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New Methods for the Study of Fast Electrode Reactions.

Talivaldis Berzins
Louisiana State University and Agricultural & Mechanical College

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NEW METHODS FOR THE STUDY OF FAST ELECTRODE REACTIONS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Talivaldis Berzins
B. S., Louisiana State University, 1952
M. S., Louisiana State University, 1953
August, 1955
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Two methods are described for the study of the kinetics of fast electrode reactions. The potential of the electrode whose kinetics is being studied is adjusted at its equilibrium value in absence of any current, and a current impulse represented by a step function (Method I) or a periodic current represented by a square wave (Method II) is passed through the electrolytic cell. The potential of the electrode is recorded during electrolysis, and the kinetic parameters for electron transfer, the rate constant $k_s$ and the transfer coefficient $\alpha$ are determined from potential-time curves.

Method I. A rigorous mathematical analysis is presented for the potential-time curves in the early stages of electrolysis when the variations of potential are only of the order of a few millivolts. The influence of the electrical double layer on potential-time curves is discussed, and equations are derived which permit the calculation of the kinetic parameters $k_s$ and $\alpha$ from experimental data. Values of $k_s$ up to $10^2 \text{cm} \cdot \text{sec}^{-1}$ can be determined easily and this method can be applied to the study of the kinetics of so-called "reversible" electrode reactions in aqueous solutions and fused salts. Experimental results for the reduction of cadmium ions on cadmium amalgam confirm the theory.
Method II. An equation for potential-time curves is derived for the steady state. The analysis of this equation shows that the rate constants up to 1 cm·sec⁻¹ could be determined; this method is thus comparable to the electrolysis with superimposed alternating voltage.

In addition, a general current-potential relationship expressed in terms of Laplace transforms is derived for electrolysis involving only small variations in potential and with mass transfer controlled solely by linear diffusion. The complete solution, including transients, for electrolysis with alternating voltage of low amplitude is given in Appendix.
CHAPTER I - INTRODUCTORY REMARKS AND REVIEW OF LITERATURE

General Current-Potential Relationship

The rate of an electrode process represented by the symbolic equation

$$Q + ne = R \quad (1-1)$$

and involving only a single rate determining step can be expressed in terms of the electric current as follows (3, 5, 6, 9, 19, 22)

$$i^d = nF \left\{ C_0 k_{th}^o \exp\left[ -\frac{\alpha nF}{RT} E \right] - C_R k_{th}^o \exp\left[ \frac{\left(1-\alpha\right) nF}{RT} E \right] \right\} \quad (1-2)$$

where the following notation is used:

- $i^d$ - the current density in amperes per square centimeter.

Cathodic currents are regarded as positive quantities.

- $n$ - the number of electrons involved in the electrode reaction (1-1).

- $F$ - the faraday.

- $R$ - the gas constant.

- $T$ - the absolute temperature.

- $C_0$ and $C_R$ - the concentrations of the substances $O$ and $R$, respectively, at the electrode-solution interface in units moles cm$^{-3}$.

- $E$ - the electrode potential in volts, referred to the normal hydrogen electrode.

- $\alpha$ - the transfer coefficient for the electrode process.

$\alpha E$ represents the fraction ($0 \leq \alpha \leq 1$) of potential $E$ which favors the cathodic reaction of process (1-1); likewise,
the fraction \((1-\alpha)\) favors the anodic reaction.

\(k_f^0, k_h^0\) and \(k_b^0, k_h^0\) - the formal rate constants at \(E=0\), in cm. sec.\(^{-1}\), for the forward and backward reactions, respectively, in the heterogeneous process represented by equation (1-1). The \(k\)'s are formal rate constants because the activity coefficients of the reacting substances are included in their values.

Equation (1-2) is written on the assumption that the number of electrons involved in the rate determining step of reaction (1-1) is equal to the number of electrons involved in the over-all reaction. Furthermore, it is assumed that species 0 is soluble in the solution and that the reduction product \(R\) is soluble either in the solution or in the electrode (as in the deposition of an amalgam forming metal on a mercury electrode). However, the modification of equation (1-2) and the subsequent treatment is trivial for the case in which \(R\) is an insoluble species (metal).

At the equilibrium potential \(E_e\) there is, by definition, electrochemical equilibrium between the species involved in reaction (1-1). Hence, the current given by equation (1-2) is equal to zero, and the following relationship is obtained.

\[
C_0 k_f^0 \exp \left[ - \frac{\alpha n F}{RT} E_e \right] = C_R k_b^0 \exp \left[ \frac{(1-\alpha) n F}{RT} E_e \right] = k_e \quad (1-3),
\]

where \(C_0\) and \(C_R\) are the concentrations of 0 and \(R\), respectively, at equilibrium. By introduction of the standard potential \(E^0\), equation (1-3) can be transformed in the following form
\[
C_0^{(1-\alpha)} C_R^\alpha k_s = k_e 
\]

(1-4)

where \( k_s \) is defined by

\[
k_s = k_{f, h}^o \exp\left[-\frac{\alpha nF}{RT} E^o\right] = k_{b, h}^o \exp\left[\frac{(1-\alpha)nF}{RT} E^o\right] \]

(1-5)

and can be identified as the rate constant at the standard potential \( E^o \).

In view of equations (1-3), (1-4), and (1-5) the general current-potential relationship (1-2) can now be rewritten in a form containing only one rate constant \( k_s \), i.e.,

\[
\bar{\mathcal{I}} = nFk_s C_0^{(1-\alpha)} C_R^\alpha \left\{ \frac{C_0}{C_0^o} \exp\left[-\frac{\alpha nF}{RT}(E-E_e)\right] - \frac{C_R}{C_R^o} \exp\left[\frac{(1-\alpha)nF}{RT}(E-E_e)\right] \right\} \]

(1-6)

When the equilibrium concentrations are equal \( (C_0^o = C_R^o = C^o) \), \( E \) is the formal standard potential \( E^o \), and one has

\[
\bar{\mathcal{I}} = nFk_s \left\{ C_0 \exp\left[-\frac{\alpha nF}{RT}(E-E_e)\right] - C_R \exp\left[\frac{(1-\alpha)nF}{RT}(E-E_e)\right] \right\} \]

(1-7)

It is seen from equation (1-6) that the current is now a function of the difference of potential \( (E-E_e) \), whereas in equation (1-2) the current depends on potential \( E \). Furthermore, the expression (1-6) contains only one rate constant \( k_s \) which, as was pointed out by Randles (29), does not depend explicitly on the choice of the zero point for the potential scale. It is, therefore, more advantageous to use the truly characteristic parameter \( k_s \) rather than \( k_{f, h}^o \) and \( k_{b, h}^o \) in comparing the kinetic characteristics of electrode processes.
The product of constants

\[ nFk_3C_0^{\alpha J}C_R^{\alpha} = \nu_0 \quad (1-8) \]

is equal to the so-called "exchange current density" which is used, particularly in the German literature, to characterize the kinetics of electrode reactions. The main drawback in the use of \( i_0 \) results from the dependence of the exchange current on the equilibrium concentrations, i.e., the equilibrium potential.

**Survey of Methods for the Determination of \( k_S \)**

Recently Rubin and Collins (32) applied the method of random flights to calculate the number of collisions between the reacting species and the electrode and, assuming that each collision results in an electron transfer, evaluated the upper limit of \( k_S \) to be of the order of \( 10^3 \) to \( 10^4 \) cm. sec\(^{-1} \) at room temperature.

Conventional polarization experiments enable one to determine values of \( k_S \) up to approximately \( 10^{-2} \) cm. sec\(^{-1} \). When this limit is exceeded, electron transfer is so rapid that current-potential relationships determined by ordinary polarization methods obey the Nernst equation, due allowance being of course made for concentration polarization. Such a situation is encountered, for example, in polarography; the limit \( k_S < 10^{-2} \) cm. sec\(^{-1} \) was precisely deduced for this type of electrolysis (10).

Recently, Gerischer and Vielstich (34) used a voltage impulse of a few millivolts represented mathematically by a
step function and generated by an electronic potentiostat) to investigate the kinetics of electrode processes. The kinetic parameters were calculated from the resulting current-time curves. However, the charging of the double layer and the resulting variation in potential interferes with the measurements, when very fast processes are involved. The time constant of the electric circuit is then of the same order of magnitude as the time during which current-time curves are observed.

Somewhat faster processes can be studied by electrolysis with superimposed sinusoidal voltage, and values (29) of \( k_s \) up to 1 cm.sec\(^{-1} \) can probably be determined. This method was applied to electrode studies by various authors; the work of Randles (28, 30), Ershler (12), Gerischer (14), and Grahame (20) should be particularly noted. The potential in this method varies periodically about the equilibrium value by a few millivolts. The alternating current is the sum of two components resulting from electron transfer (the faradaic current) and from the charging and discharging of the double layer (the capacity current). The faradaic current increases with the square root of the frequency, and the capacity current is proportional to the frequency. Thus, the capacity current is preponderant at high frequencies, and the rate of electron transfer cannot be determined. Nevertheless, high frequencies must be used for fast electron transfer processes because mass transfer (diffusion) from solution to electrode during
each alternation of the voltage wave, not the electron transfer at the interface, determines the current at low frequencies.

