

AD NO. 3647
ASTIA FILE COPY

Technical Report
to the
OFFICE OF NAVAL RESEARCH

Report No. 13
Project NR 051 - 258

THEORY OF ELECTROLYSIS AT CONSTANT CURRENT IN UNSTIRRED SOLUTION -
II. CONSECUTIVE ELECTROCHEMICAL REACTIONS

by

TALIVALDIS BERZINS AND PAUL DELAHAY

March, 1953
Department of Chemistry
Louisiana State University
Baton Rouge 3, Louisiana

ABSTRACT

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 volt: 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 laboratory¹ as well as by other investigators². Interesting results have been reported in this

¹ P. Delahay, J. Am. Chem. Soc., 73, 4944 (1951); 74, 3497, 3506 (1952); 75, 0000 (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, 74, 3500 (1952); J.E. Strassner and P. Delahay, 74, 6232 (1952).

² J. Koutecky and R. Brdicka, Collection Czechoslov. Chem. Commun., 12, 337 (1947); H. Eyring, L. Marker, and T.C. Kwok, 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. Commun., 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, New York, N. Y., 1952, pp. 268-294.

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 diffusion³, becomes very involved when there is partial kinetic control⁴. Electrolysis at constant current in unstirred solution does not

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

⁴ P. Delahay, J. Am. Chem. Soc., 75, 1190 (1953).

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 old⁵, but it was revived only recently⁶. A first paper

from this Laboratory⁷ dealt with general principles and with the treatment

⁵ H.P. Weber, Wied. Ann., 7, 536 (1879); H.J.S. Sand, Phil. Mag., 1, 45 (1901); Z. Karaoglanoff, Z. Electrochem., 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", 1950, Tamburini, Milan, pp. 117 and 279.

⁷ P. Delahay and T. Berzins, J. Am. Chem. Soc., 75, 0000 (1953).

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 distance x from the electrode. This concentration is, according to Karaoglanoff⁵

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

with

$$\theta = \frac{i_0}{n F D_R} \quad (2)$$

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 times τ corresponding to the reduction of substance O,⁸ but is valid for any value of t smaller than the transition time τ .

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.

At time τ the current through the cell is reversed, and consequently substance R is now re-oxidized 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 following condition

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

in which λ' is defined as follows

$$\lambda' = \frac{i_0'}{\pi F D_R} \quad (4)$$

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 following 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 following relationship⁹

⁹ I.N. Sneddon, "Fourier Transforms", McGraw-Hill, New York, N.Y., 1951, p. 5.

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

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

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

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:

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

The solution of this ordinary differential equation is immediate:

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

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:

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

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:

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

$$\begin{aligned}
& -\left(\frac{2}{\pi}\right)^{1/2} \frac{\theta}{\beta^2} \left\{ 1 - \exp\left[-D_R t' \beta^2\right] \right\} \\
& -\left(\frac{2}{\pi}\right)^{1/2} \frac{\lambda'}{\beta^2} \left\{ 1 - \exp\left[-D_R t' \beta^2\right] \right\} \quad (11)
\end{aligned}$$

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:

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

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 are also 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: $i_0 = i_0^1 = 10^{-2}$ amp.cm.⁻², $D_O = D_R = 10^{-5}$ cm².sec.⁻¹, $n = 1$, $C^* = 5 \times 10^{-5}$ 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_0^1 ; 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).

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 $O \rightarrow R$ and the transition time τ' for the re-oxidation process

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

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:

$$\tau' = 1/3 \tau \quad (14)$$

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' fluctuates 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 per cent) 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.

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 $t \leq \tau$.

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:

$$E = E^{\circ} + \frac{RT}{\pi F} \ln \frac{f_O}{f_R} + \frac{RT}{\pi F} \ln \frac{C^{\circ} - 2\lambda \left[\frac{D_O(\tau + t')}{\pi} \right]^{1/2} + 4\lambda \left(\frac{D_O t'}{\pi} \right)^{1/2}}{2\theta \left[\frac{D_R(\tau + t')}{\pi} \right]^{1/2} - 4\theta \left(\frac{D_R t'}{\pi} \right)^{1/2}} \quad (15)$$

The notations in equation (15) are as follows: E° is the standard potential for the couple O-R¹⁰; f_O and f_R are the activity coefficients

¹⁰ If an amalgam electrode is involved, E° is the standard potential for the amalgam.

of substances O and R; D_O is the diffusion coefficient of substance O; C° is the bulk concentration of substance O and the quantity λ is defined as follows:

$$\lambda = \frac{i_0}{n F D_O} \quad (16)$$

Equation (15) can be modified by recalling that the transition time is related to the concentration C° by the equation⁵:

$$C^\circ = 2 \lambda \left(\frac{D_O \tau}{\pi} \right)^{1/2} \quad (17)$$

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

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

with

$$E_{1/2} = E^\circ + \frac{RT}{nF} \ln \frac{f_O D_R^{1/2}}{f_R D_O^{1/2}} \quad (19)$$

It was previously shown that the potential $E_{1/2}$ for a simple reduction or oxidation process is observed at a time equal to $1/4 \tau^2$, and the

potential $E_{1/2}$ for the reduction of substance O can readily be determined experimentally. If electrochemical equilibrium is achieved at the electrode, the potential $E_{1/2}$ 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:

$$t'_{E = E_{1/2}} = 0.222 \tau' \quad (20)$$

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 accordingly¹¹.

