[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Theory of Electrolysis at Constant Current in Unstirred Solution. II. Consecutive Electrochemical Reactions

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A rigorous mathematical analysis is presented for the following types of electrode process in electrolysis at constant current in unstirred solution: 1. Cathodic process followed by re-oxidation resulting from reversal of the current through the cell; 2. reduction of a two-component system; 3. stepwise reduction of a single substance. The concentrations of the substances involved in the electrode process are derived by applying the method of integral transforms (Fourier and Laplace), and the corresponding *transition times* are calculated. Equations of the potential–time curves are also derived for cases I and III.

In case I, the transition time for the re-oxidation process is one-third of the transition time for the preceding cathodic process. The analysis of the potential–time curve enables one to make a complete study of the kinetics of the electrode process when this process involves cathodic and anodic overvoltages exceeding 0.1 v.: calculation of the rate constant at zero potential, determination of the transfer coefficient, calculation of the free energies of activation for the forward and backward electrochemical reaction, and computation of the standard potential for the couple involved. In case II, the transition time for the substance which is the more difficult to reduce, depends not only on the bulk concentration of this substance, but also on the concentration of the substance being reduced at less cathodic potentials. Quantitative relationships between the transition times for the two steps are derived. In case III, the ratio of the transition time, τ_2/τ_1 is not proportional to the ratio of the number of electrons involved in the corresponding electrode processes. Thus $\tau_2/\tau_1 = 3$ for $n_2/n_1 = 1$; $\tau_2/\tau_1 = 8$ for $n_2/n_1 = 2$, etc. Experimental results for various electrode processes confirm the theoretical treatments of the above three cases.

Introduction

There have been several attempts in the recent years to apply the polarographic method to the study of electrode processes, and several contributions in this field have been made in this Laboratory[1] as well as by other investigators.[2] Interesting results have been reported in this respect, but the main drawback of the polarographic method in such studies is the approximate nature of the quantitative treatment of the current observed with the dropping mercury electrode. It is generally feasible to give a rigorous solution of the boundary value problem being studied for the case of semi-infinite linear diffusion, but the rigorous derivation for the corresponding problem for the expanding sphere generally involves very serious difficulties. It is then necessary to adapt the solution for linear diffusion to the case of the dropping mercury electrode by a rather approximate method. Such approximations are avoided in transitory voltammetry in which the solution for linear diffusion is applicable with good accuracy. However, the mathematical treatment of currents in transitory voltammetry, which is relatively straightforward in simple cases involving pure diffusion,[3] becomes very involved when there is partial kinetic control.[4] Electrolysis at constant current in unstirred solution does not have the disadvantages of the above methods: the experimental conditions actually correspond to the case of semi-infinite linear diffusion and it is possible to solve rigorously the various boundary value problems. This method is rather old,[5] but it was revived only recently.[6] A first paper from This Laboratory[7] dealt with general principles and with the treatment of electrode processes in which the electrochemical reaction is preceded by a chemical transformation. In the present paper we discuss various processes involving two consecutive electrochemical reactions.

Case I—Cathodic Process Followed by Re-oxidation Resulting from Reversal of Current

Initial and Boundary Conditions.—Consider the electrode process in which a substance O is being reduced to a substance R. The electrolysis is carried out at constant current in an *unstirred solution,* and it is assumed that the direction of current through the cell is reversed at some stage of the electrolysis. This reversal of current results in the re-oxidation of substance R which had been produced during the preceding cathodic process. The potential–time curves obtained in this type of electrolysis can be applied to the *quantitative* interpretation of electrochemical processes, and it is therefore of interest to develop the mathematical analysis of this type of electrolysis. This is done below for experimental conditions corresponding to semi-infinite linear diffusion. Convection or migration effects will be assumed to be negligible, it being understood that the electrolysis is carried out in presence of a large excess of supporting electrolyte.

In the course of the cathodic process leading to the formation of substance R, the concentration of this substance varies with the time t elapsed since the beginning of the electrolysis and with the dis-

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(1) P. Delahay, This Journal, **73**, 4944 (1951); **74**, 3497, 3506 (1952); **75**, 1430 (1953); P. Delahay and J. E. Strassner, *ibid.*, **73**, 5219 (1951); **74**, 893 (1952); P. Delahay and T. J. Adams, *ibid.*, **74**, 1437 (1952); P. Delahay and G. L. Stiehl, *ibid.*, **74**, 3500 (1952); J. E. Strassner and P. Delahay, *ibid.*, **74**, 6232 (1952).

(2) J. Koutecky and R. Brdicka, *Collection Czechoslov. Chem. Communs.*, **12**, 337 (1947); H. Eyring, L. Marker and T. C. Kwoh, *J. Phys. Colloid Chem.*, **53**, 187 (1949); N. Tanaka and R. Tamamushi, *Bull. Chem. Soc. Japan*, **22**, 187 (1949); **22**, 227 (1949); **23**, 110 (1950); M. G. Evans and N. S. Hush, *J. chim. phys.*, **49**, C 159 (1952); A. Tockstein, *Collection Czechoslov. Chem. Communs.*, **16**, 101 (1951); J. Koutecky, *Sbornik Mezinarod. Polarog. Sjezdu Prace, 1st Cong.*, 1951, Part I, pp. 826–838. For a survey and additional references, see I. M. Kolthoff and J. J. Lingane, "Polarography," 2 Ed., Interscience Publishers, Inc., New York, N. Y., 1952, pp. 268–294.

(3) A. Sevcik, *Collection Czechoslov. Chem. Communs.*, **13**, 349 (1948); J. E. B. Randles, *Trans. Faraday Soc.*, **44**, 327 (1948); T. Berzins and P. Delahay, This Journal, **75**, 555 (1953).

(4) P, Delahay, *ibid.*, **75**, 1190 (1953).

(5) H. F. Weber, *Wied. Ann.*, **7**, 536 (1879); H. J. S. Sand, *Phil. Mag.*, **1**, 45 (1901); Z. Karaoglanoff, *Z. Elektrochem.*, **12**, 5 (1906).

(6) A. Rius, J. Llopis and S. Polo, *Anales Fis. y Quim.*, (*Madrid*), **45**, 1029 (1949); L. Gierst and A. Juliard, "Proceeding of the 2nd Meeting of the International Committee of Electrochemical Thermodynamics and Kinetics," Tamburini, Milan, 1950, pp. 117 and 279.

(7) P. Delahay and T. Berzins, This Journal, **75**, 2486 (1953).

tance x from the electrode. This concentration is, according to Karaoglanoff[5]

$$C_R(x,\tau) = 2\theta(D_R\tau/\pi)^{1/2} \exp(-x^2/4D_R\tau) - \theta x \operatorname{erfc}(x/2D_R^{1/2}\tau^{1/2}) \quad (1)$$

with

$$\theta = i_0/nFD_R \quad (2)$$

The notations in equations 1 and 2 are as follows: i_0 is the density of the current through the electrolytic cell, n the number of electrons in the reduction of substance O, F the faraday, D_R the diffusion coefficient of substance R; and "erfc" is the complement of the error function. Equation 1 was written for the *transition time* τ corresponding to the reduction of substance O,[8] but is valid for any value of t smaller than the transition time τ.

At time τ the current through the cell is reversed, and consequently substance R is now reoxidized at constant current. This anodic process proceeds at a current density i_0' which may not necessarily be the same as the density i_0 during the cathodic process. Since the current is constant, the flux at the electrode surface is constant and one can write the condition

$$[\partial C_R(x,t')/\partial x]_{x=0} = \lambda' \quad (3)$$

in which λ' is defined as

$$\lambda' = i_0'/NFD_R \quad (4)$$

Note that the concentration $C_R(x,t')$ in equation 3 is written as a function of the time t', which is related to the time t elapsed since the beginning of the reduction of substance O by the relationship

$$t' = t - \tau \quad (5)$$

This new scale of time is introduced for the sake of simplicity (see below).