Electrolysis at constant current, which was first used more than fifty years ago, has recently been revived (2, 9, 17, 24, 25, 26) but it has never been applied to the studies of fast electrode reactions. It is the purpose of this dissertation to show how this application can be made.

**Purpose of the Dissertation**

When the electron transfer process is very fast, the over-all rate of the electrode reaction is controlled by mass transfer. In order to obtain kinetic parameters for the electron transfer process, it is necessary to study the kinetics of the overall reaction before mass transfer becomes the rate controlling factor. This could be accomplished by studying the rate of an electrode process in the early stages of electrolysis, i.e., before the concentrations of reacting species at the electrode have changed to any considerable extent.

The purpose of the present investigation is to apply the above general idea by developing a method of electrolysis with a current impulse represented mathematically by a step function. In addition, electrolysis with a square wave current and transients in electrolysis with sinusoidally alternating voltage of small amplitude will be considered.
Only cases involving semi-infinite linear diffusion in an unstirred solution will be considered, since cases of spherical or cylindrical diffusion can be treated as linear diffusion problems provided that the duration of electrolysis is sufficiently short (1 sec. or less) (31), a condition which is generally fulfilled in the above-mentioned types of electrolysis. Convection effects will be neglected because of the short duration of electrolysis. Furthermore, it will be assumed that the solution being electrolyzed contains a large excess of supporting electrolyte, and that migration effects can be neglected.

\footnote{1In the mathematical treatment of diffusion the term "semi-infinite linear diffusion" implies that the diffusion takes place in a medium which is bounded by a plane at \( x = 0 \), and extends to infinity in the positive direction of the \( x \)-axis, and that the diffusion proceeds only in the direction of the \( x \)-axis.}
CHAPTER II - ELECTROLYSIS WITH A CURRENT IMPULSE REPRESENTED BY A STEP FUNCTION

Introduction

The potential of the electrode whose kinetics is being studied is adjusted to its equilibrium value in the absence of any current, and a current impulse represented by a step function is applied to the electrolytic cell. This cell may be composed of two identical polarized electrodes or of one polarized and one unpolarized electrode. The solution is not stirred and a large excess of supporting electrolyte is present in solution, i.e., diffusion is virtually the sole mode of mass transfer. The polarized electrode is a plane, and conditions of semi-infinite linear diffusion are assumed to prevail. The voltage across the cell is recorded during electrolysis, and the rate constant $k_0$ is determined from voltage-time curves.

Under the foregoing conditions of electrolysis, the concentration, $C_0(x,t)$, of the electrolyzed substance $O$ and of its reduction product $R$ are given by the solution of Fick's diffusion equation

\[ \frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} \]  

(2.1)
for the following initial and boundary conditions:\(^1\):

\[ C_0(x,0) = C_0^0, \quad x > 0, \quad t = 0 \quad (2-2a) \]

\[ C_R(x,0) = C_R^0 \]

\[ D_0 \left( \frac{\partial}{\partial x} \frac{\partial C_0(x,t)}{\partial x} \right)_{x=0} = - n \left( \frac{\partial}{\partial x} \frac{\partial C_R(x,t)}{\partial x} \right)_{x=0} = \frac{I_d}{nF} \quad (2-2b) \]

\[ C_0(x,t) \rightarrow C_0^0, \quad t > 0, \quad x \rightarrow \infty \quad (2-2c) \]

\[ C_R(x,t) \rightarrow C_R^0 \]

where the \( C_0^0 \)'s are the bulk concentrations of substances 0 and R involved in the electrode reaction (0 \( \neq \) ne \( \rightarrow \) R), the \( D_0 \)'s are the diffusion coefficients, \( I_d \) is the current density at the electrode, \( n \) the number of electrons involved in the reaction, \( F \) the faraday, \( x \) the distance from the electrode, and \( t \) the time elapsed since the beginning of electrolysis. Substances 0 and R are assumed to be soluble in solution (one of them may be insoluble in solution but soluble in the electrode as in the case of amalgam formation). This boundary value problem was solved by Sand (33) in 1900; the concentrations at the electrode surface (\( x = 0 \)) are given by

\[ C_0(x,t) = C_0^0 - \frac{2I_d}{nF} \frac{t^{1/2}}{r^{1/2}} \quad (2-2) \]

and

\[ C_R(x,t) = C_R^0 - \frac{2I_d}{nF} \frac{t^{1/2}}{r^{1/2}} \quad (2-4) \]

\(^1\)The boundary condition (2-2b) was obtained by equating the rate of diffusion of the reacting substance at the electrode surface (\( x = 0 \)) to the rate at which this substance is consumed or produced in the electrolytic process.
The time required to reach complete depletion of the substance being electrolyzed is called the transition time, and is indicated by a rapid change in the potential of the working electrode. If the transition time $\tau$ is identified with the time at which $C_0(0,t)$ in equation (2-3) becomes equal to zero, one deduces from (2-3)

$$\tau = -\frac{\pi^{1/2} n F C_0^2 D^{1/2}}{2L_d} \quad (2-5)$$

Since the variations of potential in the immediate vicinity of the transition time are often quite large (several tenth of a volt), the transition time can be measured with a good precision. Consequently, concentrations, diffusion coefficients, and particularly the product $C_0^2 D^{1/2}$, which will be frequently encountered in the subsequent expressions, can be conveniently determined from transition times.

**Simplified Determination of $k_s$ and $\alpha$**

In view of equation (2-5) the concentrations of the substances involved in the electrode reaction can be rewritten as follows

$$C_0'(t) = C_0^0 \left[ 1 - \left( \frac{\tau}{C_0^0} \right)^{1/2} \right] \quad (2-6)$$

and

$$C_R'(t) = C_R^0 \left[ 1 - \left( \frac{\tau}{C_R^0} \right)^{1/2} \right] \quad (2-7)$$

where the $\tau$'s are the transition times for the cathodic and anodic processes. Introducing the values of $C_0$ and $C_R$ given by equations (2-6) and (2-7) in the general current-potential expression (1-6) one obtains the following equation for the complete potential-time curve.
\[ i_d = nFk_s c_0^{\epsilon(1-\omega)} \left[ \frac{1 - \left( \frac{t}{t_0} \right)^{1/2}}{1 + \left( \frac{t}{t_0} \right)^{1/2}} \right] \exp \left[ -\frac{\alpha nF}{R T} \left( E - E_e \right) \right] \]

(2-8)

It follows from (2-8) that a plot of
\[ \ln \left[ \frac{1 - \left( \frac{t}{t_0} \right)^{1/2}}{1 + \left( \frac{t}{t_0} \right)^{1/2}} \right] E - E_e \]
against \( E - E_e \) should yield a straight line whose slope is
\[ \frac{\alpha nF}{R T} \] and whose intercept at \( E = E_e \) is
\[ -\ln nFk_s c_0^{\epsilon(1-\omega)} c_R \alpha \];
thus \( k_s \) and \( \alpha \) can be determined. However, the quantity being plotted as ordinate is represented by a complicated function, it is more convenient to determine \( k_s \) from measurements of potential in the early stages of electrolysis. The departure from the equilibrium potential is then of the order of a few millivolts.

If \( E - E_e \) does not exceed a few millivolts, the exponential functions is (2-8) may be replaced by the first two terms of their series expansion without any serious error. One then obtains
\[ E - E_e = -\frac{RT}{nF} \frac{i_d}{\zeta_0} + \left[ \frac{1}{t_0 \gamma_0} + \frac{1}{t_0 \gamma_0} \right] \frac{t}{\gamma_0} \]
(2-9)

where
\[ \zeta_0 = nFk_s c_0^{\epsilon(1-\omega)} c_R \alpha \]

When \( t \) is sufficiently small, the second term in the denominator in equation (2-9) becomes negligible with respect to unity and the potential-time relationship is
\[ E - E_e = -\frac{R T}{n F} \left[ \frac{i_d}{\nu_0} + \left( \frac{1}{\tau_c \alpha} + \frac{1}{\tau_a \alpha} \right) t \alpha \right] \quad (2-10) \]

If the transition times \( \tau_c \) and \( \tau_a \) are equal, equation (2-10) is valid for any value of \( t \) when \( \alpha = 0.5 \). This equation can be used also for values of \( \alpha \) different from 0.5 when the condition
\[ t < 0.1 \tau \]  \quad (2-11)

is satisfied.

It follows from (2-10) that a plot of \( E \) against \( t^\frac{1}{2} \) is linear, and that the rate constant \( k_0 \) can be readily calculated from the intercept at \( t = 0 \). This extrapolated potential has precisely the value one would calculate before concentration polarization sets in.