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, J. Amer. Chem. Soc., 63, 1018 (1941).

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 volt.

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

$$\frac{i'_0}{nF} = k_{t,h} C_R(0, t') \quad (21)$$

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

$$k_{t,h} = k_{t,h}^0 \exp \left[\frac{(1-\alpha) n F E}{RT} \right] \quad (22)$$

in which $k_{t,h}^0$ is the value of the constant at $E = 0$ (vs. the normal hydrogen electrode), and α is the transfer coefficient for the cathodic process $O \rightarrow R$. By combining equation (12) (for $x = 0$), (21) and (22), one obtains the following potential-time characteristic:

$$E = \frac{RT}{(1-\alpha)nF} \ln \frac{\pi^{1/2} D_R^{1/2}}{2k_{t,h}^0} - \frac{RT}{(1-\alpha)nF} \ln \left[(\tau+t')^{1/2} - 2t'^{1/2} \right] \quad (23)$$

According to equation (23) a plot of the logarithm of the quantity $[(\tau+t')^{1/2} - 2t'^{1/2}]$ versus E should yield a straight line whose reciprocal slope is $(RT) / (1-\alpha) n F$; 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 process⁷, 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 $k_{b,h}^{\circ}$ is calculated from the potential $t' = 0$ (see equation (23)), and the corresponding rate constant $k_{f,h}^{\circ}$ for the cathodic process is determined from the potential-time curve for the cathodic process⁷. A complete study of the kinetics of the electrochemical reaction can thus be made. Finally, the free energies of activation corresponding to $k_{f,h}^{\circ}$ and $k_{b,h}^{\circ}$ 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.

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 Sand⁵ and by Karaoglanoff⁵ 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 transition time τ_1 is equal to zero at the electrode surface, and this concentration remains equal to zero at 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:

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

$$n_1 D_{O_1} \left[\frac{\partial C_{O_1}(x, t')}{\partial x} \right]_{x=0} + n_2 D_{O_2} \left[\frac{\partial C_{O_2}(x, t')}{\partial x} \right]_{x=0} = \frac{i_0}{F} \quad (25)$$

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:

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

and

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

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 Sand⁵ and by Karaoglanoff⁵.

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) to (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 $\partial C_{O_1}(x, t') / \partial x$ 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}:

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, New York, N.Y., 1944.

$$\frac{d^2 \bar{C}_0(s, x)}{dx^2} - \frac{s}{D_0} \bar{C}_0(s, x) = - \frac{C_0(x, 0)}{D_0} \quad (28)$$

where $C_0(x, 0)$ is defined by equation (27). The solution of this equation is of the form

$$\bar{C}(s, x) = M \exp\left[-\left(\frac{s}{D_0}\right)^{1/2} x\right] + N \exp\left[\left(\frac{s}{D_0}\right)^{1/2} x\right] + \bar{C}_p(s, x) \quad (29)$$

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:

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

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

where $i = (-1)^{1/2}$; σ is a positive constant; $\Phi(p)$ is the Laplace transform of the function $-C_{0_1}(x, 0) / D_{0_1}$ 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

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

case one has:

$$\Psi(p) = p^2 - \frac{\sigma}{D_{0_1}} \quad (31)$$

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 transform¹⁶. Thus:

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

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

in which η is an auxiliary variable, and the functions $f(x)$ and $g(x)$ are defined as follows: $f(x) = -C_{0_1}(x, 0) / D_{0_1}$ and $g(x)$ is such that the function $1/\Psi(p)$ (see eq.(31)) is the Laplace transform of $g(x)$. Hence¹⁷:

¹⁷ See ref. 13, p. 296, eq.(17).

$$f(x) = \frac{1}{\left(\frac{\delta}{D_0}\right)^{1/2}} \sinh \left[\left(\frac{\delta}{D_0}\right)^{1/2} x \right] \quad (33)$$

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

$$\begin{aligned} \bar{C}_p(\delta, x) = & - \frac{C_1^0}{(D_0 \delta)^{1/2}} \int_0^x \sinh \left[\left(\frac{\delta}{D_0}\right)^{1/2} (x-\eta) \right] d\eta \\ & + \frac{\lambda}{D_0^{3/2} \delta^{1/2}} \int_0^x \left[\frac{2 D_0^{1/2} \tau_1^{1/2}}{\pi^{1/2}} \exp\left(-\frac{\eta^2}{4 D_0 \tau_1}\right) \right. \\ & \left. - \eta \operatorname{erfc}\left(\frac{\eta}{2 D_0^{1/2} \tau_1^{1/2}}\right) \right] \sinh \left[\left(\frac{\delta}{D_0}\right)^{1/2} (x-\eta) \right] d\eta \end{aligned} \quad (34)$$

or in an abridged form

$$\bar{C}_p(\delta, x) = - \frac{C_1^0}{D_0^{1/2} \delta^{1/2}} I_1 + \frac{\lambda}{D_0^{3/2} \delta^{1/2}} I_2 \quad (35)$$

