCl} = 9.3 \times 10^{-9}$

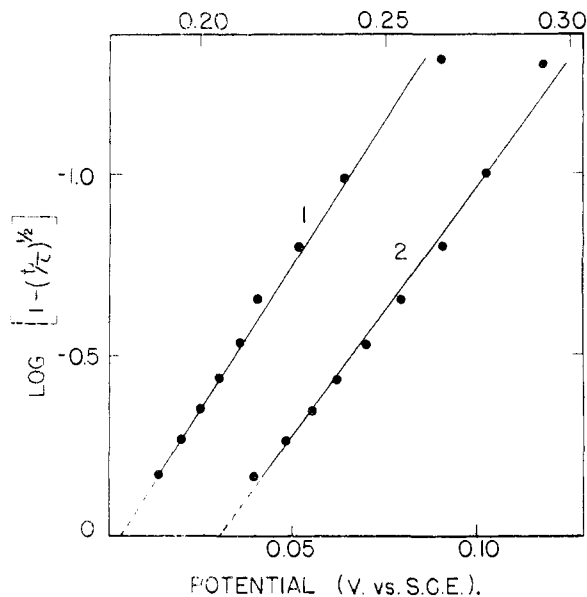


Fig. 5.—Logarithmic plot for the anodic oxidation of silver in 5 mM bromide (line 1), and 5 mM chloride (line 2, upper scale).

and $S_{\text{AgBr}} = 3.8 \times 10^{-12}$. These values are somewhat larger than the solubility products $S_{\text{AgCl}} = 2.8 \times 10^{-10}$ and $S_{\text{AgBr}} = 5.0 \times 10^{-13}$ in the literature.¹³ This is to be expected since the diameter of the particle of AgCl formed in the anodic process is possibly a few ångströms. Hence, the solubility of those particles is higher than the value for larger particles.¹⁴ Furthermore, the experimental errors and the approximate nature of the above treatment are reflected in the values of the solubility products deduced from potential-time curves.

It is worth noting that the product $i_0\tau^{1/2}$ is independent of current density in the anodic oxidation of silver under the conditions prevailing in our experiments (Table I). This result is to be expected from equation 6 provided that the diffusion of silver ion through the film of silver bromide is not rate determining. The foregoing considerations are then essentially valid.

TABLE I

$i_0\tau^{1/2}$ for the anodic oxidation of Ag in 5 mM KBr		
$i_0 \times 10^{-3}$, amp. cm. ⁻²	τ , sec.	$i_0\tau^{1/2}$
0.198	166.0	2.50
.328	53.6	2.40
.365	41.5	2.35
.401	35.8	2.40
.418	32.5	2.38
.486	20.7	2.22
.584	17.7	2.46
		av. 2.39

The determination of transition times for the anodic oxidation of metals could possibly be useful in chemical analysis. Substances (organic reagents, etc.) forming insoluble salts could be determined. Frequent calibration of the electrode would be essential since there is never a perfectly uniform attack of the metal, *i.e.*, the area of the electrode changes from one series of experiments to another.

Experimental

The results on the catalytic reduction of Ti(IV) were obtained with a dropping mercury electrode used as stationary electrode. Rather high current densities were utilized, and a mercury pool electrode would have required currents up to approximately 0.2 amp. Potential-time curves were recorded in a small fraction of the drop life, and the area of the mercury drop did not change appreciably during recording.^{15a,b} The schematic diagram of the apparatus is shown in Fig. 6. When switch 5 is closed, the mercury drop is dislodged from the capillary by a magnetic hammer.¹⁶ The time relay (thyatron circuit) is triggered, and after a given time, relay RL 2 closes the electrolysis circuit of cell CE. This circuit is fed by the power supply with electronic regulation P. The area of the mercury drop at the time of the recording of the potential-time was computed from the rate of flow of the mercury and from the time for which relay RL 2 was adjusted; the electrode was assumed to be a sphere.

(13) W. M. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," 2nd Ed., Prentice-Hall Book Co., New York, N. Y., 1952, p. 191.

(14) I. M. Kolthoff and E. B. Sandell "Textbook of Quantitative Inorganic Analysis," The Macmillan Book Co., New York, N. Y., 1943, p. 102.

(15) (a) L. Gierst and A. Juliard, *Int. Comm. Electrochem. Therm. Kin.*, Proceedings of the 2nd Meeting, Tamburini, Milan, 1950, pp. 117 and 229; (b) L. Gierst and A. Juliard, *J. Phys. Chem.*, **57**, 701 (1953).

(16) (a) This method has been utilized by several authors: V. A. Taimmergahl, *Zavodskaya Lab.*, **15**, 1370 (1949); (b) L. Airey and A. A. Smales, *Analyst*, **75**, 287 (1950); (c) E. Wahlin, *Radiometer Polarographics*, **1**, 113 (1952).