Extrapolation to time \( t = 0 \) is useful because the potential does not vary abruptly at \( t = 0 \) on account of the charging (or discharging) of the double layer. If \( C_1 \) is the differential capacity of the double layer, the charging time \( t_1 \) is
\[ t_1 = \left| \frac{C_1 (E - E_e)}{i_d} \right| \quad (2-12) \]

The capacity \( C_1 \) is supposed to be independent of \( E \) in (2-12), a permissible simplification since \( E - E_e \) is of the order of a few millivolts. The quantity of electricity \( i \tau_1 \) must be 'small' in comparison with the quantity of electricity involved in the electron transfer process. The order of magnitude of the quantities involved in the calculation of
$k_s$ can be obtained by considering the case in which $k_s = 1$ cm$^{-1}$ sec$^{-1}$. This is the upper limit of $k_s$ which can be obtained by electrolysis with superimposed alternating voltage. For the data $n = 1$, $i_d = 0.02$ amp$^{-2}$, $C^0 = 5 \times 10^{-6}$ mole$^{-3}$ cm$^{-3}$, $T = 298.1^0$, one calculates $(E - E_e) = 1.08 \times 10^{-3}$ volt at $t = 0$. The time for charging the double layer is $1.1 \times 10^{-6}$ sec., for $C_1 = 20$ microfar$^{-2}$, and one verifies $(D = 10^{-5}$ cm$^{-2}$ sec$^{-1}$) that condition (2-11) is satisfied for $t < 5 \times 10^{-4}$ second. The recording of potential-time curves is thus entirely feasible, since oscilloscopes with a sensitivity of 50 microvolts per cm. are commercially available ("Tektronix" model 531 with amplifier type 53E). By similar calculations one can show that values of $k_s$ up to $10^2$ cm$^{-1}$ sec$^{-1}$ might be measured; values of $E - E_e$ at $t = 0$ are then of the order of 0.1 millivolt.

It was assumed in the foregoing treatment that the charging (or discharging) of the electrical double layer and the electrode reaction are two consecutive processes. This is a simplification which will not be made in the subsequent treatment where these two processes, charging of the double layer and electron transfer, will be considered as simultaneous processes.

**Boundary Value Problem for the Case in Which the Double Layer Capacity is Considered**

The behavior of the electrolytic cell can be conveniently studied by considering its equivalent circuit, as represented
in Fig. I. If one assumes that the reference electrode of the cell is not polarized, the properties of the cell are essentially determined by the characteristics of the polarized working electrode and by the electrolyte resistance $R_e$ in the cell. The behavior of the working electrode is characterized by the following two processes: the charging or discharging of the electrical double layer at the electrode-solution interface and the electron transfer across it. Consequently, in the course of electrolysis the total current $i_d$ at the electrode-solution interface can be decomposed into two components: the faradaic current, $i_f$, crossing the interface by virtue of the electrochemical reaction and the capacity current, $i_c$, being used to charge (or discharge) the double layer.

Since the total current is the sum of these two components it is convenient to regard the interface as electrically equivalent to two impedances in parallel. The impedance to the capacity current is then that of the double layer and may be represented by a simple capacitance provided that only small variations of potential are encountered$^1$. Thus, the density of the capacity current, $i_c$, is given by

$$i_c = -C_c \frac{d(E-E_e)}{dt} \quad (2-13)$$

$^1$In general the double layer capacity varies with potential, but when variations of potential are of the order of a few millivolts it may be regarded, for all practical purposes, as a constant quantity.
Figure 1
Equivalent Circuit of Electrolytic Cell with One Polarizable Electrode
where $C_1$ is the differential capacity of the double layer in units farads per square centimeter. The impedance ($Z$) to the faradaic current $i_f$ is not ordinarily representable in any simple fashion, but the value of the density of the faradic current is related to the potential difference $E-E_e$ and the concentrations of the reacting species by equation (1-6), i.e.,

$$i_f = \frac{L_0}{C_0} \exp \left[ - \frac{\alpha n F}{RT} (E-E_e) \right] - \frac{C_0}{C_0^o} \exp \left[ \frac{(1-\alpha) n F}{RT} (E-E_e) \right] \tag{2-14}$$

where

$$L_0 = nFK_s C_0^o \frac{\alpha}{C_R^o} = \text{exchange current} \tag{2-14a}$$

If the total current density $i_d$ through the cell is maintained constant in the course of electrolysis, the sum of $i_c$ and $i_f$ is also a constant quantity. Thus

$$i_c + i_f = i_d = \text{constant} \tag{2-15}$$

In order to obtain a mathematical expression for the potential-time curves one has to solve the boundary value problem given by equations (2-1) and (2-2), but where the boundary condition (2-2b) is replaced by the following system of boundary conditions

$$i_d = - C_\ell \frac{d(E-E_e)}{dt} + nFD_0 \left( \frac{\partial C_0(x,t)}{\partial x} \right)_{x=0} \tag{2-16}$$
The above system of boundary conditions was obtained from equations (2-13), (2-14), (2-15), and from the condition that the density of faradaic current $i_f$ can be expressed in terms of fluxes of reacting substances at the electrode surface as follows

\[ nFD_0 \left( \frac{\partial C_0(x,t)}{\partial x} \right)_{x=0} = \nu_0 \left( \frac{\partial C_0(x,t)}{\partial x} \right) \]  

\[ D_R \left( \frac{\partial C_R(x,t)}{\partial x} \right)_{x=0} = \nu_0 \left( \frac{\partial C_0(x,t)}{\partial x} \right) \]  

Since the boundary conditions themselves are expressed by a system of nonlinear differential equations, the solution of the boundary value problem is arduous. The solution of this boundary value problem can be obtained more easily, for small values of time, when the linearization of the boundary condition (2-17) is possible. Under these conditions a relationship between the faradaic current and the potential can be derived in terms of Laplace transforms without prescribing any explicit functional dependence of current or potential on time. Since the Laplace transform of capacity

---

In diffusion processes the flux is defined as the number of moles of a substance diffusing through a unit area per unit time.
current can be obtained from (2-13), the transform of the potential difference \((E-E_e)\) is easily calculated from equation (2-15). The potential difference \((E-E_e)\) as function of time can be obtained from its Laplace transform by performing the inverse transformation.

**General Current-Potential Relationship when Linearization of (2-17) is Permissible**

When the potential \(E\) of the polarized electrode does not depart more than a few millivolts from the equilibrium potential \(E_e\) (the potential observed when no current flows through the cell), i.e., when \(E-E_e \ll RT/nF\), the exponential functions in (2-17) may be replaced by the first two terms of their series expansions without any appreciable error. Furthermore, if the relative concentrations of the reacting species are negligible with respect to unity, one obtains the following linearized form for the boundary condition

\[(2-17) (14)\]

\[
\left( \frac{\partial \psi_0(x,t)}{\partial x} \right) = \lambda_0 \left[ \psi_0(0,t) - \psi_R(0,t) - \frac{nF}{RT}(E-E_e) \right] \tag{2-20}
\]

where \(\psi_0(x,t)\) and \(\psi_R(x,t)\) are the relative concentrations defined by

\[
\psi_0(x,t) = \frac{C_0(x,t)-C_0^o}{C_0^o} \quad \text{and} \quad \psi_R(x,t) = \frac{C_R(x,t)-C_R^o}{C_R^o} \tag{2-21}
\]

and \(\lambda_0\) is

\[
\lambda_0 = \frac{\lambda_0}{nF D_0 C_0^o} \tag{2-22}
\]
Since the sum of the fluxes of substances 0 and R is equal to zero at the electrode surface (see equation (2-19)), an equation similar to (2-20) can be written for the flux of substance R. Thus

\[
\left( \frac{\partial \Psi_R(x,t)}{\partial x} \right) = -\lambda_R \left[ \Psi_0(0,t) - \Psi_R(0,t) - \frac{nF}{RT} (E-E_0) \right] \quad (2-23)
\]

where

\[
\lambda_R = \frac{\epsilon_0}{nF D_R C^0_R} \quad (2-24)
\]

Equations (2-20) and (2-23) are the new boundary conditions. The potential difference, \( E-E_0 \), in (2-20) and (2-23) is a certain function of time, with only the restriction mentioned at the beginning of this section.

The initial conditions can be expressed in terms of the relative concentrations as follows

\[
\Psi_0(x,0) = \Psi_R(x,0) = 0 \quad \text{for} \quad x \geq 0 \quad (2-25)
\]

Furthermore one has

\[
\Psi_0(x,t) \to 0 \quad \text{and} \quad \Psi_R(x,t) \to 0 \quad (2-26)
\]

for \( x \to \infty \) and \( t \geq 0 \).

This boundary value problem will be solved by means of Laplace integral transforms\(^1\) (7, 8) with respect to the variable \( t \). After the transformation Fick’s diffusion equation (2-1) (expressed in terms of the relative concentrations) is reduced to the following ordinary differential

\[^1\text{The notation of Churchill’s text (8) will be used during subsequent derivations. Laplace transform } \tilde{f}(s) \text{ of a function } f(t) \text{ is defined by this author as follows:}
\]

\[
\tilde{f}(s) = \int_0^\infty \exp(-st) f(t) \, dt,
\]

\( s \) being the parameter resulting from the transformation.
The solutions of equations (2-27) and (2-28), when bounded for \( x \to \infty \), are as follows

\[
\bar{\Psi}_0(x,s) = M \exp \left[ - \frac{\frac{s^2}{4} x}{D_0^{\nu_0}} \right] \tag{2-29}
\]

and

\[
\bar{\Psi}_R(x,s) = N \exp \left[ - \frac{\frac{s^2}{4} x}{D_R^{\nu_R}} \right] \tag{2-30}
\]

where \( M \) and \( N \) are integration constants. These are determined from the transforms of the boundary conditions (2-20) and (2-23). Thus

\[
M = \frac{nF}{RT} \lambda_0 \frac{D_0^{\nu_0}}{S^{\nu_0} + \lambda_0 D_0^{\nu_0} + \lambda_R D_R^{\nu_R}} \tag{2-31}
\]

and

\[
N = - \frac{nF}{RT} \lambda_R \frac{D_R^{\nu_R}}{S^{\nu_R} + \lambda_0 D_0^{\nu_0} + \lambda_R D_R^{\nu_R}} \tag{2-32}
\]

\( \bar{E}(s) \) being the Laplace transform of \( (E - E_e) \).