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:

$$\begin{aligned} \bar{C}_0(\tau, x) = & M' \exp(-qx) + N' \exp(qx) + \frac{C^0}{\tau} \\ & - \frac{\lambda}{D_0 \tau} \left[\frac{1}{\pi^{1/2} a} \exp(-a^2 x^2) - x \operatorname{erfc}(ax) \right] \\ & - \frac{\lambda}{2 D_0^{1/2} \tau^{3/2}} \exp\left(qx + \frac{q^2}{4a^2}\right) \operatorname{erfc}\left(ax + \frac{q}{2a}\right) \\ & - \frac{\lambda}{2 D_0^{1/2} \tau^{3/2}} \exp\left(-qx + \frac{q^2}{4a^2}\right) \operatorname{erf}\left(ax - \frac{q}{2a}\right) \end{aligned} \quad (36)$$

with

$$q = \frac{\tau^{1/2}}{D_0^{1/2}} \quad a = 1/2 \tau_1^{1/2} D_0^{1/2} \quad (37)$$

The integration constants M' and N' in equation (36) 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 $C_0(x, t)$ is bounded for x from 0 to ∞ , it follows that $N' = 0$ in

equation (36). The other integration constant M' is determined by expressing that the transform of the boundary condition (24) is fulfilled.

Thus $C_0(0, s) = 0$, and

$$M' = \frac{\lambda}{2 D_0^{1/2} s^{3/2}} \exp\left(\frac{q^2}{4 a^2}\right) \operatorname{erfc}\left(\frac{q}{2 a}\right) \quad (38)$$

It is the derivative $\partial C_0(x, t) / \partial x$ for $x = 0$ in which we are interested, and consequently we can directly differentiate $\bar{C}_0(s, x)$ 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:

$$\left(\frac{\partial \bar{C}_0(s, x)}{\partial x}\right)_{x=0} = \frac{\lambda}{D_0} \left\{ \frac{1}{s} - \frac{1}{s^{1/2}} \cdot \frac{1}{s^{1/2}} \exp(\tau, s) \operatorname{erfc}\left[(\tau, s)^{1/2}\right] \right\} \quad (39)$$

The inverse transform of $1/s$ is simply 1 and the transform of the second term between braces can be evaluated by the convolution¹⁸. By

¹⁸ See ref. 13, p. 36.

noting that the transform of $1/s^{1/2}$ is $1/\pi^{1/2} t^{1/2}$, and the transform of

$$\frac{1}{z^{1/2}} \exp(\tau, \tau) \operatorname{erfc} \left[(\tau, \tau)^{1/2} \right]$$

is $1 / [\pi (\tau' + \tau_1)]^{1/2}$, one has

$$\left[\frac{\partial C_{O_1}(x, t')}{\partial x} \right]_{x=0} = \frac{\lambda}{D_{O_1}} \left[1 - \frac{1}{\pi} \int_0^t \frac{dz}{z^{1/2} (\tau_1 + t' - z)^{1/2}} \right] \quad (40)$$

which upon integration yields:

$$\left[\frac{\partial C_{O_1}(x, t')}{\partial x} \right]_{x=0} = \frac{\lambda}{D_{O_1}} \left[\frac{1}{2} + \frac{1}{\pi} \operatorname{arc sin} \left(\frac{\tau_1 - t'}{\tau_1 + t'} \right) \right] \quad (41)$$

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 $t' = 0$.

DERIVATION OF THE FUNCTION $C_{O_2}(0, t')$.

The boundary condition (25) can now be rewritten by introducing in it the value of $\partial C_{O_1}(x, t') / \partial x$ for $x = 0$ from equation (41).

Thus

$$\left[\frac{\partial C_{O_2}(x, t')}{\partial x} \right]_{x=0} = \frac{\mu}{\pi_2 D_{O_2}} \left[\frac{1}{2} - \frac{1}{\pi} \arcsin \frac{\tau_1 - t'}{\tau_1 + t'} \right] \quad (42)$$

μ being defined by

$$\mu = i_0 / F \quad (43)$$

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 transform. It is advantageous to introduce the function $h(x, t')$ defined by

$$h(x, t') = C_2^0 - C_{O_2}(x, t') \quad (44)$$

By solving the transform of the diffusion equation one obtains (note that $h(x, x)$ is bounded for $x \rightarrow \infty$) the solution

$$\bar{h}(s, x) = M \exp \left[- \left(\frac{s}{D_{O_2}} \right)^{1/2} x \right] \quad (45)$$

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

$$\left[\frac{\partial \bar{h}(x, s)}{\partial x} \right]_{x=0} = \frac{\mu}{\pi_2 D_{O_2}} \left\{ \frac{1}{s} \exp(\tau_1, s) \operatorname{erfc} \left[(\tau_1, s)^{1/2} \right] \right\} \quad (46)$$

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

$$\bar{h}(s, x) = \frac{\mu}{n_2 D_{O_2}^{1/2}} \frac{1}{s^{3/2}} \exp(\tau_1 s) \operatorname{erfc} \left[(\tau_1 s)^{1/2} \right] \exp \left[- \left(\frac{s}{D_{O_2}} \right)^{1/2} x \right] \quad (47)$$