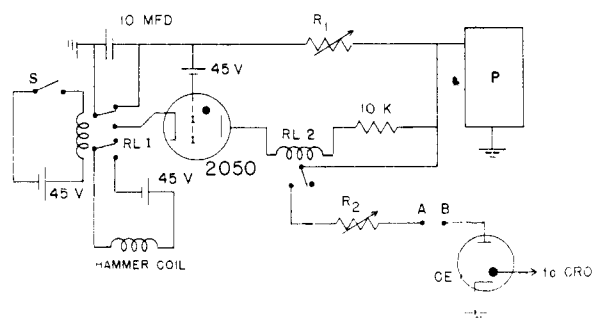


Fig. 6.—Schematic diagram of apparatus for electrolysis with the dropping mercury electrode.

A difficulty was encountered in the application of this method: the electrolysis current was still flowing through the cell when the drop detached itself from the capillary; the current density for the newly forming drop was then very large and the supporting electrolyte was reduced; this resulted in the plugging of the capillary. This difficulty was overcome by inserting in AB a time relay which opened the electrolysis circuit a given time after the closing of relay RL 2, but before the fall of the drop.

The composition of the solution in the experiments with Ti(IV) was: 0.2 oxalic acid, approximately 1 mM titanous sulfate, and varying amounts of hydroxylamine chloride. The purity of the latter substance was determined by titration with potassium permanganate after the addition of ferric ion.¹⁷ The concentration of titanium was not determined exactly because it is the ratio (τ_0/τ_d) which is of importance, and not the absolute value of τ_0 . The same amount of titanium salt was of course used in all experiments.

Potential-time curves for the anodic oxidation of silver were determined with a pen-and-ink recorder and the instrument previously discussed.¹⁶ The area of the silver electrode (foil) was approximately 1 cm.².

Appendix

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Transition Time for Spherical Diffusion.—The dropping mercury electrode has been utilized as stationary electrode in this and other investigations,^{14,15} and it appeared useful to derive the value of the transition time for the case of mass transfer controlled by spherical diffusion. The solution of this problem is as follows.

The equation for spherical diffusion

$$\frac{\partial C(r,t)}{\partial t} = D \left[\frac{\partial^2 C(r,t)}{\partial r^2} + \frac{2}{r} \frac{\partial C(r,t)}{\partial r} \right] \quad (27)$$

must be solved for the conditions $C(r,0) = C^0$, $(\partial C(r,t)/\partial r)_{r=r_0} = i_0/nFD$, $C(r,t) \rightarrow C^0$ for $r \rightarrow \infty$, r being the distance from the center of the spherical electrode, and r_0 the radius of the electrode.

Equation 27 can be transformed into the form $\partial \chi(r,t)/\partial t = D \partial^2 \chi(r,t)/\partial r^2$ by setting $\chi(r,t) = rC(r,t)$. The equation in $\chi(r,t)$ is solved for the above initial and boundary conditions—expressed in terms of $\chi(r,t)$ —by applying the Laplace transformation.¹⁸ The concentration at $r = r_0$ is

$$C(r_0,t) = C^0 - \frac{i_0 r_0}{nFD} \left\{ 1 - \exp\left(\frac{Dt}{r_0^2}\right) \operatorname{erfc}\left[\frac{(Dt)^{1/2}}{r_0}\right] \right\} \quad (28)$$

The transition time τ is defined by the condition $C(r_0,t) = 0$, or by the equation

$$\frac{C^0}{\lambda r_0} = 1 - \exp\left(\frac{D\tau}{r_0^2}\right) \operatorname{erfc}\left[\frac{(D\tau)^{1/2}}{r_0}\right] \quad (29)$$

where $\lambda = i_0/nFD$. Two particular cases of (29) are of interest, namely, when τ is very small or very large. In the former case $(D\tau/r_0^2) \ll 1$; hence $\exp(D\tau/r_0^2) \approx 1$ and $\operatorname{erfc}[(D\tau)^{1/2}/r_0] \approx 1 - [2/(\pi)^{1/2}][(D\tau)^{1/2}/r_0]$. Equation 29 takes then the same form as formula 6 for linear diffusion.

(17) W. W. Scott "Standard Methods of Chemical Analysis," D. Van Nostrand and Co., New York, N. Y., 1927, p. 352.

(18) See details in G. Mamantov's M.S. thesis (June, 1954).

Thus, the product $i_0\tau^{1/2}$ for spherical diffusion approaches the value $i_0\tau^{1/2}$ for linear diffusion when the current density is sufficiently large. The opposite case can be analyzed by expanding the error function in (29) for large arguments and by retaining the first two terms in the series. Equation 29 is transformed into the relationship which shows that the

$$i_0\tau^{1/2} \frac{r_0}{C^0 n F D} = \frac{1}{\frac{1}{\tau^{1/2}} - \frac{r_0}{\pi^{1/2} D^{1/2} \tau}} \quad (30)$$

product $i_0\tau^{1/2}$ becomes infinite when τ approaches zero. One concludes from the foregoing discussion of equation 29 that the product $i_0\tau^{1/2}$ is not independent of current density in the case of symmetrical spherical diffusion.