The boundary value problem is now completely stated. Equation 1, which gives the distribution of substance R at time $t' = 0$, is the initial condition for the present problem; formula 3 expresses the boundary condition. The concentration of substance R will be derived below by solving the differential equation expressing Fick's second law.

Derivation of the Concentration $C_R(x,t')$.—The function $C_R(x,t)$ will be derived by applying the Fourier cosine transform which is defined by the relationship[9]

$$\bar{C}_R(p,t') = (2/\pi)^{1/2}\int_0^\infty C_R(x,t') \cos px\, dx \quad (6)$$

in which p is the variable resulting from the transformation and x is the variable with respect to which the transform is taken. By this transform, the partial differential equation expressing Fick's second law is transformed into an ordinary differential equation. From (6) one deduces

$$\left(\frac{2}{\pi}\right)^{1/2}\int_0^\infty \frac{\partial^2 C_R(x,t')}{\partial x^2}\cos px\, dx = -\left(\frac{2}{\pi}\right)^{1/2}\left(\frac{\partial C_R(x,t')}{\partial x}\right)_{x=0} - p^2\bar{C}_R(p,t') \quad (7)$$

as one can readily ascertain by two consecutive integrations by parts and by noting that the concentration $C_R(x,t')$ and the derivative $\partial C_R(x,t')/\partial x$ approach zero when x becomes infinite. The first term on the right-hand of (7) is known from condition 3, and this is why the cosine transform and not the sine transform is used here. The transform of the equation expressing Fick's second law is

$$d\bar{C}_R(p,t')/dt = -(2/\pi)^{1/2}D_R\lambda' - D_Rp^2\bar{C}_R(p,t') \quad (8)$$

The solution of this ordinary differential equation is immediate

$$\bar{C}_R(p,t') = -\left(\frac{2}{\pi}\right)^{1/2}\frac{\lambda'}{p^2} + \frac{M}{D_Rp^2}\exp(-D_Rp^2t') \quad (9)$$

The integration constant M in (9) is determined by satisfying the transform of the initial condition 1. This transform is obtained by combining (1) and (6) and by calculating the resulting integrals by parts. After several consecutive integrations by parts one obtains

$$\bar{C}_R(p,0) = \left(\frac{2}{\pi}\right)^{1/2}\frac{\theta}{p^2}[1 - \exp(-D_R\tau p^2)] \quad (10)$$

Introducing now $\bar{C}_R(p,0)$ from (10) in equation 9, one readily calculates M, and finally obtains the following transform of the solution

$$\bar{C}_R(p,t) = \left(\frac{2}{\pi}\right)^{1/2}\frac{\theta}{p_2}\{1 - \exp[-(D_R\tau + D_Rt')p^2]\} - \left(\frac{2}{\pi}\right)^{1/2}\frac{\theta}{p^2}\{1 - \exp[-D_Rt'p^2]\} - \left(\frac{2}{\pi}\right)^{1/2}\frac{\lambda'}{p^2}\{1 - \exp[D_Rt'p^2] \quad (11)$$

The three terms on the right-hand of equation 11 are of the same form as the transform of the initial condition 10, and consequently the function $C_R(x,t)$ is the sum of three groups of terms having the same form as the initial condition 1. Thus

$$C_R(x,t') = 2\theta\left[\frac{D_R(\tau + t')}{\pi}\right]^{1/2}\exp\left[-\frac{x^2}{4D_R(\tau + t')}\right] - \theta x \operatorname{erfc}\left\{\frac{x}{2[D_R(\tau + t')]^{1/2}}\right\} - 2(\theta + \lambda')\left(\frac{D_Rt'}{\pi}\right)^{1/2}\exp\left(-\frac{x^2}{4D_Rt'}\right) + (\theta + \lambda')\, x \operatorname{erfc}\left[\frac{x}{(2D_Rt')^{1/2}}\right] \quad (12)$$

The correctness of the above derivation was established by verifying that the solution 12 satisfies the differential equation expressing Fick's second law. The initial and boundary conditions also are satisfied.

As an example, the variations of the function $C_R(x,t)$ with x and for given times of electrolysis are shown in Fig. 1. This diagram was constructed for the following data: $i_0 = i_0' = 10^{-2}$ amp. cm.$^{-2}$, $D_O = D_R = 10^{-5}$ cm.^{2} sec.$^{-1}$, $n = 1$, $C^\circ = 5 \times 10^{-6}$ mole. cm.$^{-3}$. Note that the concentration *vs.* x curves exhibit a maximum for $t' > 0$, and that the slope of the tangent to the curve at $x = 0$ is constant, as it should in view of condition 3. Furthermore, the concentration at a sufficient distance from the electrode *increases* during the re-oxidation process; this is to be expected since substance R diffuses toward the region of the solution in which its concentration is lowered. Of course, for large values of t', $C_R(x,t')$ ultimately approaches zero.

Transition Time τ'.—Because the concentrations of substances O and R at the electrode surface vary during the re-oxidation process, the corresponding electrode potential varies. At the *transition time* τ', the concentration of substance R is by definition equal to zero, and consequently the electrode potential becomes infinite. Actually, this merely implies that at times $t' > \tau'$ the oxidation of substance R proceeds at a rate which corresponds to a current of density smaller than i_0'; as a result, the potential moves toward more anodic values until another anodic process (oxidation of the solvent, oxidation of the electrode) occurs. The transition time τ' is therefore characterized by a sudden variation of potential as shown in Fig. 2 (this diagram is discussed below).

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[8] For a detailed discussion of the properties of transition time see ref. 7; τ corresponds to the time of electrolysis at which the concentration of substance O *at the electrode surface* becomes equal to zero.

[9] I. N. Sneddon, "Fourier Transforms," McGraw–Hill Book Co., Inc., New York, N. Y., 1951, p. 8.

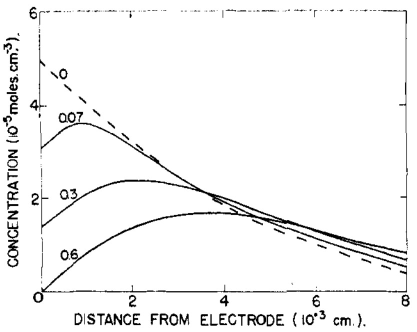

Fig. 1.—Variation of the concentration of substance R during the re-oxidation process. The number on each curve is the time t'.

The value of τ' is readily deduced from equation 12 by introducing the condition $C_R(0,t') = 0$. This leads to the following relationship between the transition time τ for the reduction process O → R and the transition time τ' for the re-oxidation process

$$\tau' = \frac{\theta^2}{(\theta + \lambda')^2 - \theta^2}\,\tau \qquad (13)$$

The quantities θ and λ' in this equation are defined by equations 2 and 4, respectively. If the current densities i_0 and i_0' are equal, equation 13 takes the remarkably simple form

$$\tau' = {}^1/_3\tau \qquad (14)$$

Equation 14 shows that the transition time for the re-oxidation process is equal to one third of the transition time for the preceding cathodic process the current density being the same in both processes. This conclusion was verified experimentally for a few electrode processes, and the results are summarized in Table I. It is seen from this table that values of the ratio τ/τ' fluctuate around 3; the average value of the 16 listed values is 3.02, whereas the theoretical value is 3. The relatively large errors (up to 6–7%) are to be expected because of the use of a cathode-ray oscillograph as recorder (see below): the length on the trace corresponding to the time τ' was less than 1 inch, and consequently the accuracy on τ' was poor.