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

$$\frac{1}{s^{1/2}} \exp(\tau_1 s) \operatorname{erfc} \left[(\tau_1 s)^{1/2} \right]$$

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

$$h(0, t') = \frac{\mu}{n_2 \pi^{1/2} D_0^{1/2}} \int_0^t \frac{dz}{(\tau_1 + z)^{1/2}} \quad (48)$$

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

$$C_{O_2}(0, t') = C_2^0 - \frac{2 i_0}{\pi^{1/2} n_2 F D_{O_2}^{1/2}} \left[(\tau_1 + t')^{1/2} - \tau_1^{1/2} \right] \quad (49)$$

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

$$C_{O_2}(0, t') = C_2^0 - \frac{2 i_0}{\pi^{1/2} n_2 F D_{O_2}^{1/2}} t'^{1/2} \quad \text{for } \tau_1 = 0 \quad (50)$$

This is precisely the value derived by Sand⁵. 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_2 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

$$\tau_2 = \beta^2 + 2\beta \tau_1^{1/2} \quad (51)$$

with

$$\beta = \frac{\pi^{1/2} n_2 F D_{O_2} C_2^0}{2 i_0} \quad (52)$$

Equation (51) shows that the transition time τ_2 not only depends on the bulk concentration of O_2 , 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: $n_1 = n_2$, $C_1^0 = C_2^0$, $D_{O_1} = D_{O_2}$. By recalling the value of the transition time τ_1 for the first step⁵

$$\tau_1^{1/2} = \frac{\pi^{1/2} n_1 F D_{O_1}^{1/2} C_1^0}{2 i_0} \quad (53)$$

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

$$\tau_2 = 3 \tau_1 \quad (54)$$

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 $C_{O_2}(0, t')$ is equal to zero for $t' = \tau_2$, it follows from equation (49) that the product $i_0 \left[(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2} \right]$, 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 $i_0 \tau_1^{1/2}$ which is independent of current density⁵. Equation (49) also shows that the concentration C_2^* is proportional to the quantity $\left[(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2} \right]$, 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 $i_0 \left[(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2} \right]$ 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 $i_0 \left[(\tau_1 + \tau_2)^{1/2} - \tau_1^{1/2} \right]$ are 2.06, 1, 0.766, and 0.312.¹⁹

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.

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.

CASE III. STEPWISE REDUCTION OF A SINGLE SUBSTANCE

The stepwise reduction of a substance O according to the equations



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 Sand⁵, 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

$$\begin{aligned} & (\pi_1 + \pi_2) F D_0 \left[\frac{\partial C_0(x, t')}{\partial x} \right]_{x=0} \\ & + \pi_2 F D_{R_1} \left[\frac{\partial C_{R_1}(x, t')}{\partial x} \right]_{x=0} = i_0 \end{aligned} \quad (57)$$

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 (1st step). Equation (57) is the boundary condition for the present problem. This condition can be modified by replacing the derivative $\partial C_C(x, t') / \partial x$ for $x = 0$ by its value derived for Case II (equation (41)). After a few simple transformations, the boundary condition becomes:

$$\begin{aligned} & \left[\frac{\partial C_{R_1}(x, t')}{\partial x} \right]_{x=0} = \frac{i_0}{\pi_2 F D_{R_1}} \\ & \frac{(\pi_1 + \pi_2) i_0}{\pi_1 \pi_2 F D_{R_1}} \left[\frac{1}{2} + \frac{1}{\pi} \arcsin \frac{\tau_1 - t'}{\tau_1 + t'} \right] \end{aligned} \quad (58)$$

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_{R_1} and $\delta^{1/2} / D_{R_1}$ be replaced by D_{O_1} and $\delta^{1/2} / D_{O_1}$, 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

$$\left[\frac{d\bar{C}_{R_1}(x, s)}{dx} \right]_{x=0} = \frac{i_0}{\pi_2 F D_{R_1} s}$$

$$-\frac{(\pi_1 + \pi_2) i_0}{\pi_1 \pi_2 F D_{R_1}} \left\{ \frac{1}{2s} - \frac{1}{s} \exp(\tau_1 s) \operatorname{erfc}[(\tau_1 s)^{1/2}] \right\} \quad (59)$$

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

$$\bar{C}_{R_1}(0, s) = \frac{2 i_0 \tau_1^{1/2}}{\pi^{1/2} \pi_1 F D_{R_1}^{1/2}} \frac{1}{s} - \frac{i_0}{\pi_2 F D_{R_1}} \frac{1}{s^{3/2}} \exp(\tau_1 s) \operatorname{erfc}[(\tau_1 s)^{1/2}] \quad (60)$$

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

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

TRANSITION TIME.

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

$$\tau_2 = \tau_1 \left[2 \left(\frac{n_2}{n_1} \right) + \left(\frac{n_2}{n_1} \right)^2 \right] \quad (62)$$

For example, when n_1 and n_2 are equal, the transition time τ_2 is equal to 3 τ_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

²⁰ The composition of the supporting electrolyte in the reduction of uranyl ion was exactly the same as that Kolthoff and Harris (J. Am. Chem.