By calculating \( \left( \partial \bar{\Psi}_0(x,s)/\partial x \right)_{x=0} \) and expressing this function in terms of the Laplace transform of the faradaic current \( \bar{i}_f(s) \) one obtains the following current-potential relationship

\[
\bar{i}_f(s) = - \frac{nF}{RT} \lambda_0 \left[ \bar{E}(s) - \frac{\alpha \bar{E}(s)}{S^{\nu_0}} \right] \tag{2-33}
\]
where  

$$\alpha = \frac{i_0}{nF} \left( \frac{1}{D_0 C_0} + \frac{1}{D_R C_R} \right) \quad (2.34)$$

If the conditions stated at the beginning of this section are fulfilled in the course of electrolysis, the equation (2-33) gives a general current-potential relationship, since no explicit functional dependence of current or potential on time was prescribed in its derivation.

**Influence of the Double Layer Capacitance on Potential-Time Curves.**

In the early stages of electrolysis with constant current, the conditions are such that the equation (2-33) is applicable. Furthermore, the equation (2-13) giving the capacity current also holds and can be expressed in terms of Laplace transforms as follows (8)

$$\tilde{I}_C(s) = -C_\ell s \tilde{E}(s) + \tilde{I}_e (E-E_e)_{t \to +0} \quad (2.35)$$

where $\tilde{E}(s)$ is the transform of $(E-E_e)$.  

Since, in the present case, $(E-E_e) \to 0$ as $t \to +0$ and the sum of the faradaic and capacity currents is equal to the total current density, which is maintained at a constant value $i_d$, one obtains from (2-15)

$$\frac{i_d}{s} = -C_\ell s \tilde{E}(s) - \frac{nF}{RT} i_0 \left[ \tilde{E}(s) - \frac{a \tilde{E}(s)}{s^{\nu_0} + a} \right] \quad (2.36)$$

From which the Laplace transform of the potential can easily be calculated. Thus

$$\tilde{E}(s) = \frac{i_d}{C_\ell} s^{\nu_0/2} \frac{s^{\nu_0} + a}{s^{\nu_0} + b} \quad (2.37)$$
with

\[ b = \frac{nF \cdot C_0}{RT \cdot C_e} \quad (2-38) \]

By factorization of the denominator in (2-37) and application of the theory of partial fractions, one can transform (2-37) to the following form

\[ \tilde{E}(s) = -\frac{I\cdot C_0}{C_e(\gamma - \beta)} \left[ \frac{I}{S(\frac{1}{\nu} + \beta)} - \frac{I}{S(\frac{1}{\nu} + \gamma)} + \frac{\alpha}{S^{\frac{1}{\nu}}(\frac{1}{\nu} + \beta)} - \frac{\alpha}{S^{\frac{1}{\nu}}(\frac{1}{\nu} + \gamma)} \right] \quad (2-39) \]

where

\[ \beta = \frac{\alpha}{2} + \left( \frac{\alpha}{4} - b \right) = \frac{\alpha}{2nF} \left( \frac{1}{D_0^{\frac{1}{\nu}}C_0^{\frac{1}{\nu}}} + \frac{1}{D_0^{\frac{1}{\nu}}C_0^{\frac{1}{\nu}}} \right) + \left[ \frac{\alpha}{2nF^2} \left( \frac{1}{D_0^{\frac{1}{\nu}}C_0^{\frac{1}{\nu}}} + \frac{1}{D_0^{\frac{1}{\nu}}C_0^{\frac{1}{\nu}}} \right) - \frac{nF \cdot C_0}{RT \cdot C_e} \right] \quad (2-40) \]

\[ \gamma = \frac{\alpha}{2} - \left( \frac{\alpha}{4} - b \right) = \frac{\alpha}{2nF} \left( \frac{1}{D_0^{\frac{1}{\nu}}C_0^{\frac{1}{\nu}}} + \frac{1}{D_0^{\frac{1}{\nu}}C_0^{\frac{1}{\nu}}} \right) + \left[ \frac{\alpha}{2nF^2} \left( \frac{1}{D_0^{\frac{1}{\nu}}C_0^{\frac{1}{\nu}}} + \frac{1}{D_0^{\frac{1}{\nu}}C_0^{\frac{1}{\nu}}} \right) - \frac{nF \cdot C_0}{RT \cdot C_e} \right] \quad (2-41) \]

The potential as a function of time can be obtained easily from (2-39) by means of the convolution integral.\(^1\)

Thus, by noting that the inverse transform \((7,8)\) of \(1/s\) and \(1/s^{3/2}\) are 1 and \(2(t/\pi)^{1/2}\), respectively, and that the inverse transform of \((s^2 + \beta)^{-1}\) is

\[ \left( \frac{1}{\pi \cdot t} \right)^{1/2} = \beta \exp(\beta^2 t) \text{erfc}(\beta \sqrt{t}) \]

one has

\[ E - E_0 = -\frac{I\cdot C_0}{C_e(\gamma - \beta)} \int_0^t \exp(\beta^2 \tau) \text{erfc}(\beta \sqrt{\tau}) d\tau - \beta \int_0^t \exp(\beta^2 \tau) \text{erfc}(\beta \sqrt{\tau}) d\tau \quad (2-42) \]

where the notation "erfc" represents the complementary error function having the quantity between brackets as argument.

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\(^1\)The inverse transform of a product of transforms \(\tilde{f}_1(s) \cdot \tilde{f}_2(s)\) is given by the following convolution integral \((8)\)

\[ \int_0^t f_1(t - \tau) f_2(\tau) d\tau \]
The two similar integrals in (2-42) can be evaluated by integration once by parts. Thus

\[ E - E_e = \frac{I_d}{C_e(\gamma/\beta)} \left( \frac{\alpha}{\beta} \left[ \exp(\beta^2t) \text{erfc}(\beta \frac{t}{\pi}) + 2\beta(\frac{t}{\pi})^{1/2} - 1 \right] \right) \]  

where \( \beta \) and \( \gamma \) are defined by (2-40) and (2-41).

Discussion of Equation (2-43).

As one can see from (2-43) the variation of potential in electrolysis with a current step is given by a rather involved function of time when the influence of the double layer is taken into account. However, it will be shown later that for ordinary experimental conditions the potential-time curve can be expressed by an equation which has the same functional dependence on time as the simple equation (2-10).

In the subsequent discussion it will be assumed for the sake of simplicity that \( C_0 = C_R = 3^0 \) and \( D_0 = D_R = D \). This obviously constitutes a special case, but the modification for other cases is trivial. The constants \( \beta \) and \( \gamma \) given by (2-40) and (2-41) can now be written in the following form

\[ \beta = \frac{k_s}{D_R} \left[ 1 + \left( 1 - \frac{n^2 F^2 C^0 D}{RT C_R k_s} \right)^{1/2} \right] \]  

and

\[ \gamma = \frac{k_e}{D_R} \left[ 1 - \left( 1 - \frac{n^2 F^2 C^0 D}{RT C_R k_s} \right)^{1/2} \right] \]  

Inspection of the last two equations shows that \( \beta \) and \( \gamma \) can be either real or complex quantities depending on whether the quantity

\[ \frac{n^2 F^2 D C^0}{RT C_R k_s} \]
is smaller or larger than unity. When
\[ \frac{n^2F^2Dc^0}{kTc_e k_s} < 1 \]  
(2-46)
\[ \beta \text{ and } \gamma \text{ are real.} \]

By taking the following representative values: \( n = 1 \), \( T = 300^\circ K \), \( \nu = 10^{-5} \text{cm}^2 \text{sec}^{-1} \), \( C_1 = 2 \times 10^{-5} \text{farads cm}^{-2} \), \( C^0 = 10^{-6} \text{moles cm}^{-3} \), one deduces from (2-46) that \( \beta \) and \( \gamma \) are real when \( k_s \) is of the order of unity or larger.

**Potential-time curves when \( \beta \text{ and } \gamma \text{ are real.}**

The influence of the double layer can be seen by comparing the potential-time curves obtained from equation (2-43) with the curves calculated from the simplified equation (2-10) which was derived with the assumption that the double layer capacity was equal to zero. This is done in Fig. 2. The potential-time curves are constructed for a cathodic process from the following data: \( n = 2 \), \( T = 300^\circ K \), \( C_1 = 2 \times 10^{-5} \text{farad cm}^{-2} \), \( D = 1 \times 10^{-5} \text{cm}^2 \text{sec}^{-1} \), \( C^0 = 5 \times 10^{-6} \text{mole cm}^{-3} \), and \( k_s = 10^2 \text{ cm sec}^{-1} \). Curve I corresponds to the case in which the double layer capacity is not taken into account while curve II represents the potential-time relationship embodied in equation (2-43). It is seen from Fig. 2, (1) that the potential along curve II varies less rapidly than for curve I, and (2) that there is no initial "jump" in potential when the effect of the double layer is taken into account. This is to be expected since the double layer capacity must be progressively charged as the potential departs from its equilibrium value.