TABLE I

DATA ON THE TRANSITION TIMES FOR VARIOUS RE-OXIDATION PROCESSES

	Thallium[a]				Cadmium[b]			
τ^e	3.30	3.14	3.03	1.44	3.55	2.38	1.36	1.26
τ'^e	1.14	1.06	1.00	0.50	1.26	0.828	0.442	0.423
τ/τ'	2.89	2.96	3.03	2.88	2.82	2.88	3.07	2.98
	Zinc[c]				Quinone[d]			
τ^e	2.46	1.67	0.907	0.865	3.00	2.93	1.10	0.884
τ^e	0.78	0.538	0.313	0.282	0.965	0.965	0.345	0.276
τ/τ'	3.15	3.10	2.93	3.06	3.11	3.05	3.19	3.20

[a] 10^{-2} *M* thallium nitrate in 1 *M* potassium nitrate. [b] 10^{-2} *M* cadmium sulfate in 1 *M* potassium nitrate. [c] 10^{-3} *M* zinc sulfate in 2 *M* ammonium hydroxide and 2 *M* ammonium chloride. [d] 10^{-3} *M* quinone in buffer of *p*H 6.9 and *M* potassium nitrate. [e] Transition times in seconds at different current densities.

Two examples of potential–time curves are shown in Fig. 2. Note that the current was reversed very slightly *before* the transition time was reached. This procedure is justified because equation 1 and the above treatment are valid when the reversal of current occurs at any time t which is smaller or equal to the transition time τ. Equation 1, however, does not hold for values of t larger than τ, and consequently it is advisable in the experimental verification to reverse the current for $t \leqslant \tau$.

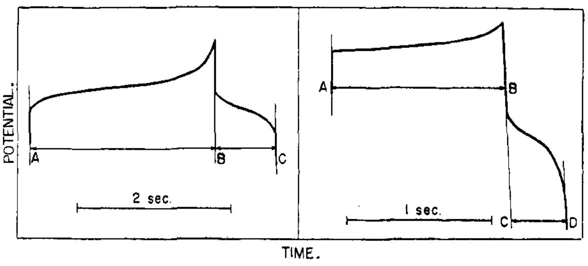

Fig. 2.—Potential-time curves for the reduction—and subsequent re-oxidation—of cadmium ion (left) and zinc tetrammine ion. See data in Table I. Note that one has approximately AB = 3 BC (left), and AB = 3 CD (right).

Potential–Time Curves.—The method involving the reversal of the current would be of little practical value if it were not for the possibility of studying the kinetics of electrochemical reactions by the present method. The characteristics of potential–time curves which are useful in such studies will now be established.

Case in which there is electrochemical equilibrium at the electrode.—If electrochemical equilibrium is achieved at the electrode, the potential is given by the Nernst equation, and the application of this equation requires the knowledge of the functions $C_R(0,t')$ and $C_O(0,t')$. The former concentration is given by equation 12 in which x is made equal to zero; the concentration $C_O(0,t')$ can be derived by following exactly the same method as the one which led to equation 12. There is no need for repeating the derivation here, and the equation for the potential–time curve can be written directly. Thus

$$E = E^0 + \frac{RT}{nF}\ln\frac{f_O}{f_R} + \frac{RT}{nF}\ln\frac{C^0 - 2\lambda\,[D_O(\tau + t')/\pi]^{1/2} + 4\lambda\,(D_Ot'/\pi)^{1/2}}{2\theta[D_R(\tau + t')/\pi]^{1/2} - 4\theta\,(D_Rt'/\pi)^{1/2}} \qquad (15)$$

The notations in equation 15 are as follows: E^0 is the standard potential for the couple O–R[10]; f_O and f_R are the activity coefficients of substances O and R; D_O is the diffusion coefficient of substance O; C^0 is the bulk concentration of substance O; and the quantity λ is defined as

$$\lambda = i_O/nFD_O \qquad (16)$$

Equation 15 can be modified by recalling that the transition time τ is related to the concentration C^0 by the equation[5]

$$C^0 = 2\lambda(D_O\tau/\pi)^{1/2} \qquad (17)$$

By combining (15) and (17) one finally has

$$E = E_{1/2} + \frac{RT}{nF}\ln\frac{\tau^{1/2} - [(\tau + t')^{1/2} - 2t'^{1/2}]}{(\tau + t')^{1/2} - 2t'^{1/2}} \qquad (18)$$

with

$$E_{1/2} = E^0 + \frac{RT}{nF}\ln\frac{f_OD_R^{1/2}}{f_RD_O^{1/2}} \qquad (19)$$

It was previously shown that the potential $E_{1/2}$ for a simple reduction or oxidation process is observed at a time

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[10] **If an amalgam electrode is involved, E^0 is the standard potential for the amalgam.**

equal to $^1/_4\ \tau$,[7] and the potential $E_{1/4}$ for the reduction of substance O can readily be determined experimentally. If electrochemical equilibrium is achieved at the electrode, the potential $E_{1/4}$ for the *re-oxidation process* is observed at a time t' for which the logarithm on the right-hand of (18) is equal to zero. This condition leads to second degree equation in t' whose solution is

$$t'_{E=E_{1/4}} = 0.222\tau' \qquad (20)$$

Summarizing, in case of electrochemical reversibility, the potential at time $\tau/4$ for the cathodic process should be equal to the potential at the time t' given by equation 20. This procedure can be used to determine whether or not electrochemical equilibrium is achieved at the electrode. This method, however, leads to erroneous conclusions when the electrochemical reaction is followed by a chemical transformation. In that case the concentrations of substance R might be greatly decreased, and the potential–time curve is shifted according.[11]

An example of potential-time curve for a reversible process is shown in Fig. 2 (curve on the left) for the reduction of cadmium ion and the subsequent oxidation of cadmium (see conditions of electrolysis in Table I). The potential $E_{1/4}$ for the re-oxidation process in Fig. 2 (left) (see equation 20) is somewhat more anodic than the potential $E_{1/4}$ for the cathodic process, but this difference is merely caused by the ohmic drop between the tip of the reference electrode and the mercury pool on which the electrochemical reaction being studied occurs. We have developed an instrument in which potential–time curves are recorded with a pen-and-ink instrument, and we were able to verify (in collaboration with Mr. C. C. Mattax) that the potentials $E_{1/4}$ for the cathodic and anodic processes were the same in the case of cadmium. We also verified that $E_{1/4}$ for the same system is virtually equal to the half-wave potential, the difference being less than 0.005 v. The detailed description of these investigations will be reserved for a subsequent paper.

Irreversible Electrochemical Reaction.—We consider the case in which the cathodic and anodic overvoltages are large enough at the current density i_0 to allow one to neglect the effect of the backward process in writing the equations for the rate of the electrochemical reaction. This condition is verified in the great majority of irreversible electrode processes, since the above simplification is justified when the overvoltages (cathodic and anodic) exceed, say, 0.1 v.