Soc., 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).

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 substances 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:

$$D_0 \left[\frac{\partial C_0(x, t')}{\partial x} \right]_{x=0} + D_{R_1} \left[\frac{\partial C_{R_1}(x, t')}{\partial x} \right]_{x=0} + D_{R_2} \left[\frac{\partial C_{R_2}(x, t')}{\partial x} \right]_{x=0} = 0 \quad (63)$$

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

$$\left[\frac{\partial C_{R_2}(x, t')}{\partial x} \right]_{x=0} = - \frac{i_0}{n_2 F D_{R_2}} \left[\frac{1}{2} - \frac{1}{\pi} \operatorname{arcc} \sin \frac{\tau_1 - t'}{\tau_1 + t'} \right] \quad (64)$$

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:

$$C_{R_2}(0, t') = \frac{2 i_0}{\pi^{1/2} n_2 F D_{R_2}^{1/2}} \left[(\tau_1 + t')^{1/2} - \tau_1^{1/2} \right] \quad (65)$$

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:

$$E = (E_{1/2})_{R_1-R_2} + \frac{RT}{n_2 F} \ln \frac{(\tau_1 + \tau_2)^{1/2} - (\tau_2 + t')^{1/2}}{(\tau_1 + t')^{1/2} - \tau_1^{1/2}} \quad (67)$$

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 $t'_{E_{1/2}}$ 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 process⁷.

EXPERIMENTAL

The experimental method applied in this investigation was identical to that previously reported⁷. 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.

ACKNOWLEDGMENT. The authors are indebted to the Office of Naval Research for the support of this investigation.

APPENDIX - EVALUATION OF THE INTEGRALS I_1 AND I_2
OF EQUATION (35)

The integral I_1 is directly obtained from tables. Thus:

$$I_1 = \frac{D_0}{\mathcal{J}} \left\{ \cosh \left[\left(\frac{\mathcal{J}}{D_0} \right)^{1/2} x \right] - 1 \right\} \quad (69)$$

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

$$v = \frac{1}{\pi^{1/2} a} \exp(-a^2 \eta^2) - \eta \operatorname{erfc}(a\eta) \quad (70)$$

$$du = \sinh \left[\left(\frac{J}{D_{01}} \right)^{1/2} (x - \eta) \right] d\eta \quad (71)$$

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

$$I_3 = \int_0^x \cosh \left[\left(\frac{J}{D_{01}} \right)^{1/2} (x - \eta) \operatorname{erfc}(a\eta) \right] d\eta \quad (72)$$

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

$$I_4 = \int_0^x \exp(-a^2 \eta^2) \sinh \left[\left(\frac{J}{D_{01}} \right)^{1/2} (x - \eta) \right] d\eta \quad (73)$$

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

TABLE I

DATA ON THE TRANSITION TIMES FOR VARIOUS RE-OXIDATION PROCESSES

	Thallium ^a				Cadmium ^b			
2°	3.30	3.14	3.03	1.44	3.55	2.38	1.36	1.26
2'	1.14	1.06	1.00	0.50	1.26	0.828	0.442	0.423
2/2'	2.89	2.96	3.03	2.88	2.82	2.88	3.07	2.98
	Zinc ^c				Quinone ^d			
2°	2.46	1.67	0.907	0.865	3.00	2.93	1.10	0.884
2'	0.78	0.538	0.313	0.282	0.965	0.965	0.345	0.276
2/2'	3.15	3.10	2.95	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 pH 6.9 and 1 M potassium nitrate

^e Transition times in seconds at different current densities

TABLE II
 DATA FOR THE ELECTROLYSIS OF MIXTURES
 OF CADMIUM AND ZINC IONS

Solution I ^a				Solution II ^a			
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}	
1.32	2.70	1.32	0.13	2.50	1.56	0.58	
1.96	1.28	0.25	0.22	1.17	0.685	0.54	
3.18	0.42	0.0878	0.21	0.42	0.307	0.65	
4.81	0.182	0.0612	0.32	0.202	0.123	0.58	
9.39	0.050	0.015	0.30	-	-	-	
		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	0.81	1.21	2.54	1.65	
3.18	0.435	0.385	0.78	0.442	0.87	1.54	
4.81	0.178	0.161	0.77	0.19	0.40	1.59	
9.39	0.046	0.0377	0.70	0.0477	0.102	1.59	
		average	0.77		average	1.59	

^a Concentration of cadmium ion: 3×10^{-3} M in all cases. Concentration of zinc ion: 3×10^{-4} M (sol.I), 7.5×10^{-4} M (sol.II), 10^{-3} M (sol.III), 2×10^{-3} M (sol.IV). Supporting electrolyte: 1 M potassium nitrate.

TABLE III
 DATA FOR THE STEPWISE REDUCTION OF OXYGEN
 AND URANYL ION

Oxygen ^a			Uranyl ion ^b		
τ_1	τ_2	τ_2 / τ_1	τ_1	τ_2	τ_2 / τ_1
sec.	sec.		sec.	sec.	
1.29	3.84	2.97	0.264	2.14	7.97
0.716	2.09	2.92	0.139	1.09	7.86
0.328	1.02	3.11	0.090	0.71	7.89
0.128	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 2×10^{-4} per cent.