As a result, the faradaic current is smaller than the total current through the cell and the effect of concentration polarization is less pronounced than for the simplified case.
Figure 2
Influence of the Double Layer Capacity on Potential-Time Curves
in which the double layer capacity is considered to be equal to zero.

It is seen from equation (2-43) that the functional dependence of potential on time is characterized by two functions of the following generalized form: $2T/\pi^{1/2}$ and $\exp(T^2) \text{erfc}(T)$, where $T$ is either $\beta t^{1/2}$ or $\gamma t^{1/2}$. The relative importance of these two functions in determining the dependence of potential on time can be deduced from the plot given in Fig. 3 where the ratio of $\exp(T^2) \text{erfc}(T)$ to $2T/\pi^{1/2}$ is plotted versus $T$. This plot shows that when the value of the argument $T$, i.e., $\beta t^{1/2}$ or $\gamma t^{1/2}$, is larger than $7$ the term containing the error function becomes much smaller than the term $2T/\pi^{1/2}$. From equations (2-44) and (2-45) one concludes that $\gamma < \beta$ as long as real values of $\beta$ and $\gamma$ are concerned. Therefore, one deduces that when $\gamma t^{1/2}$ is larger than, say, $7$ the terms containing the error function may be neglected in equation (2-43); the error resulting from this simplification is then less than $1$ per cent. In view of equations (2-45) and (2-46) one concludes that the above condition ($\gamma t^{1/2} > 7$) is fulfilled for the times longer than $5 \times 10^{-5}$ sec., when the same representative values of $n$, $T$, $C_1$, $C_0$, and $D$ as given in connection with equation (2-46) are used to estimate the value of $\gamma$.

Thus, for sufficiently long times, equation (2-43) can be written in the following simplified form
Lot of the ratio of $\ln\exp(T^2)\text{erfc}(1)$ to $2\pi\sqrt{T}$. 

Diagram showing a curve with the function $\frac{\sqrt{2\pi}\exp(T^2)\text{erfc}(T)}{2T}$ plotted against $T$. 

The title of the diagram reads: "Lot of the ratio of $\ln\exp(T^2)\text{erfc}(1)$ to $2\pi\sqrt{T}$".
Potential-time curves when $\alpha$ and $\gamma$ are complex.

It follows from equations (2-44) and (2-45) that, if the condition

$$\frac{n^2F^2DC^0}{RTCeKs} > 1$$

is satisfied, $\alpha$ and $\gamma$ are conjugate complex quantities.

This causes some difficulties in the evaluation of the complete potential-time curves because values of the error functions of complex arguments are not tabulated. However, equation (2-43) can be transformed into a real form by the following procedure. The error function can be expanded in a uniformly convergent series (7), and the resulting series, as was shown by Born (4), can be separated into real and imaginary parts. By replacing the error functions in (2-43) by their series expansion and by rearranging the terms, one can show that the imaginary parts cancel out and equation (2-43) is transformed in a real form.

The resulting equation is too complicated for any practical purpose. But it can be shown that, if the absolute value of $\alpha t^2$ and $\gamma t^2$ is larger than unity, the values of the series resulting from the expansion of the error function are negligible with respect to the term containing the square root of time. An expression for potential-time curves which is identical with equation (2-47) is thus obtained.
Determination of \( k_\alpha \) and \( \alpha \)

It follows from (2-47) that the plot of \((E-E_0)\) against \( t^\frac{1}{2} \) is linear as it is for the case when the double layer capacity is assumed to be equal to zero (equation (2-10)). However, the intercept at \( t = 0 \) in the complete treatment is characterized by two terms: one term, containing the rate constant \( k_\alpha \), which is the same as in (2-10), and an additional second term expressing the influence of the double layer capacity.

The rate constant can still be obtained from the intercept at \( t = 0 \) provided that the term containing \( k_\alpha \) is not negligible with respect to the capacity term. By assuming that the term containing the rate constant should not be less than one tenth of the capacity term, and by taking the following representative values: \( n = 2 \), \( T = 300^\circ \text{K} \), \( D_0 = D_R = 10^{-5} \text{cm}^2 \text{sec}^{-1} \), \( C_l = 2 \times 10^{-5} \text{farad cm}^{-2} \), \( C_0^o = C_R^o = 10^{-5} \text{mole cm}^{-3} \), one deduces from (2-47) that the values of \( k_\alpha \) up to 100 cm sec\(^{-1}\) could easily be determined.

Since the intercept at \( t = 0 \) is given by the difference of the two terms, it is more convenient to evaluate the term containing the rate constant from the intercept at

\[
(2-48)
\]

The intercept, \( (E-E_0)_t^\frac{1}{2} \), where \( t^\frac{1}{2} \) is given by (2-48), is related (see equation (2-47)) to the rate constant by the equation

\[
-(E-E_0)_t^\frac{1}{2} = \frac{RT \nu d}{nF \nu_0} = \frac{RT}{n^2F^2} \frac{L_d}{k_\alpha C_0^{o^{1-\alpha}} C_R^{\alpha}} \quad (2-49)
\]
The slope, $S$, of the linear plot of $(E-E_0)$ against $t^{\frac{1}{2}}$ is

$$S = \frac{2 \mu d \frac{RT}{n^2 F^2}}{} \left( \frac{1}{C_0 R^\alpha} + \frac{1}{C_R R^\alpha} \right) \quad (2-50)$$

and, consequently, the very simple expression for $t_i^{\frac{1}{2}}$,

$$t_i^{\frac{1}{2}} = \frac{n i_d}{\mu d} S \quad (2-51)$$

is obtained from (2-48) and (2-50).

When the bulk concentrations of the reacting species are different, the intercept at $t_i^{\frac{1}{2}}$ contains the transfer coefficient $\alpha$ which must then be known to calculate the rate constant $k_s$. The transfer coefficient can be determined from a logarithmic plot of the exchange current against the concentration of one reacting species (16), while the concentration of the other reactant is kept constant. A straight line whose slope is either $\alpha$ or $(1-\alpha)$ is obtained, and $\alpha$ is thus readily determined. This method follows from the definition of the exchange current in equation (1-8).

Summarizing, one can conclude that electrolysis with a current impulse appears to be a promising method for studies of fast electrode reactions.
CHAPTER III - ELECTROLYSIS WITH A CURRENT REPRESENTED BY A SQUARE-WAVE

The conditions of electrolysis are supposed to be the same as in the previous method except that the current through the cell is now a square-wave function of time. The electrode potential varies periodically, and the rate constant \( k_s \) is deduced from the potential-time relationship. The concentrations of species \( O \) and \( R \) at the electrode surface are calculated by solving Fick's diffusion equation (2-1) for linear diffusion for the conditions given by equation (2-2), but where \( i_d \) is now a square-wave function of time.

Calculation of Concentrations \( C_O(x, t) \) and \( C_R(x, t) \)

The substitutions

\[
\frac{\partial C_O}{\partial t} - D \frac{\partial^2 C_O}{\partial x^2} = \frac{\partial C_R}{\partial t} - D \frac{\partial^2 C_R}{\partial x^2}
\]

are made, and the initial and boundary conditions (2-2) are expressed in terms of \( \phi_O(x, t) \) and \( \phi_R(x, t) \). The solution of Fick's diffusion equation (2-1) for linear diffusion is obtained by using the Laplace transformation, with respect to the variable \( t \), and the transform \( \phi_O(x, s) \) when \( \phi_O(x, s) \) is bounded for \( x \to \pm \infty \). It is

\[
\phi_O(x, s) = \exp \left[ -\left( \frac{s}{D} \right)^{1/2} x \right]
\]

where \( s \) is the parameter introduced by the transformation. The same equation in which \( D_R \) is substituted for \( D_O \) and \( M \) is replaced by another integration constant \( N \) holds for \( \phi_R(x, s) \).
The Laplace transform of the square wave, $\text{Sq}(t,\tau)$, with the amplitude $I_m$ and the period $2\tau$ is (8)

$$L\left[ \text{Sq}(t,\tau) \right] = \frac{I_m}{s} \frac{\tanh \frac{\tau s}{2}}{s}, \quad (3-3)$$

In view of the (3-3) one deduces from the transforms of the boundary conditions

$$\left( \tilde{Q}_0 (\nu, \sigma) = M = \frac{I_m}{\pi F C_0} \frac{\tanh \frac{s \sigma}{2}}{s \sigma} \right) \quad (3-4)$$

and the same value for $N = \tilde{Q}_Q (0, s)$ (with $D_R$ instead of $D_0$).

Since the transform (3-4) does not appear in the tables, it must be determined by the use of inversion theorem for the Laplace transformation. This theorem states (7) that the function $v(t)$ can be obtained from its Laplace transform $\tilde{v}(s)$ by means of the following complex inversion integral

$$v(t) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} \exp \left[ s \nu \right] \tilde{v}(s) ds \quad (3-5)$$

where $c$ is to be so large that all the singularities of $\tilde{v}(p)$ lie to the left of the line $\left\{ c = \alpha, \nu \leq \alpha \right\}$. The variable $p$ is written instead of $s$ in (3-5) to emphasize the fact that $\tilde{v}(p)$ is regarded as a function of a complex variable.