If one assumes that the electrochemical reaction is of the first order one has

$$i_0'/nF = k_{\mathrm{b.h}}\ C_{\mathrm{R}}(0,t') \qquad (21)$$

in which $k_{\mathrm{b.h}}$ is rate constant (heterogeneous) for the re-oxidation process. This rate constant is an exponential function of the electrode potential E of the form

$$k_{\mathrm{b,h}} = k^0{}_{\mathrm{b,h}} \exp\left[\frac{(1-\alpha)nFE}{RT}\right] \qquad (22)$$

in which $k^0{}_{\mathrm{f,h}}$ is the value of the constant at $E = 0$ (*vs.* the normal hydrogen electrode), and α is the transfer coefficient for the cathodic process O → R. By combining equation 12 (for $x = 0$), (21) and (22), one obtains the following potential–time characteristic

$$E = \frac{RT}{(1-\alpha)nF} \ln \frac{\pi^{1/2} D_{\mathrm{R}}{}^{1/2}}{2k^0{}_{\mathrm{b,h}}} - \frac{RT}{(1-\alpha)nF} \ln\, [(\tau + t')^{1/2} - 2t'^{1/2}| \qquad (23)$$

According to equation 23 a plot of the logarithm of the quantity $[(\tau + t')^{1/2} - 2\ t'^{1/2}]$ *vs.* E should yield a straight line whose reciprocal slope is $(RT)/(1-\alpha)nF$; the value of $(1 - \alpha)$ can thus be determined from the potential–time curve for the re-oxidation process. Since α can also be calculated from the experimental potential–time curve for the *cathodic* process,[7] it is possible to verify by the present method that the sum $\alpha + (1 - \alpha)$ is indeed equal to unity. If there are kinetic complications (consecutive electrochemical reactions, dismutation, etc.) this sum will generally be different from unity, and such complications can therefore be detected. The rate constant $k^0{}_{\mathrm{b,h}}$ is calculated from the potential at time $t' = 0$ (see equation 23), and the corresponding rate constant $k^0{}_{\mathrm{f,h}}$ for the cathodic process is determined from the potential–time curve for the cathodic process.[7] A complete study of the kinetics of the electrochemical reaction can thus be made. Finally, the free energies of activation corresponding to $k^0{}_{\mathrm{f,h}}$ and $k^0{}_{\mathrm{b,h}}$ can be evaluated by application of the absolute rate theory, and consequently the standard free energy change for the electrode process can be determined. Standard potentials for markedly irreversible processes can thus be evaluated by the present method.

The preceding discussion dealt with re-oxidation processes, and it is a trivial matter to transpose the treatment to the opposite case in which an anodic process is followed by cathodic reduction.

An example of potential–time curve for an irreversible system is shown in Fig. 2 (curve on the right) for the case of the reduction of zinc tetrammine ion and the subsequent oxidation of zinc (see conditions of electrolysis in Table I). Note that the cathodic and anodic potential–time curves are well separated (by approximately 0.5 v.). No attempt was made to calculate any datum for the electrochemical reaction in the present case, because the accuracy of oscillographic recordings on a 5 inch screen is not sufficient. The required accuracy can be obtained with the pen-and-ink instrument already mentioned. A detailed experimental study of potential–time curves will be reported in a subsequent paper. The present experimental study, however, establishes the correctness of the present treatment.

Case II—Two Consecutive Electrochemical Reactions Involving Different Substances

Initial and Boundary Conditions.—We consider the case in which two substances O_1 and O_2 are reduced at sufficiently different potentials to yield a potential–time curve exhibiting two distinct steps. The reduction products are R_1 and R_2, and the number of electrons n_1 and n_2, respectively. It is also assumed that O_1 is the substance which is reduced at less cathodic potentials.

The characteristics of the potential–time curve for the first step are not influenced by the presence of substance R_2 in solution, and consequently the simple treatment developed by Sand[5] and by Karaoglanoff[5] is applicable. This is not so, however, for the second step, and the quantitative treatment for this case will be developed here. As for Case I, it will be assumed that the experimental conditions correspond to semi-infinite linear diffusion, and that the effects of migration and convection are negligible.

The concentration of substance O_1 at the transi-

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(11) We have also developed the treatment of this case, and this matter will be taken up in a subsequent publication; for an example in polarography, see L. I. Smith, I. M. Kolthoff, S. Wawzonek and P. M. Ruoff, THIS JOURNAL, **63**, 1018 (1941).

tion time τ_1 is equal to zero at the electrode surface, and this concentration remains equal to zero as the electrode proceeds. Substance O_1, however, continues to diffuse toward the electrode at which it is immediately reduced. As a result, the current through the cell is the sum of two components corresponding to the reduction of substances O_1 and O_2, respectively. Thus

$$C_{O_1}(0,t') = 0 \qquad (24)$$

$$n_1 D_{O_1}[\partial C_{O_1}(x,t')/\partial x]_{x=0} + N_2 D_{O_2}[\partial C_{O_2}(x,t')/\partial x]_{x=0} = i_0/F \qquad (25)$$

where the D's are the diffusion coefficients. Note that equation 24 and 25 are written in terms of the time t' defined by the condition $t' = t - \tau_1$.

The initial conditions are

$$C_{O_2}(x,0) = C_2^0 \qquad (26)$$

and

$$C_{O_1}(x,0) = C_1^0 - \frac{2\lambda D_{O_1}{}^{1/2}\tau_1{}^{1/2}}{\pi^{1/2}}\exp\left(-\frac{x^2}{4D_{O_1}\tau_1}\right) + \lambda x \operatorname{erfc}\left(\frac{x}{2D_{O_1}{}^{1/2}\tau_1{}^{1/2}}\right) \qquad (27)$$

In equations 26 and 27, C_1^0 and C_2^0 are the bulk concentrations of substances O_1 and O_2, and λ is defined by equation 16. Equation 26 simply expresses that the concentration of substance O_2 is constant before electrolysis. Equation 27 gives the distribution of substance O_1 at the transition time τ_1; equation 27 was originally derived by Sand[5] and by Karaoglanoff.[5]

Derivation of $\partial C_{O_1}(x,t')/\partial x$ for $x = 0$.—The procedure adopted in solving the boundary value stated by equations 24 and 27 is as follows: firstly, the derivative $\partial C_{O_1}(x,t')/\partial x$ for $x = 0$ will be derived by solving the diffusion equation for conditions 24 and 27; the resulting value of $\partial C_O(x,t')/\partial x$ for $x = 0$ will be introduced in (25), and the function $C_{O_2}(x,t')$ will then be derived by solving the diffusion equation for the resulting boundary condition and for the initial condition 26. We determined the derivative $\partial C_{O_1}(x,t')/\partial x$ for $x = 0$ by two methods, namely, the Laplace and Fourier transformations. Both methods yielded the same result and only the derivation based on the use of the Laplace transformation will be discussed here.

By taking the Laplace transform of the diffusion equation with respect to time one obtains the following ordinary differential equation[12,13]

$$\frac{d^2\bar{C}_{O_1}(s,x)}{dx^2} - \frac{s}{D_{O_1}}\bar{C}_{O_1}(s,x) = -\frac{C_{O_1}(x,0)}{D_{O_1}} \qquad (28)$$

where $C_{O_1}(x,0)$ is defined by equation 27. The solution of this equation is of the form

$$\bar{C}(s,x) = M\exp[-(s/D_{O_1})^{1/2}x] + N\exp[(s/D_{O_1})^{1/2}x] + \bar{C}_p(s,x) \qquad (29)$$

where M and N are integration constants and $\bar{C}_p(s,x)$ is a particular solution of equation 28. This particular solution is given by the relationship[14]

$$\bar{C}_p(s,x) = \frac{1}{2\pi i}\int_{\gamma - i\infty}^{\gamma + i\infty}\frac{\Phi(p)}{\psi(p)}\exp(px)dp \qquad (30)$$

where $i = (-1)^{1/2}$; γ is a positive constant; $\Phi(p)$ is the Laplace transform of the function $-C_{O_1}(x,0)/D_{O_1}$ with respect to x (using p instead of s to avoid confusion with the previous transformation); and $\psi(p)$ is the symbolic formulation of equation 28.[15] In the present case one has

$$\psi(p) = p^2 - (s/D_{O_1}) \qquad (31)$$

The integral 30 in which $\psi(p)$ is replaced by its value from (31) can be evaluated by applying the Faltung theorem for the Laplace transform.[16] Thus

$$\bar{C}_p(s,x) = \int_0^x f(\eta)g(x-\eta)d\eta \qquad (32)$$

in which η is an auxiliary variable, and the functions $f(x)$ and $g(x)$ are defined as follows: $f(x) = -C_{O_1}(x,0)/D_{O_1}$ and $g(x)$ is such that the function $1/\psi(p)$ (see eq. 31) is the Laplace transform of $g(x)$. Hence[17]