LIST OF FIGURES

- Fig. 1. Variation of the concentration of substance R during the re-oxidation process. The number on each curve is the time t' .
- Fig. 2. Potential-time curves for the reduction - and subsequent re-oxidation - of cadmium ion (left) and zinc tetramine ion. See data in Table I. Note that one has approximately $AB = 3 BC$ (left), and $AB = 3 CD$ (right).
- 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 .
- 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).

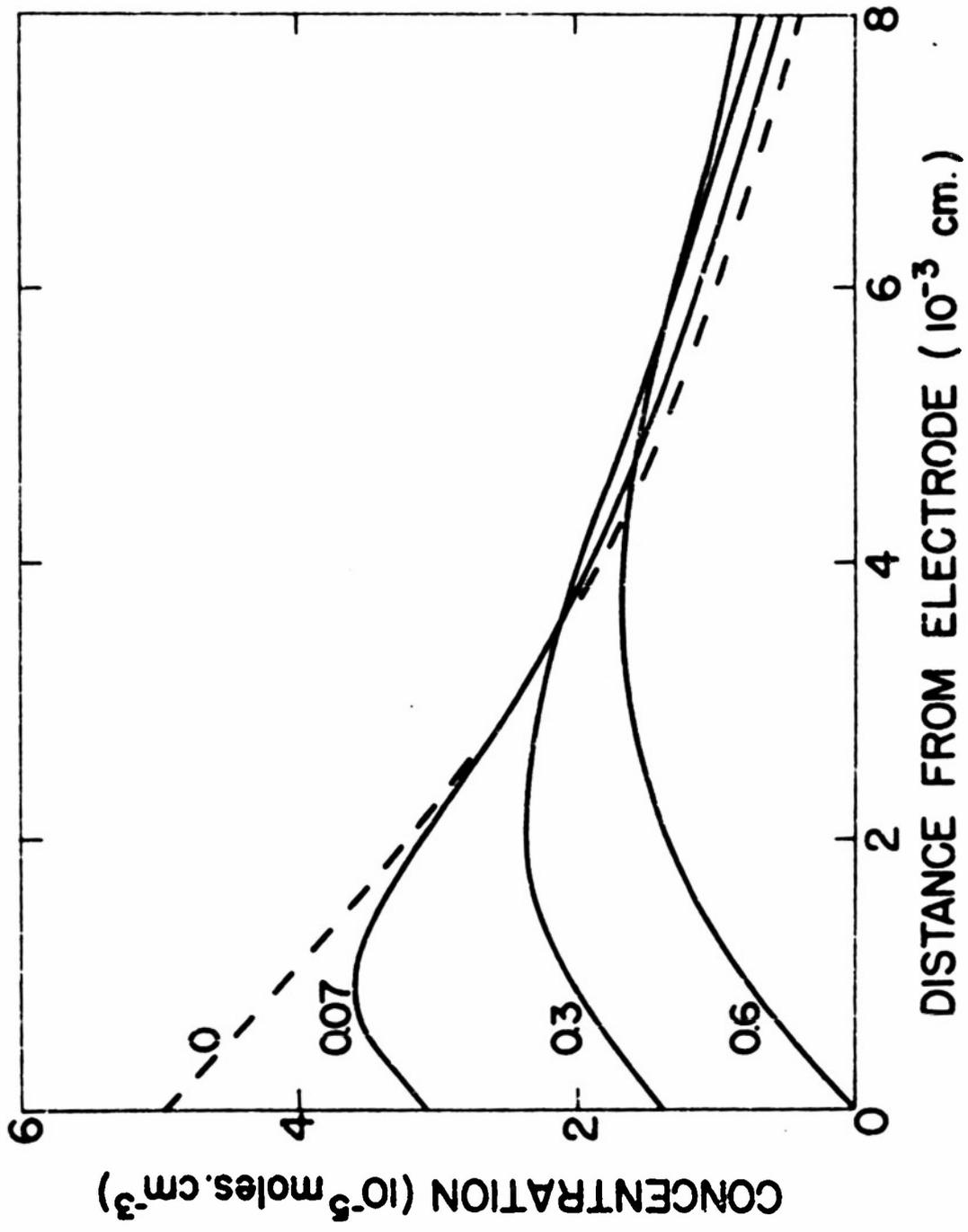
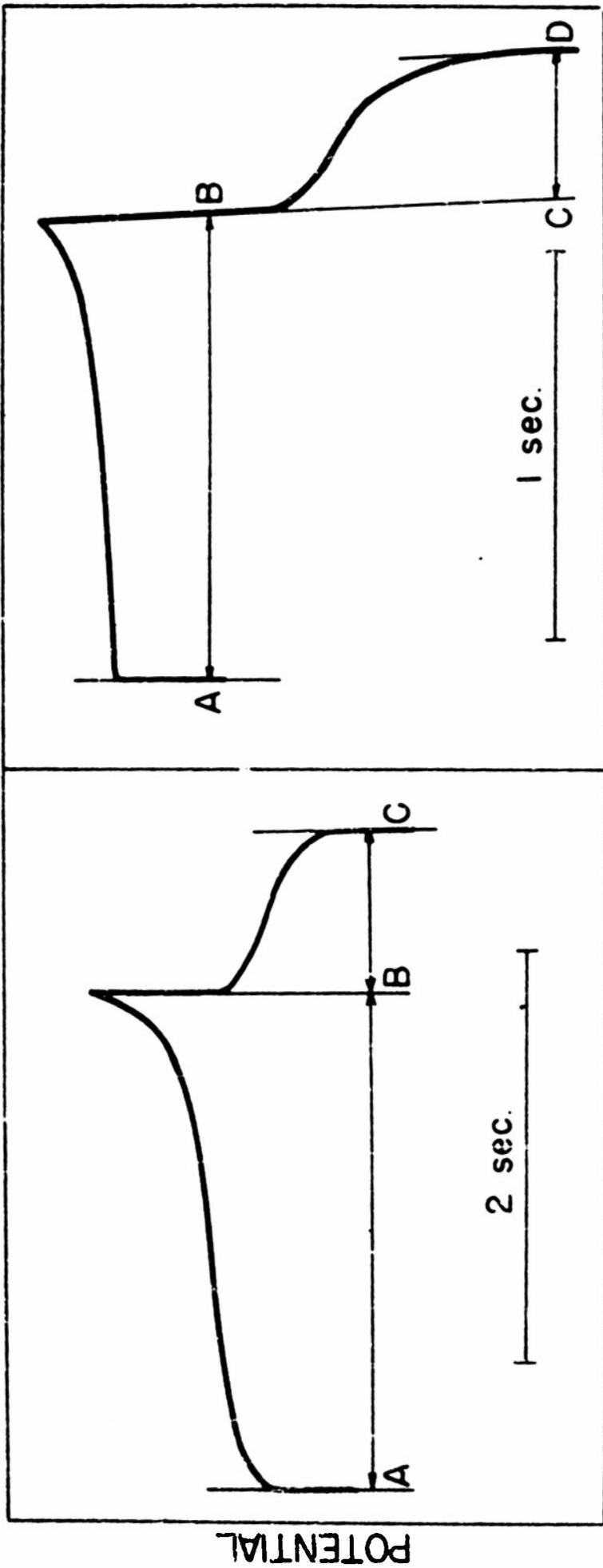