By applying the inversion theorem (3-5), to equation (3-4) one obtains for $x = 0$

$$\tilde{Q}_0 (0, \nu) = \frac{I_m}{\pi F C_0} \int_{c-i\infty}^{c+i\infty} \exp \left[ s \nu \right] \frac{\tanh \frac{s \nu}{2}}{s \nu} ds \quad (3-6).$$

The integrand of the contour integral in (3-6) has a branch point at $p = 0$, and simple poles for $\cosh \left( \frac{\tau}{2} p \right) = 0$, i.e., for $p = -i(2q+1) \tau /\tau$ with the integer $q$ varying from
The steady state part of $\phi_0(0,t)$ is given by the sum of the residues at the poles. Thus, the steady state solution is

$$\phi_0(0,t) = \sum_{q=-\infty}^{q=+\infty} \lim_{p \to -l(2q+1)\pi \over t} \frac{\exp[pt] \sinh \frac{tp}{c}}{p^{3/2}} \times \frac{[p + l(2q+1)\pi]}{\cosh \frac{tp}{c}}$$

or

$$\phi_0(0,t) = \sum_{q=-\infty}^{q=+\infty} \lim_{p \to -l(2q+1)\pi \over t} \frac{\exp[-l(2q+1)\pi t]}{[-l(2q+1)]^{1/2}}$$

By taking into account the relationships

$$l^1/2 = (1/2)^{1/2} / (1+i) = \exp[\frac{l \pi}{\mu}]$$

$$l^{1/2} = (1/2)^{1/2} / (1-i) = \exp[-\frac{l \pi}{\mu}]$$

the equation (3-8) can be transformed into

$$\phi_0(0,t) = \sum_{q=-\infty}^{q=+\infty} \lim_{p \to -l(2q+1)\pi \over t} \frac{\cos\left[(2q+1)\frac{\pi t}{c} + \frac{\pi}{2}\right]}{(2q+1)^{1/2}}$$

The expression for $\phi_R(0,t)$ is identical to (3-9) except that $D_R$ is substituted for $D_0$, and that a plus sign precedes the second member. The values of $C_0(0,t)$ and $C_R(0,t)$ are

1The complete solutions $\phi_0(x,t)$ and $\phi_R(x,t)$ including the transients were obtained but they were too complicated for any practical use. However, the complete solutions were used to verify the correctness of the derivation by showing that they satisfied the differential equation expressing Fick's second law (2-1). The initial and boundary conditions were also satisfied.
readily obtained in view of the definition of $\varphi_0$ and $\varphi_R$.

Thus the steady state concentration of substance 0 at $x=0$ is

$$C_0(0,t) = C_0^0 + \frac{4I_m}{\pi^{1/2}nFD_0q'} \cos \left[ \frac{(2q+1)\pi x}{\tau} + \frac{\pi}{4} \right]$$

where $I_m$ is the amplitude of the square wave current, and $\tau$ is the half-period. This equation holds for $C_R(0,t)$ except that the second term on the right-hand side is preceded by a minus sign and $D_R$ is substituted for $D_0$.

**Potential-Time Curves**

The complete potential-time curves can be obtained by substituting the $C(0,t)$'s in the general current-potential equation (1-6). This leads to a complicated expression; it is more fruitful to consider the case where the current density and the frequency of the square wave are selected in such a manner that the variations of potential for the steady state do not exceed a few millivolts. The current-potential relationship given by (2-20) is then applicable and, if one assumes for the sake of simplicity that $C_0^0 = C_R^0 = C^0$ and that $D_0 = D_R = D$, one readily obtains the potential-time relationship for the steady state by introducing the concentrations at $x=0$ in (2-20). Thus

$$-(E - E_0) = \left\{ \frac{RT}{n^2F^2k_sc^0} \left[ \frac{R}{\pi^{1/2}nFD_0C_0} \sum_{q=0}^{q=\infty} \frac{\cos \left[ (2q+1)\pi x/\tau + \pi/4 \right]}{(2q+1)^{3/2}} \right] \right\}$$

(3.11)
where $i_d(t)$ is either $+I_m$ or $-I_m$. Values of the series in this equation are plotted against the fraction of the period in Fig. 4. The series is equal to $1.68876 / 2^{t/2}$ or $1.20$ at $t = 2NT$, and $-1.20$ at $t = (2N+1)T$, where $N$ is an integer. Values of this series were calculated from the tabulated values of a similar series computed by Glaisher (18).

The first term on the right-hand side of (3-11) accounts for the kinetics of electron transfer, and the other term results from variations of the reagent concentrations at the electrode surface. The latter term must not be larger than, say, ten times the term in $k_s$ if the rate constant is to be determined. Thus the condition

$$k_s < 10D^{1/2}T^{1/2}$$

must be satisfied. Since $D$ is of the order of $10^{-5} \text{cm}^2 \text{sec}^{-1}$, values of $k_s$ up to $0.1 \text{ cm/sec}^{-1}$ can easily be determined, $T$ being then larger than $10^{-4} \text{ sec}$. Values of $k_s$ up to $1 \text{ cm/sec}^{-1}$ could possibly be determined. This method is thus comparable to electrolysis with superimposed alternating voltage. A useful procedure for obtaining $k_s$ would be to determine $E-E_e$ at various frequencies, and deduce $k_s$ from a plot of $E-E_e$ against $T^4$. The ohmic drop must be compensated in such measurements, for example, by the procedure described in Chapter IV.
VALUES OF SERIES

FRACTION OF PERIOD

Fig. 4. Values of the series in relation (I-II)
CHAPTER IV - EXPERIMENTAL METHODS

The apparatus used in the experimental studies consisted of the following essential components: the electrolytic cell, the bridge to compensate the electrolyte resistance, and the generator of current impulses. These are described below.

The Electrolytic Cell

The kinetics of the discharge of cadmium ions on cadmium amalgam was studied to verify the theory developed in Chapter II because kinetic data for this reaction are available in the literature (16). The electrolytic cell used in this investigation was essentially the same as the one used by Gerischer (15) in the study of the cadmium - cadmium amalgam system by electrolysis with superimposed sinusoidal voltage. The cell was composed of two amalgam electrodes of identical composition (Fig. 5): a hanging amalgam drop was used as the working electrode while an amalgam pool with about 200 times larger area served as the reference electrode. The amalgam was made to flow at a constant rate through an ordinary polarographic capillary, and the amalgam drops formed at the end of capillary were caught in a groove on a small glass plate attached to the capillary with such an inclination that the drops rolled slowly along the groove. The capillary, held in the vertical position by a close fitting glass sleeve, could be rotated about its axis in such a fashion that the
Figure 5
Electrolytic cell with hanging drop electrode

hanging drop electrode

Pt

Pt

to amalgam reservoir

amalgam pool

N₂
drops rolling along the groove touched the tip of a small platinum wire serving as the terminal for the working electrode. The platinum wire was sealed in glass and only its tip about 0.1 mm long was left uncovered. Since mercury (or amalgam) does not adhere to platinum, traces of gold were deposited on the tip of the platinum wire by electroplating. After this treatment of the tip, drops of mercury, or amalgam, adhered to the wire very easily and remained hanging for any period of time. The hanging drop was renewed by collecting additional drops on the platinum tip until the limit of adhesion was exceeded and the drop detached itself. A new drop of identical size was replaced on the platinum tip. The size of the drop was determined by collecting a known number of drops and weighing them.

The hanging drop electrode is preferable to the dropping mercury electrode in this type of investigation because it has a constant area and does not require a device for synchronizing the operation of the electrical equipment with the fall of the drop. The small contamination of gold in mercury does not interfere with measurements since gold is a nobler element than mercury.

Solutions were freed from dissolved oxygen before electrolysis by bubbling nitrogen according to conventional polarographic practice. This gas was also passed through the cell before each measurement in order to eliminate any gradient of concentration.
Compensation for the Electrolyte Resistance

In general the ohmic drop across the cell is much larger than the potential changes in the early stages of electrolysis, and an adequate compensation must be provided. This was achieved by incorporating the cell in a bridge circuit as shown schematically in Fig. 6. The cell CE containing only the supporting electrolyte (amalgam electrodes replaced by identical Hg electrodes) was placed in the fourth arm of the bridge, while the adjustable resistance $R_3$, in series with a variable capacitor $C_1$, served as the equivalent circuit for the cell. The bridge was fed by an oscillator having an output voltage of a few millivolts\(^1\) with the frequency of $10^3$ cycles per second. By setting $R_1 = R_2$ and by adjusting $R_3$ and $C_1$ the bridge was balanced, a cathode-ray oscilloscope CRO with a preamplifier (not shown in the diagram) being used as the balance indicator. The capacitor $C_1$ was then removed from the circuit and the cell replaced by a variable resistance $R_4$, and the bridge was rebalanced by adjusting $R_4$. The rebalanced bridge was then connected to the constant current generator (described below), and a current was determined by measuring the ohmic drop in the resistance $R_1$ by means of a Leeds and Northrup student potentiometer. In order to maintain the same current distribution in the balanced bridge during the recording of potential-time curves, resistance

\(^{1}\text{Voltage of a small amplitude had to be applied to the bridge to obtain a good balance because the double layer capacity changes with the potential.}\)
R₁ was so high that the voltage drop across it exceeded more than 100 times the counter e.m.f. of the cell developed during electrolysis.