$$g(x) = \frac{1}{(s/D_{O_1})^{1/2}}\sinh[(s/D_{O_1})^{1/2}x] \qquad (33)$$

In view of equations 32, 33, and the definition of the function $f(x)$, the particular solution $\bar{C}_p(s,x)$ is

$$\bar{C}_p(s,x) = -\frac{C_1^0}{(D_{O_1}, s)^{1/2}}\int_0^x \sinh\left[\left(\frac{s}{D_{O_1}}\right)^{1/2}(x-\eta)\right]d\eta + \frac{\lambda}{D_{O_1}{}^{3/2}s^{1/2}}\int_0^x\left[\frac{2D_{O_1}{}^{1/2}\tau_1{}^{1/2}}{\pi^{1/2}} - \eta\operatorname{erfc}\left(\frac{\eta}{2D_{O_1}{}^{1/2}\tau^{1/2}}\right)\right] \times \sinh\left[\left(\frac{s}{D_{O_1}}\right)^{1/2}(x-\eta)\right]d\eta \qquad (34)$$

or in an abridged form

$$\bar{C}_p(s,x) = -\frac{C_1^0}{D_{O_1}{}^{1/2}s^{1/2}}I_1 + \frac{\lambda}{D_{O_1}{}^{3/2}s^{1/2}}I_2 \qquad (35)$$

I_1 and I_2 corresponding to the integrals of equation 34. These integrals are evaluated in appendix I, and the complete solution of equation 28 is

$$\begin{aligned}\bar{C}_{O_1}(s,x) = {} & M'\exp(-qx) + N'\exp(qx) + \frac{C_1^0}{s} \\ & - \frac{\lambda}{D_{O_1}s}\left[\frac{1}{\pi^{1/2}a}\exp(-a^2x^2) - x\operatorname{erfc}(ax)\right] \\ & - \frac{\lambda}{2D_{O_1}{}^{1/2}s^{3/2}}\exp\left(qx + \frac{q^2}{4a^2}\right)\operatorname{erfc}\left(ax + \frac{q}{2a}\right) \\ & - \frac{\lambda}{2D_{O_1}{}^{1/2}s^{3/2}}\exp\left(-qx + \frac{q^2}{4a^2}\right)\operatorname{erf}\left(ax - \frac{q}{2a}\right)\end{aligned} \qquad (36)$$

with

$$q = s^{1/2}/D_{O_1}{}^{1/2};\ a = {}^1/_2\tau_1{}^{1/2}D_{O_1}{}^{1/2} \qquad (37)$$

The integration constants M' and N' in equation 37 are different from the constants M and N of equation 29, because terms in $\exp(-qx)$ and $\exp(qx)$ in the particular solution have been included in the first two terms on the right-hand of equation 36. Since the function $C_O(x,t)$ is bounded for x from 0 to ∞, it follows that $N' = 0$ in equation 36. The other integrations constant M' is determined by expressing that the transform of the boundary condition 24 is fulfilled. Thus, $C_{O_1}(0,s) = 0$, and

$$M' = \frac{\lambda}{2D_O{}^{1/2}s^{3/2}}\exp\left(\frac{q^2}{4a^2}\right)\operatorname{erfc}\left(\frac{q}{2a}\right) \qquad (38)$$

It is the derivative $\partial C_{O_1}(x,t')/\partial x$ for $x = 0$ in which we are interested, and consequently we can directly differentiate $\bar{C}_{O_1}(s,x)$ with regard to x and introduce the value $x = 0$ in the resulting equation. After regrouping terms and introducing the values of q and a from (37), one finally obtains

$$\left[\frac{\partial C_{O_1}(s,x)}{\partial x}\right]_{x=0} = \frac{\lambda}{D_{O_1}}\left\{\frac{1}{s} - \frac{1}{s^{1/2}} \times \frac{1}{s^{1/2}}\exp(\tau_1 s)\operatorname{erfc}[(\tau_1 s)^{1/2}]\right\} \qquad (39)$$

The inverse transform of $1/s$ is simply 1 and the transform of the second term between braces can be evaluated by the convolution.[18] By noting that the transform of $1/s^{1/2}$ is $1/\pi^{1/2}t^{1/2}$, and the transform of

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(12) H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, London, 1947, p. 246.

(13) We use here the notations of R. V. Churchill, "Modern Operational Mathematics in Engineering," McGraw-Hill Book Co., Inc. New York, N. Y., 1944.

(14) See ref. 9, p. 37, equation 94.

(15) For a discussion of the D method see, for example, M. Morris and O. E. Brown, "Differential Equations," Prentice-Hall, Inc., New York, N. Y., 1946, p. 75.

(16) See ref. 9, p. 30, equation 69.

(17) See ref. 13, p. 296, eq. 17.

(18) See ref. 13, p. 36.

$$\frac{1}{s^{1/2}}\exp(\tau_1 s)\,\mathrm{erfc}\,[(\tau_1 s)^{1/2}]$$

is $1/[\pi(t' + \tau_1)]^{1/2}$, one has

$$\left[\frac{\partial C_{\mathrm{O}_1}(x,t)}{\partial x}\right]_{x=0} = \frac{\lambda}{D_{\mathrm{O}_1}}\left[1 - \frac{1}{\pi}\int_0^t \frac{\mathrm{d}z}{z^{1/2}(\tau_1 + t' - z)^{1/2}}\right] \tag{40}$$

which upon integration yields

$$\left[\frac{\partial C_{\mathrm{O}_1}(x,t')}{\partial x}\right]_{x=0} = \frac{\lambda}{D_{\mathrm{O}_1}}\left[\frac{1}{2} + \frac{1}{\pi}\arcsin\left(\frac{\tau_1 - t'}{\tau_1 + t'}\right)\right] \tag{41}$$

The result embodied in equation 41 was also derived by a different method (Fourier transform); furthermore, equation 41 is verified for $t' = 0$ and for $t' = \infty$. This establishes the correctness of the above treatment.

Values of the ratio of the flux of O_1 for $t' = 0$ and $x = 0$ to the flux for $t' > 0$ and $x = 0$ are plotted against t'/τ_1 in Fig. 3. This diagram shows that the contribution of the reduction of substance O_1 to the total current is indeed very important. For example, at time $t' = \tau_1$, the flux is still one-half of its initial value at time $t' = 0$.

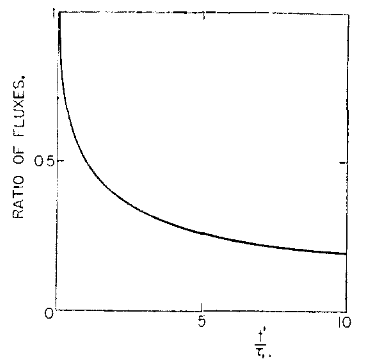

Fig. 3.—Variations of the ratio of the flux of substance O_1 at $x = 0$ and time t' to the flux of this substance at $x = 0$ and time $t' = 0$. Abscissas are calculated in terms of the ratio t'/τ_1.