FIG.1



TIME

FIG. 2

2

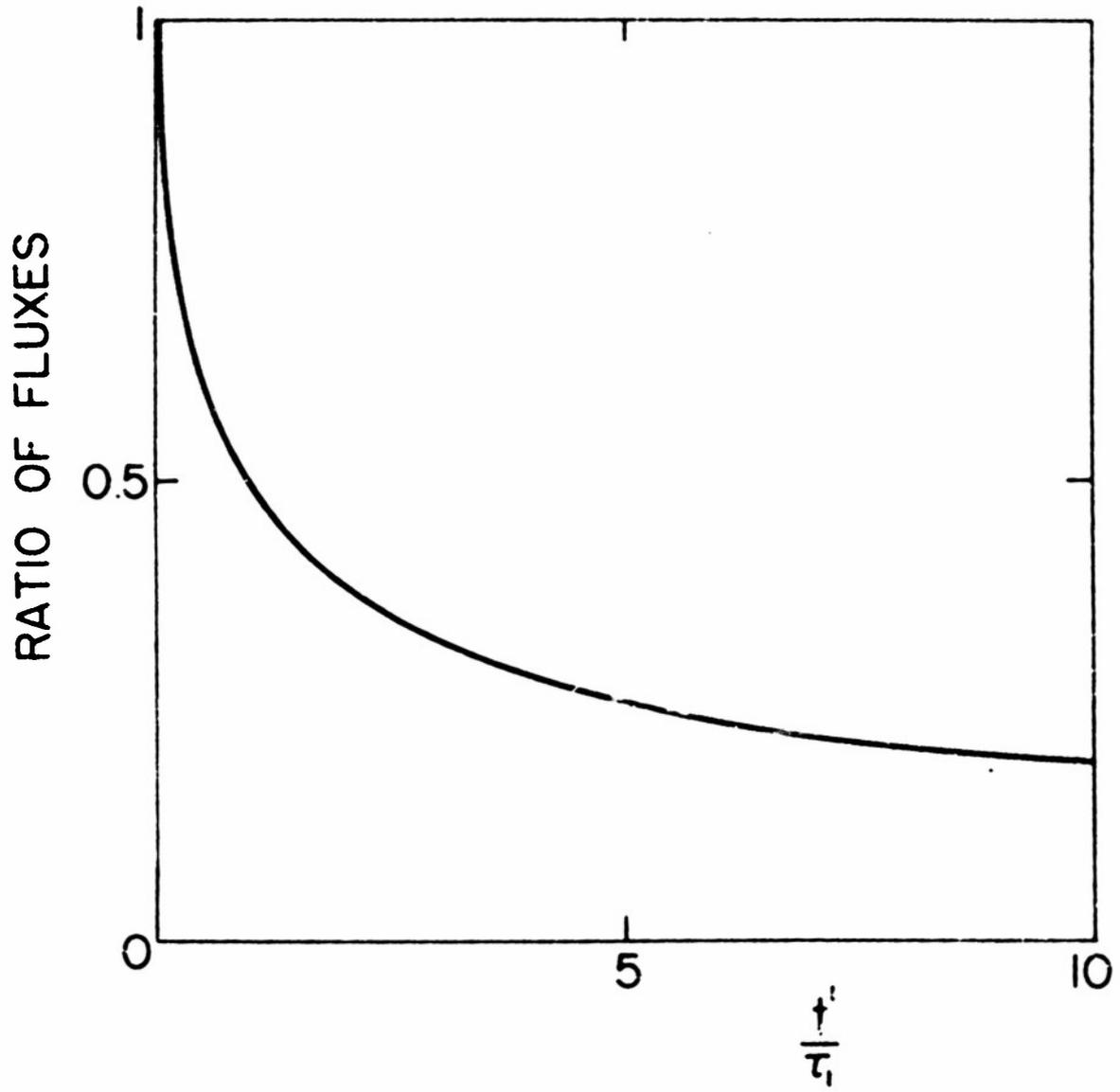