Adjustment of R₃ could also be made with direct current (capacitor C₁ being removed and cell containing the system to be investigated), but the solution had to be stirred to avoid concentration polarization, and in order to make the overvoltage virtually equal to zero the current through the cell must be much smaller than the current used during the recording of potential-time curves. A sensitive galvanometer could be used as the balance indicator.

**Generation of Current Step**

The generation of a current step with a very steep front is a necessary requirement in this investigation. The electrical circuit for generation of such current steps is shown schematically in Fig. 7. This circuit was fundamentally the same as the one often used in conventional electrolysis at constant current except that an electronic switch rather than a mechanical relay was used to initiate the flow of current.

The bridge AB containing the electrolytic cell, in series with a variable resistance R₅ and a thyatron, T₁, was connected to a constant voltage power supply having an output voltage of 300 volts. The resulting circuit has two stable states: the thyatron is either conducting or non-conducting. Both states are stable since the first is maintained by the
Sweep Synchronization

Figure 7
Schematic Circuit Diagram of Current Step Generator
negative grid bias (-22.5 volts) and the second by the nature of the gas discharge. The circuit passes from the non-conducting to the conducting state when the grid of the thyatron receives a suitable triggering signal as described below. The circuit then remains in the conducting state, provided that the current through the thyatron is high enough to maintain a continuous discharge.

When currents lower than the minimum discharge current (approx. 1 ma for the thyatron type 2050) were desired through the bridge, an additional resistor $R_6$ was connected parallel to the bridge. The extinguishing of the thyatron was accomplished by opening the plate or cathode circuit momentarily.

The method of triggering the thyatron circuits is as follows. The control grid-to-cathode voltage is increased to a point beyond a critical value, and eventually the tube will fire. However, the direct application of the triggering signal to the grid of the thyatron results in the introduction of a transient in the main circuit. This difficulty was overcome by feeding the trigger signal to the thyatron grid through a diode, $6H6$, (11). Using the triggering circuit shown in Fig. 7 and improving the response of the power supply by connecting a large condenser $C_2$ (100 microfarads) across its output terminals, the firing of the thyatron, i.e., the switching on of the current, was accomplished in approximately $10^{-7}$ second and only a small transient,
lasting less than a microsecond, was superimposed on the constant current.

**Recording of Potential-Time Curves**

By closing the double pole double throw relay, $S_1S_2$, which was adjusted in such a manner as to close $S_2$ slightly before $S_1$, the bridge circuit AB containing the electrolytic cell was connected to the constant current generator, and the triggering signal from a 45 volt battery was applied to the grid of the thyatron $T_1$ (Fig. 7). The same signal was used to trigger the horizontal sweep of the recording oscilloscope. Relay $S_1S_2$ was actuated by closing switch $S_3$ manually.

In order to interrupt the electrolysis before secondary electrode reactions (decomposition of the solvent or supporting electrolyte) could occur, it was necessary to disconnect the cell from the current generator after a definite time of electrolysis. This was accomplished by connecting a biased thyatron $T_2$ in parallel with the relay coil. After a definite interval of time, which was determined by the values of the resistance $R_7$ and the capacitor $C_3$, the thyatron $T_2$ became conductive, thus shortening out the relay coil and opening the electrolysis circuit.

The voltage across the electrolytic cell during electrolysis was recorded with a calibrated cathode-ray oscilloscope (Tektronix oscilloscope, model 531 with the differential preamplifier 53D/54D having a maximum sensitivity of 1 millivolt per centimeter). Since the voltage drop across the
cell due to the electrolyte resistance was compensated by the adjusted resistance $R_3$ (Fig. 6), the oscilloscope recorded only changes in potential of the working electrode during the course of electrolysis.

The oscillograms were photographed on 35 mm film and readings were made from enlarged images.
The kinetics of the discharge of cadmium ions on cadmium amalgam was studied to check the theory developed in Chapter II. The system Cd\textsuperscript{++}/Cd(amalgam) was selected for this purpose because its kinetics has been thoroughly investigated (16) from the studies of electrolysis with sinusoidal voltages. Furthermore, this system has one of the largest rate constants \( k_s \) so far determined.

Four Cd\textsuperscript{++}/Cd(amalgam) systems - having identical composition in the amalgam phase, but differing in the concentration of Cd\textsuperscript{++}-ion in the solution phase - were studied. The cadmium amalgam used in this investigation was prepared by dissolving a known amount of metallic cadmium in mercury. During its preparation, storage, and use the amalgam was kept under an inert (nitrogen) atmosphere to avoid any oxidation of the amalgam by atmospheric oxygen. The composition of the four Cd\textsuperscript{++}/Cd(amalgam) systems was as follows:

\[
\begin{align*}
\text{System I} & \quad 1.0 \times 10^{-3} \\
\text{System II} & \quad 5.0 \times 10^{-4} \\
\text{System III} & \quad 2.5 \times 10^{-4} \\
\text{System IV} & \quad 1.0 \times 10^{-4}
\end{align*}
\]

while the amalgam containing 0.6 mole per cent of cadmium \((4.0 \times 10^{-4} \text{ mole cm}^{-3})\) was used in all four cases. All determinations were carried out at \(25 \pm 0.1^\circ\text{C}\).
Potential-time curves for the four above mentioned systems were recorded during the electrolysis with the current density of $9.30 \times 10^{-4}$ amp. cm.$^{-2}$ as described in Chapter IV. Two examples of potential-time curves (for system I and IV) are shown in Fig. 8.

According to the treatment developed in Chapter II the potential-time relationship should be of the form (see equation (2-47))

$$E - E_e = K_1 t^{1/2} + K_2$$

where $K_1$ and $K_2$ are constants independent of time. The constant $K_2$ is related in a simple manner to the exchange current defined by equation (1-8). It follows from (5-1) that the exchange current can be determined from the plot of potential against square root of time. A detailed procedure for calculations of the exchange current from this plot was given on page 29. The data necessary to evaluate the exchange currents were obtained from the plots shown in Fig. 9 and are summarized in Table I. Exchange currents were calculated from the intercepts at $t^{1/2} = t_{i}^{1/2}$ by means of the equation (2-49). The values of $t_{i}^{1/2}$ at which the intercepts were determined were computed from the slopes of the straight lines shown in Fig. 9, the current density and the differential capacity of the double layer $C_1$ (see equation (2-51)). The last quantity ($C_1$) was determined by measuring the capacity of the electrolytic cell with the AC bridge (Fig. 6). The amplitude of the alternating voltage applied to the bridge did not exceed a few millivolts and the voltage had a frequency
### TABLE I

**DATA FOR CALCULATION OF EXCHANGE CURRENTS**

<table>
<thead>
<tr>
<th>Concentration of Cd⁺⁺</th>
<th>Slope at ( t_\frac{1}{2} )</th>
<th>Intercept at ( t_\frac{1}{2} )</th>
<th>Exchange Currents</th>
<th>( k_s )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>10</td>
<td>2.42</td>
<td>7.16</td>
<td>0.40</td>
</tr>
<tr>
<td>II</td>
<td>5.0</td>
<td>4.90</td>
<td>14.5</td>
<td>0.70</td>
</tr>
<tr>
<td>III</td>
<td>2.5</td>
<td>9.80</td>
<td>29.0</td>
<td>1.20</td>
</tr>
<tr>
<td>IV</td>
<td>1.0</td>
<td>24.1</td>
<td>71.1</td>
<td>2.45</td>
</tr>
</tbody>
</table>

**Units:**
- (a) \( 10^{-7} \) mole cm\(^{-3} \)
- (b) \( 10^{-2} \) volt sec
- (c) \( 10^{-4} \) sec
- (d) millivolts
- (e) \( 10^{-3} \) amp cm
- (f) \( 10^{-2} \) cm sec

---

51
of 30 kilocycles per second. It was shown by Gerischer (15) that under these conditions the capacitive impedance of the cell containing the system \( \text{Cd}^{++}/\text{Cd( amalgam)} \) was virtually equal to the differential double layer capacity of the polarized electrode. The capacity of the polarized electrode determined in the foregoing manner was found to be \( C_1 = 3.5 \times 10^{-5} \text{ farad. cm}^{-2} \).

The transfer coefficient \( \alpha \) was determined from the variation of the exchange current with the concentration of \( \text{Cd}^{++}-\text{ion} \). In view of the definition of the exchange current \( i_o = nFk_s C_0 C_Q^{\alpha} \) the logarithmic plot of \( i_o \) versus \( C_0 \) should yield a straight line having a slope equal to \( (1-\alpha) \). This is indeed the case (Fig. 10). From the slope of this straight line in Fig. 10 one calculates the value, \( \alpha = 0.21 \).

The rate constant \( k_s \) was calculated from the exchange currents using the above determined value for the transfer coefficient \( \alpha \) (\( \alpha = 0.21 \)). The results are shown in the last column of Table I, the average value of \( k_s \) being \( 4.5 \times 10^{-2} \text{ cm.sec}^{-1} \).