Derivation of the Function $C_{\mathrm{O}_2}(0,t')$.—The boundary condition 25 can now be rewritten by introducing in it the value of $\partial C_{\mathrm{O}_1}(x,t')/\partial x$ for $x = 0$ from equation 41. Thus

$$\left[\frac{\partial C_{\mathrm{O}_2}(x,t')}{\partial x}\right]_{x=0} = \frac{\mu}{n_2 D_{\mathrm{O}_2}}\left[\frac{1}{2} - \frac{1}{\pi}\arcsin\frac{\tau_1 - t'}{\tau_1 + t'}\right] \tag{42}$$

μ being defined by

$$\mu = i_0/F \tag{43}$$

The problem is to solve the diffusion equation for the initial condition 26 and the boundary condition 42, and this will be done by applying the Laplace transformation. It is advantageous to introduce the function $\mathrm{h}(x,t')$ defined by

$$\mathrm{h}(x,t') = C_2^0 - C_{\mathrm{O}_2}(x,t') \tag{44}$$

By solving the transform of the diffusion equation one obtains (note that $\mathrm{h}(s,x)$ is bounded for $x \to \infty$) the solutions

$$\bar{\mathrm{h}}(s,x) = M\exp\left[-\left(\frac{s}{D_{\mathrm{O}_2}}\right)^{1/2}x\right] \tag{45}$$

in which the integration constant M is determined by satisfying the transform of the boundary condition 42. This transform is obtained by integration by parts, and the following result is obtained

$$\left[\frac{\partial\bar{\mathrm{h}}(x,s)}{\partial x}\right]_{x=0} = \frac{\mu}{n_2 D_{\mathrm{O}_2}}\left\{\frac{1}{s}\exp(\tau_1 s)\,\mathrm{erfc}\,[(\tau_1 s)^{1/2}]\right\} \tag{46}$$

After having determined M from (45) and (46), one finally deduces the following transform of the function $\mathrm{h}(x,t')$

$$\bar{\mathrm{h}}(s,x) = \frac{\mu}{n_2 D_{\mathrm{O}_2}{}^{1/2}}\frac{1}{s^{3/2}}\exp(\tau_1 s)\,\mathrm{erfc}\,[(\tau_1 s)^{1/2}] \times \exp\left[-\left(\frac{s}{D_{\mathrm{O}_2}}\right)^{1/2}x\right] \tag{47}$$

Since only the concentration of O_2 at the electrode surface is needed, the value $x = 0$ can be introduced in equation 47. The inverse transform of the resulting equation is again derived by applying the convolution. Thus, by noting that the inverse transform of $1/s$ is 1, and the inverse transform of

$$\frac{1}{s^{1/2}}\exp(\tau_1 s)\,\mathrm{erfc}\,[(\tau_1 s)^{1/2}]$$

is $1/[\pi(\tau_1 + t')]^{1/2}$ one has

$$\mathrm{h}(0,t') = \frac{\mu}{n_2\pi^{1/2}D_{\mathrm{O}}{}^{1/2}}\int_0^t \frac{\mathrm{d}z}{(\tau_1 + z)^{1/2}} \tag{48}$$

The integral in equation 48 is immediate, and after returning to the function $C_{\mathrm{O}_2}(0,t')$, one finally obtains the concentration of O_2 at the electrode surface

$$C_{\mathrm{O}_2}(0,t') = C_2^0 - \frac{2i_0}{\pi^{1/2}n_2 F D_{\mathrm{O}_2}}[(\tau_1 + t')^{1/2} - \tau_1^{1/2}] \tag{49}$$

This is the remarkably simple final result of the above long derivation. If the transition time τ_1 is made equal to zero, *i.e.*, if only substance O_2 is present in solution, equation 49 takes the form

$$C_{\mathrm{O}_2}(0,t') = C_2^0 - \frac{2i_0}{\pi^{1/2}n_2 F D_{\mathrm{O}_2}{}^{1/2}}t'^{1/2} \text{ for } \tau_1 = 0 \tag{50}$$

This is precisely the value derived by Sand.[5] It is interesting to find that equation 49 for the consecutive reduction of two substances is of the same form as equation 50 for the reduction of a single substance; the only difference between equations 49 and 50 is that the square root of the time elapsed since the beginning of electrolysis in equation 50 is replaced by the difference $[(\tau_1 + t')^{1/2} - \tau_1^{1/2}]$ in equation 49.

Transition Time for the Second Step of the Potential–Time Curve.—The transition time τ for the second step of the potential–time curve is determined by the condition that the concentration of substance O_2 at the electrode surface be equal to zero. Hence, the right-hand member of (49) is equal to zero for $t' = \tau_2$. By solving the resulting equation in τ_2 one deduces

$$\tau_2 = \beta^2 + 2\beta\tau_1^{1/2} \tag{51}$$

with

$$\beta = \pi^{1/2}n_2 F D_{\mathrm{O}_2}{}^{1/2}C_2^0/2i_0 \tag{52}$$

Equation 51 shows that the transition time τ_2 not only depends on the bulk concentration of C_2^0, but also on the bulk concentration of substance O_1 which is reduced at less negative potentials. This is understandable, since substance O_1 continues to be reduced while the reduction of substance O_2 proceeds. The influence of the reduction of O_2 can be evaluated by considering the following case: $n_1 = n_2$, $C_1^0 = C_2^0$, $D_{\mathrm{O}_1} = D_{\mathrm{O}_2}$. By recalling the value of the transition time τ_1 for the first step[5]

$$\tau_1^{1/2} = \pi^{1/2}n_1 F D_{\mathrm{O}_1}{}^{1/2}C_1^0/2i_0 \tag{53}$$

one concludes from equations 51 and 53 that the transition time τ_2 is

$$\tau_2 = 3\tau_1 \tag{54}$$

The transition time τ_2 would have been equal to τ_1, had substance O_1 not been present. The increase in transition time resulting from the presence of substance O_1 is therefore very pronounced.

Since $C_{\mathrm{O}_2}(0,t')$ is equal to zero for $t' = \tau_2$, it follows from equation 49 that the product $i_0[(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2}]$, for given conditions of electrolysis, is independent of the current density i_0. In the case of the reduction of a single substance it is the product $i_0\tau^{1/2}$ which is independent of current density.[5] Equation 49 also shows that the concentration C_2^0 is proportional to the quantity $[(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2}]$, and this property can be applied in analytical determinations.

We also derived the equation of the second step of the potential–time curve, but the resulting equation does not lead to any interesting conclusion.

The above treatment was verified experimentally for mixtures of cadmium and zinc ions. The results summarized in Table II show that the product $i_0[(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2}]$ is indeed independent of the current density. The average values of this product are also proportional to the concentration of zinc ion: the ratios of concentrations are 2, 1, 0.75 and 0.30, whereas the corresponding ratios of the average values of the product $i_0[(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2}]$ are 2.06, 1, 0.766 and 0.312.[19] The experimental errors are those one would expect for recording on a 5-inch screen of a cathode-ray oscillograph. Finally, Table II shows that the experimental determination of zinc ion in presence of a tenfold excess of cadmium leads to very uncertain results (solution I). This conclusion could easily be generalized.

TABLE II

DATA FOR THE ELECTROLYSIS OF MIXTURES OF CADMIUM AND ZINC IONS

Current 10^{-3} amp.	τ_1, sec.	τ_2, sec.	$i[(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2}]$, 10^{-3} amp. sec.$^{1/2}$	τ_1, sec.	τ_2, sec.	$i[(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2}]$, 10^{-3} amp. sec.$^{1/2}$
	Solution I[a]			Solution II[a]		
1.32	2.70	1.32	0.13	2.50	1.56	0.58
1.96	1.28	0.25	.22	1.17	0.685	.54
3.18	0.42	.0878	.21	0.42	.307	.65
4.81	.182	.0612	.32	0.202	.123	.58
9.39	.050	.015	.30	....	...	..
		Average	0.24		Average	0.59
	Solution III[a]			Solution IV[a]		
1.32	2.62	2.24	0.77	....	...	..
1.96	1.22	1.07	.81	1.21	2.54	1.65
3.18	0.435	0.385	.78	0.442	0.87	1.54
4.81	.178	.161	.77	.19	.40	1.59
9.39	.046	.0377	.70	.0477	.102	1.59
		Average	0.77		Average	1.59

[a] Concentration of cadmium ion: $3 \times 10^{-3} M$ in all cases; concentration of zinc ion: $3 \times 10^{-4} M$ (soln. I), $7.5 \times 10^{-4} M$ (soln. II), $10^{-3} M$ (soln. III), $2 \times 10^{-3} M$ (soln. IV); supporting electrolyte: 1 M potassium nitrate.