The validity of equation 29 was verified experimentally and the results are shown in Fig. 7. The calculated curve is in fair agreement with the experimental points. The departure from theory at low current densities results mainly from the growth of the drop during the recording of the potential-time curves. At low current densities the transition time is of the order of several tenths of a second, and the area of the drop at the transition time is larger than the average area of the drop during recordings at higher current densities. As a result, low current densities are smaller than the calculated values of i_0 , and the product $i_0\tau^{1/2}$ is larger than expected. The reduction of a few metallic ions also was studied, but the results were somewhat erratic possibly because of interference by convection.

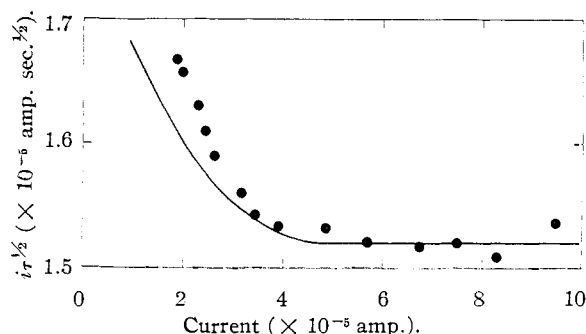


Fig. 7.—Variations of $i_0\tau^{1/2}$ with current for the reduction of 1 mM potassium chromate in 1 N sodium hydroxide on the dropping mercury electrode.

Transition for Processes Controlled by Linear Diffusion and by Electric Migration in a Uniform Field.—In calculating transition times one generally assumes that the effect of migration of the electrolyzed species (ion) can be neglected. In general this procedure is justified when a large excess of supporting electrolyte is present. It is then said that the supporting electrolyte “carries” the current and that the effect of migration of the reducible or oxidizable ion is negligible. This is undoubtedly so at low current densities, but at high current densities this may not be the case. Consider for example a current density of 10^{-2} amp. cm^{-2} and assume that the reducible oxidizable ion carries only 1% of the current. This fraction of the current may correspond to an appreciable transport of substance by migration, and consequently the transition time is different

from the value obtained for mass transfer solely controlled by diffusion. The transition time will be derived for the case in which the intensity of the electric field is constant. This simplified case is of practical interest since a large excess of supporting electrolyte is generally present in solution, and the field intensity is not appreciably affected by variations of the concentration of the reducible or oxidizable ion.

Fick’s equation for linear diffusion must be modified as

$$\partial C(x,t)/\partial t = D\partial^2 C(x,t)/\partial x^2 + u\varphi\partial C(x,t)/\partial x \quad (31)$$

where u is the ionic mobility of the ion being reduced or oxidized and φ is the intensity of the electric field which is assumed to be constant for a given current density.

This equation must be solved for the initial condition $C(x,0) = C^0$ (C^0 bulk concentration) and for the boundary condition

$$D[\partial C(x,t)/\partial x]_{x=0} + u\varphi C(0,t) = \frac{i_0}{nF} \quad (32)$$

One has also $C(x,t) \rightarrow C^0$ for $x \rightarrow \infty$.

The solution of this problem as obtained by the Laplace transformation¹⁸ is for $x = 0$

$$C(0,t) = C^0 - \frac{\lambda - ac^0}{2D} \left[at + \frac{2D + a^2t}{a} \operatorname{erf} \left(\frac{at^{1/2}}{2D^{1/2}} \right) + 2 \left(\frac{Dt}{\pi} \right)^{1/2} \exp \left(-\frac{a^2t}{4D} \right) \right] \quad (33)$$

where $a = u\varphi$ and $\lambda = i_0/nF$.

The transition time τ is obtained by prescribing the condition $C(0,\tau) = 0$. When the condition

$$\frac{a^2t}{4D} \leq 0.1 \quad (34)$$

is fulfilled, one can make the approximations

$$\operatorname{erf} \left(\frac{at^{1/2}}{2D^{1/2}} \right) \approx a \frac{t^{1/2}}{\pi^{1/2} D^{1/2}} \quad (35)$$

and

$$\exp \left(-\frac{a^2t}{4D} \right) = 1 - \frac{a^2t}{4D} \quad (36)$$

By introducing these approximations in (33) and noting that $\varphi = \rho i_0$ where ρ is the resistivity of the solution, one deduces from the condition $C(0,\tau) = 0$ the equation

$$(i_0\tau^{1/2})^3 + \frac{2\pi^{1/2}D^{1/2}}{u\rho} (i_0\tau^{1/2})^2 + \frac{8D}{u^2\rho^2} (i_0\tau^{1/2}) - \frac{4\pi^{1/2}nFD^{3/2}C^0}{u^2\rho^2(1 - u\rho nFC^0)} = 0 \quad (37)$$

The value of $i_0\tau^{1/2}$ and consequently that of $\tau^{1/2}$ can be computed by solving (37). It should be noted that the value of $i_0\tau^{1/2}$ obtained in this fashion is independent of current density since none of the coefficients in (37) contains i_0 . In conclusion the product $i_0\tau^{1/2}$ is independent of current density even in the case of partial mass transfer by migration. This conclusion is valid provided that condition (34) is fulfilled.

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