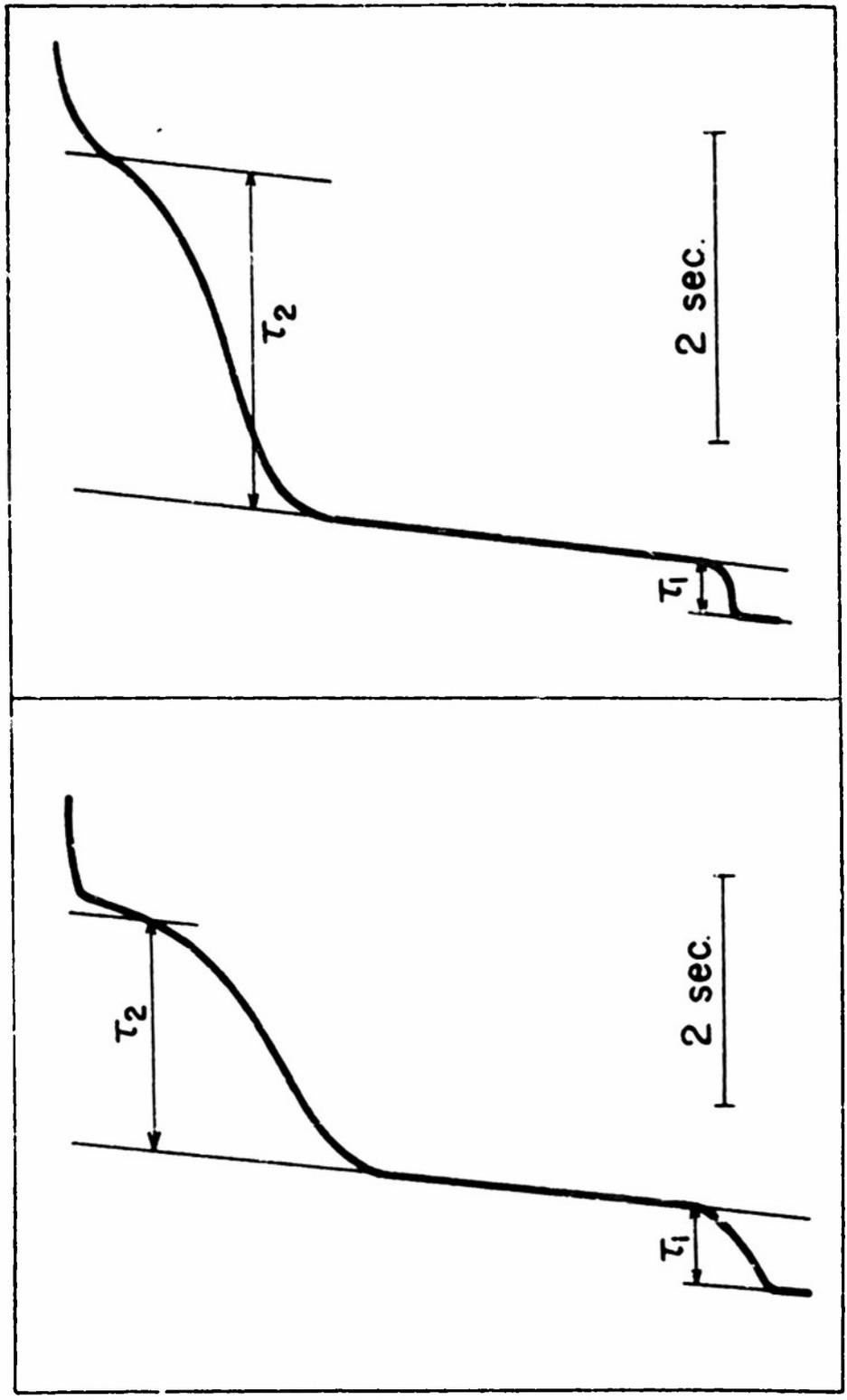


FIG. 3



TIME

FIG.4