Case III—Stepwise Reduction of a Single Substance

The stepwise reduction of a substance O according to the equations

$$O + n_1e = R_1 \qquad (55)$$

$$R_1 + n_2e = R_2 \qquad (56)$$

will now be treated for the case in which the substances O and R_1 are reduced at sufficiently different potentials to yield a potential–time curve exhibiting two steps. As in the previous cases, the problem will be solved for conditions of semi-infinite diffusion, the effects of migration and convection being assumed to be negligible.

The transition time τ_1 for reaction 55 can be calculated on the basis of the treatment developed by Sand,[5] but this is not so for the transition time τ_2 corresponding to the second step. After the transition time τ_1, the concentration of substance O at the electrode surface is equal to zero, but this substance continues to diffuse toward the electrode where it is reduced directly to R_2 in a process involving $n_1 + n_2$ electrons. Furthermore, substance R_1 which was produced in the first step of the electrolysis (equation 55) diffuses toward the electrode at which it is reduced according to reaction 56. As a result, the current through the cell is the sum of two components according to the formula

$$(n_1 + n_2)FD_0\left[\frac{\partial C_O(x,t')}{\partial x}\right]_{x=0} + n_2FD_{R_1}\left[\frac{\partial C_{R_1}(x,t')}{\partial x}\right]_{x=0} = i_0 \qquad (57)$$

which is written in terms of the time t' defined by the relationship $t' = t - \tau_1$, t being the time elapsed since the beginning of the electrolysis (first step). Equation 57 is the boundary condition for the present problem. This condition can be modified by replacing the derivative $\partial C_O(x,t')/\partial x$ for $x = 0$ by its value derived for Case II (equation 41). After a few simple transformations, the boundary condition becomes

$$\left[\frac{\partial C_{R_1}(x,t')}{\partial x}\right]_{x=0} = \frac{i_0}{n_2FD_{R_1}} - \frac{(n_1 + n_2)i_0}{n_1n_2FD_{R_1}}\left[\frac{1}{2} + \frac{1}{\pi}\text{arc sin}\,\frac{\tau_1 - t'}{\tau_1 + t'}\right] \qquad (58)$$

Note that equation 58 is written in an expanded form to show the similarity between the present boundary condition and that expressed by equation 41. Equation 1 as written with the diffusion coefficient D_{R_1} instead of D_R gives the distribution of substance R_1 at time τ_1, and consequently this formula expresses the initial condition for the present problem.

Derivation of the Concentration C_{R_2} $(0,t')$.—The above boundary value problem will be solved by applying the Laplace transformation as in Case II. The treatment is similar as that previously discussed, and equation 36 holds for this case provided that D_{O_1} and $s^{1/2}/D_{O_1}$ be replaced by D_{R_1} and $s^{1/2}/D_{R_1}$, respectively. The integration constant N is again equal to zero, and M is defined by satisfying the transform of the boundary condition 58, *i.e.*, the condition

$$[\mathrm{d}\bar{C}_{R_1}(x,s)/\mathrm{d}x]_{x=0} = i_0/n_2FD_{R_1}s - \frac{(n_1 + n_2)i_0}{n_1n_2FD_{R_1}}\left\{\frac{1}{2s} - \frac{1}{s}\exp(\tau_1s)\,\text{erfc}\,[(\tau_1s)^{1/2}]\right\} \qquad (59)$$

After rearranging the terms one finally arrives at the following transform of the solution of $x = 0$

$$\bar{C}_{R_1}(0,s) = \frac{2i_0\,\tau_1^{1/2}}{\pi^{1/2}n_1FD_{R_1}^{1/2}} \times \frac{1}{s} - \frac{i_0}{n_2FD_{R_1}}\frac{1}{s^{3/2}}\exp\,(\tau_1s)\,\text{erfc}\,[(\tau_1s)^{1/2}] \qquad (60)$$

The inverse transform is performed by applying the convolution as for equation 39, and this leads to the solution

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[19] Note that the solutions of cadmium and zinc ions were not standardized, and consequently the absolute concentrations of these substances are not known exactly. However, the various solutions were prepared by dilution of a single zinc solution, and the ratios of zinc ion concentrations are only affected by the errors resulting from dilution.

$$C_{R_1}(0,t') = \frac{2i_0}{\pi^{1/2}n_2FD_{R_1}^{1/2}}\left[\frac{n_1+n_2}{n_1}\,\tau_1^{1/2} - (\tau_1+t')^{1/2}\right] \quad [61)$$

Transition Time.—The transition time, obtained by equating to zero the concentration $C_{R_1}(0,t')$, is

$$\tau_2 = \tau_1[2(n_2/n_1) + (n_2/n_1)^2] \quad (62)$$

For example, when n_1 and n_2 are equal, the transition time τ_2 is equal to $3\tau_1$; likewise for $n_2/n_1 = 2$, one has $\tau_2/\tau_1 = 8$.

The above treatment was verified experimentally for the stepwise reduction of oxygen and uranyl ion. Data obtained at different current densities are listed in Table III, and two examples of potential–time curves are shown in Fig. 4. The average experimental results $\tau_2/\tau_1 = 2.97$ for oxygen and $\tau_2/\tau_1 = 7.91$ for uranyl ion are in good agreement with the theoretical values $3(n_2/n_1 = 1)$ and $8(n_2/n_1 = 2)$ one computes from equation 62.[20] It is to be noted that the exact determination of τ_1 and τ_2 on the potential–time curve for uranyl ion (Fig. 4 on the right) is difficult when the complete curve is recorded on a 5 inch screen of a cathode-ray oscillograph. Hence, the curve of Fig. 4 is given merely to show the general shape of the potential–time curve thus obtained. More reliable results were obtained by recording the potential curve for the first step (τ_1) separately and by using an expanded scale of time.

TABLE III

DATA FOR THE STEPWISE REDUCTION OF OXYGEN AND URANYL ION

Oxygen[a]			Uranyl ion[b]		
τ_1, sec.	τ_2, sec.	τ_2/τ_1	τ_1, sec.	τ_2, sec.	τ_2/τ_1
1.29	3.84	2.97	0.264	2.14	7.97
0.716	2.09	2.92	.139	1.09	7.86
.328	1.02	3.11	.090	0.71	7.89
.128	0.368	2.88	. . .	. .	. .
	Average	2.97		Average	7.91

[a] 1 *M* lithium chloride saturated with oxygen at 25°. [b] 10^{-3} *M* uranyl nitrate in 0.1 *M* potassium chloride and 0.01 *M* hydrochloric acid. Thymol present at a concentration of $2 \times 10^{-4}\%$.

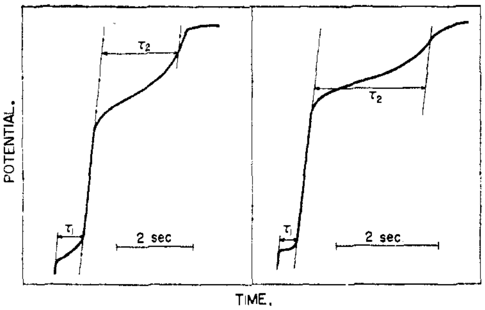

Fig. 4.—Potential-time curves for the stepwise reduction of oxygen (left) and uranyl ion. See data in Table III. Note that one has approximately $\tau_2 = 3\tau_1$ (left) and $\tau_2 = 8\tau_1$ (right).