It should be noted that the values of the kinetic parameters \( k_s = 4.5 \times 10^{-2} \text{ cm.sec}^{-1} \) and \( \alpha = 0.21 \) obtained by the present method are in good agreement with those \( (k_s = 4.2 \times 10^{-2} \text{ cm.sec}^{-1} \) and \( \alpha = 0.18 \) obtained by Gerischer (16) for the same system from studies of electrolysis with sinusoidally alternating voltage.
A graph showing the relationship between \( \log i_0 \) and \( \log C_{\text{Cd}^{++}}^0 \), with a straight line indicating a linear correlation.
In order to verify the equation (2-8) of the complete potential-time curve the variation of potential for system IV was recorded in the course of electrolysis with the current density of 9.30 x 10^{-4} \text{amp. cm}^{-2}. The plot of

$$\log \left\{ 1 - \left( \frac{t}{t_c} \right)^{1/2} - \exp \left[ \frac{nF}{RT} (E - E_e) \right] \right\}$$

against $E - E_e$ was constructed from the obtained potential-time curve. The resulting plot shown in Fig. 11 gives a straight line as predicted by equation (2-8) but the precision is rather poor as compared with the linear plots shows in Fig. 9. This is to be expected, since the small size of the screen of the cathode-ray oscilloscope prevents the recording of wide variations in potential with high accuracy. Furthermore, equation (2-8) represents only an approximate expression for potential-time curves because, in its derivation, the influence of the double layer capacity was not taken into account. One calculates (equation (2-8)), from the slope of the straight line in Fig. 11, a value of the transfer coefficient, $\alpha = 0.23$

On the basis of the foregoing results one may conclude that electrolysis with a current impulse is a valuable method for studies of fast electron transfer processes. This method could be applied to determine the rate constants for so-called "reversible" electrode reactions in aqueous solutions and, particularly, in fused salts where the electron transfer is too rapid to be studied by any other methods developed so far.
Theoretical analyses of electrolysis with sinusoidally alternating voltage have been developed by various authors during the last fifty years (12, 13, 14, 20, 29). The current-potential relationships derived by these authors are valid only when the system being electrolyzed has attained a steady state, and no information is available about the nature and significance of the transitory state. The knowledge of transients is of interest in polarography with superimposed alternating voltage where direct measurements of the current amplitude are made.

Since, in this method, the potential of the polarized electrode varies periodically about its equilibrium value (observed when no current flows through the cell) by a few millivolts, the general current-potential relationship (2-33) is applicable to the derivation of the current as a function of time.

Expressing the potential as a function of time during electrolysis by

\[ E(t) = e \sin(\omega t + \epsilon) \]  

one obtains, after introducing the Laplace transform of \( E(t) \) in (2-33), the following expression for the transform of current

\[ \ldots \]
\[
\overline{L}(s) = -\frac{nF}{R_T} \nu_0 e^{\frac{\omega \cos \xi}{s^2 + \omega^2}} + \frac{s \sin \xi}{s^2 + \omega^2}
\]

\[
- \alpha \left[ \cos \xi \frac{\omega}{(s^2 + \omega^2)(s^2 + \alpha)} + \sin \xi \frac{s}{(s^2 + \omega^2)(s^2 + \alpha)} \right]
\]

where \( i_0 \) and \( \alpha \) are defined by (2-14a) and (2-34), respectively. The inverse transform of current is obtained by applying the convolution integral. Thus

\[
\overline{I}(t) = -\frac{nF}{R_T} \nu_0 e^{\frac{\omega \cos \xi}{s^2 + \omega^2}} + \frac{s \sin \xi}{s^2 + \omega^2}
\]

By several integrations by parts one obtains

\[
\overline{I}(t) = -\frac{nF}{R_T} \nu_0 e^{\frac{\omega \cos \xi}{s^2 + \omega^2}} + \frac{s \sin \xi}{s^2 + \omega^2}
\]

\[
- \alpha \cos \xi \int_0^t \sin \left[ \omega (t - \tau) \right] \left[ \frac{1}{\pi \tau} \right] - \alpha \exp (at) \text{erfc}(at^\frac{1}{2}) d\tau
\]

\[
- \alpha \sin \xi \int_0^t \cos \left[ \omega (t - \tau) \right] \left[ \frac{1}{\pi \tau} \right] - \alpha \exp (at) \text{erfc}(at^\frac{1}{2}) d\tau
\]

\[
\text{(A-3)}
\]

\[
\text{By several integrations by parts one obtains}
\]

\[
\overline{I}(t) = -\frac{nF}{R_T} \nu_0 e^{\frac{\omega \cos \xi}{s^2 + \omega^2}} + \frac{s \sin \xi}{s^2 + \omega^2}
\]

\[
- \alpha \cos \xi \int_0^t \sin \left[ \omega (t - \tau) \right] \left[ \frac{1}{\pi \tau} \right] - \alpha \exp (at) \text{erfc}(at^\frac{1}{2}) d\tau
\]

\[
- \alpha \sin \xi \int_0^t \cos \left[ \omega (t - \tau) \right] \left[ \frac{1}{\pi \tau} \right] - \alpha \exp (at) \text{erfc}(at^\frac{1}{2}) d\tau
\]

\[
\text{(A-4)}
\]
where \( C \) and \( S \) are the Fresnel integrals

\[
C(\beta) = \int_0^\beta \cos \left( \frac{\pi y^2}{2} \right) dy \quad \text{and} \quad S(\beta) = \int_0^\beta \sin \left( \frac{\pi y^2}{2} \right) dy
\]

These integrals can be expressed \((27)\) by

\[
C(\beta) = \frac{1}{2} + \frac{K+H}{\pi \nu_o} \sin \frac{\pi \beta^2}{2} - \frac{K-H}{\pi \nu_o} \cos \frac{\pi \beta^2}{2} \quad (A-5)
\]

\[
S(\beta) = \frac{1}{2} - \frac{K-H}{\pi \nu_o} \sin \frac{\pi \beta^2}{2} - \frac{K+H}{\pi \nu_o} \cos \frac{\pi \beta^2}{2} \quad (A-6)
\]

where the functions \( K+H \) and \( K-H \), which were calculated by Miller and Gordon \((27)\), are shown in Fig. 12. The combination of \((A-4)\), \((A-5)\), and \((A-6)\) yields, after some algebraic transformations,

\[
L(t) = \frac{\pi}{RT} \exp \left( \frac{a t}{\nu_o} \right) \left[ \frac{\omega^{\nu_o}}{[\alpha^2 + (2w)^{\nu_o}]^2 + \omega} \right] \sin \left[ \omega t + \phi - \tan^{-1} \left( \frac{\omega}{\alpha + (\omega^2)^{\nu_o}} \right) \right]
\]

\[
+ T_1 + T_2 + T_3
\]

\[(A-7)\]

with

\[
T_1 = \frac{\omega^{\nu_o}}{[\alpha^2 + (2w)^{\nu_o}]^2 + \omega} \exp \left( \frac{a t}{\nu_o} \right) \text{erfc} \left( \frac{\alpha \omega^{\nu_o}}{\nu_o} \right)
\]

\[
T_2 = \frac{\omega^{\nu_o}}{[\alpha^2 + (2w)^{\nu_o}]^2 + \omega} \frac{K+H}{\pi \nu_o}
\]

\[
T_3 = -\frac{\omega^{\nu_o}}{[\alpha^2 + (2w)^{\nu_o}]^2 + \omega} \frac{K-H}{\pi \nu_o}
\]
The T's in (A-7) are the transients and the other term represents the steady state solution which is identical to that derived previously by other authors for the steady state. The phase shift of the current with respect to the voltage is

\[ \frac{\pi}{4} - \tan^{-1} \frac{(\omega/2)^{1/2}}{a + (\omega/2)^{1/2}} \]

and is equal to \( \pi/4 \) when \( a \) is infinite. This result was established many years ago by Warburg (20) for a process entirely controlled by diffusion.

The relative importance on the transients can be judged from Fig. 13 which shows a logarithmic plot of the initial absolute values of the transients and the amplitude of the steady state term against the dimensionless group \( a^2/\omega \).

The relative values of the transients with respect to the steady state term are plotted in Fig. 14 against \( \omega t \) for three values of \( \varepsilon \) and for \( a^2/\omega = 1 \). It is seen that transients vanish rapidly - after a few cycles - and that they should not prevent direct measurement of the amplitude of the alternating current in A.. C. polarography.
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VITA

Talivaldis Berzins was born June 19, 1924, in Litene, Latvia. He received his elementary education in the local public school, and entered State High School at Ķalvi, Latvia, from which he graduated in 1943.

In 1945 he went to Germany and stayed there until 1950. While in Germany, he attended the Baltic University in Hamburg for three years.

In 1950 he entered the United States and continued his education in the Louisiana State University, where he received the Bachelor of Science Degree in June, 1952.

He enrolled in the Graduate School of Louisiana State University in 1952 and received the degree of Master of Science in June, 1953. He is now a candidate for the degree of Doctor of Philosophy.
Candidate: Talivaldis Berzins

Major Field: Chemistry

Title of Thesis: New Methods for the Study of Fast Electrode Reactions

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination: 7/2/55