Derivation of $C_{R_2}(0,t)$.—In order to derive the equation for the potential–time curve (see below) for the second step it is necessary to know the concentrations $C_{R_1}(0,t')$ and $C_{R_2}(0,t')$. The former concentration is given by equation 61, and the latter will now be calculated. Substance R_2 is produced either by reduction of substance O or by reduction of substance R_1. Hence, the sum of the fluxes of substances O, R_1, and R_2 at the electrode surface is equal to zero. Thus

$$D_0\left[\frac{\partial C_O(x,t')}{\partial x}\right]_{x=0} + D_{R_1}\left[\frac{\partial C_{R_1}(x,t')}{\partial x}\right]_{x=0} + D_{R_2}\left[\frac{\partial C_{R_2}(x,t')}{\partial x}\right]_{x=0} = 0 \quad (63)$$

Equation 63 is the boundary condition for the present problem. The initial condition on the other hand is: $C_{R_2}(x, 0) = 0$. Equation 63 can be rewritten by combining it with equations 41 and 58, and the following boundary condition is obtained in this manner

$$\left[\frac{\partial C_{R_2}(x,t')}{\partial x}\right]_{x=0} = -\frac{i_0}{n_2FD_{R_2}}\left[\frac{1}{2} - \frac{1}{\pi}\arcsin\frac{\tau_1 - t'}{\tau_1 + t}\right] \quad (64)$$

The solution is derived by applying the Laplace transformation as in the previous section, the integration constant being determined by satisfying the transform of equation 64. After inverse transformation, one obtains by using the convolution as in the case of equation 47, the concentration $C_{R_2}(0,t')$. Thus

$$C_{R_2}(0,t') = \frac{2i_0}{\pi^{1/2}n_2FD_{R_2}^{1/2}}[(\tau_1+t')^{1/2} - \tau_1^{1/2}] \quad (65)$$

Potential–Time Curve.—In case of electrochemical equilibrium the equation for the potential–time curve for the second step of the electrode process (reaction 56) is obtained by introducing in the Nernst equation the concentrations from (61) and (65). The resulting equation can be rewritten by taking into account that according to (61) one has

$$\frac{n_1+n_2}{n_1}\,\tau_1^{1/2} = (\tau_1+\tau_2)^{1/2} \quad (66)$$

Thus

$$E = (E_{1/2})_{R_1-R_2} + \frac{RT}{n_2F}\ln\frac{(\tau_1+\tau_2)^{1/2} - (\tau_2+t')^{1/2}}{(\tau_1+t')^{1/2} - \tau_1^{1/2}} \quad (67)$$

where the potential $(E_{1/2})_{R_1-R_2}$ is defined in the similar fashion as the potential $E_{1/2}$ for the system O–R_1 in equation 19. The time at which the potential E is equal to $(E_{1/2})_{R_1-R_2}$ is obtained by equating to unity the argument of the logarithm term in (67). After simple transformations one obtains

$$t'_{E_{1/2}} = \frac{\tau_2}{4} + \frac{1}{2}\frac{n_2}{n_1}\tau_1 \quad (68)$$

For example if $n_1 = n_2$, one has $\tau_2 = 3\tau_1$, and the potential $E_{1/2}$ is observed at $t' = \tau_2/4 + \tau_2/6$ or $5\tau_2/12$. The time is one-fourth of the transition time in the reduction of a single substance in a one-step process.[7]

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[20] The composition of the supporting electrolyte in the reduction of uranyl ion was exactly the same as that Kolthoff and Harris (THIS JOURNAL, **68**, 1175 (1946)) used in one phase of their study of the polarography of uranium. This is why thymol was added although it might not have been needed in the electrolysis at constant current. Note that the above authors found $n_2/n_1 = 2.12$ from polarographic waves for the conditions listed in Table III. This abnormality possibly does not exist in the constant current method, since the ratio τ_2/τ_1 for $n_2/n_1 = 2.12$ is 8.50, whereas the average experimental value of τ_2/τ_1 is 7.91. This point, however, cannot be settled here on account of the relatively large experimental errors (see Fig. 4).

Experimental

The experimental method applied in this investigation was identical to that previously reported.[7] The reversal of current in the experiments on re-oxidation process was controlled by a D.P.D.T. relay which was actuated manually by closing a tap key. Experimental results were discussed above.

Conclusion

It is possible to develop a rigorous mathematical analysis of potential–time curves for the three types of electrode processes discussed in the present paper. Rigorous interpretations of potential–time curves can be developed for cases for which only *approximate* treatments are available in polarography and/or transitory voltammetry (see Case I and ref. 7), and consequently the constant current method appears more advantageous than the former two methods in electrochemical kinetics. Further work in this direction will be discussed in a subsequent paper.

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APPENDIX: EVALUATION OF THE INTEGRALS I_1 AND I_2 OF EQUATION 35

The integral I_1 is directly obtained from tables. Thus

$$I_1 = \frac{D_O}{s}\left\{\cosh\left[\left(\frac{s}{D_{O_1}}\right)^{1/2}x\right] - 1\right\} \qquad (69)$$

The integral I_2 is evaluated by successive integrations by parts. In the first integration one sets

$$V = (1/\pi^{1/2}a)\exp(-a^2\eta^2) - \eta\,\mathrm{erfc}(a\eta) \qquad (70)$$

$$\mathrm{d}u = \sinh[(s/D_{O_1})^{1/2}(x - \eta)]\mathrm{d}\eta \qquad (71)$$

where a is defined by equation 37. After integration, this leads to a third integral

$$I_3 = \int_0^x \cosh\left[\left(\frac{s}{D_{O_1}}\right)^{1/2}(x - \eta)\,\mathrm{erfc}\,(a\eta)\right]\mathrm{d}\eta \qquad (72)$$

which is evaluated by setting erfc $(a\,\eta)$ as v and the remaining terms as du. The following fourth integral is obtained in this manner

$$I_4 = \int_0^x \exp(-a^2\eta^2)\sinh[(s/D_{O_1})^{1/2}(x - \eta)]\mathrm{d}\eta \qquad (73)$$

and this integral is calculated by substituting for the hyperbolic sine the corresponding exponential functions. After collecting terms, one finally obtains equation 36.

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Ultracentrifugal Properties of Human γ-Globulins Prepared by Electrophoresis–Convection[1,2]

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Ultracentrifuge studies have been carried out on fractions of γ-globulin, separated from normal human sera by electrophoresis–convection. 90–99% of these preparations sedimented as a single component with an extrapolated sedimentation constant of 6.56 Svedberg units. By analysis of the spreading of the sedimenting boundary with time, it was found that these γ-globulins possess a distribution of sedimentation constants with a standard deviation of ±0.32 Svedberg unit. The unsymmetrical form of this distribution is due to the different sedimentation properties of pseudoglobulin and euglobulin. The standard deviations of the distributions of sedimentation constants for pseudoglobulin and euglobulin are about 5% of the mean. There is no correlation between the electrophoretic heterogeneity of γ-globulin and its heterogeneity with respect to sedimentation constant.

Introduction

Development in recent years of chemical and physical methods for the fractionation of human and animal blood plasma and serum has made possible the separation of γ-globulin in a state of high purity. This electrophoretic component of serum is of particular interest to the immunologist and immunochemist since it contains antibodies against a variety of pathogenic agents and other antigens. In addition to being indispensable in following the fractionation and assuring uniformity of the product, physical chemical measurements on γ-globulin yield information as to its molecular characteristics, thus giving insight into its reactions and immunological properties. An example of such a measurement is afforded by the method of sedimentation velocity, which permits determination of the mean size and shape of the globulin molecules and the heterogeneity with respect to these parameters.

A number of investigators have carried out ultracentrifugal studies on γ-globulin, prepared by the low-temperature ethanol fractionation procedure.[3–7] These preparations contained at least three components with average sedimentation constants of s = 7 Svedberg units, s = 8–12 and s = 18–20. The per cent. of the normal component with s = 7 varied from 89–57%, with a corresponding increase in the heavier components. Some preparations contained about 5% of a slow-moving component with sedimentation constant s = 4–5. This component presumably represented albumin, at least in part. By analysis of the spreading of

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(2) Presented before the Division of Physical and Inorganic Chemistry at the 123rd Meeting of the American Chemical Society, Los Angeles, California, March, 1953.

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