

THEORY AND APPLICATION OF
CHRONOPOTENTIOMETRY FOR
MEASURING HETEROGENEOUS
ELECTRON TRANSFER KINETICS

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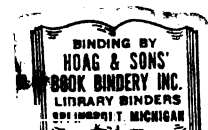
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ABSTRACT

THEORY AND APPLICATION OF CHRONOPOTENTIOMETRY FOR MEASURING HETEROGENEOUS ELECTRON TRANSFER KINETICS

By

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A new method for measuring heterogeneous electron transfer kinetics is described and developed theoretically. The method is based on using chronopotentiometry with current reversal to observe directly the overpotential associated with a kinetically controlled redox reaction. A simple equation is derived which relates observed overpotential to current density, bulk concentration of the depolarizer, and the standard rate constant, k_s . It is estimated by calculation that the method is useful for measuring rate constants in the range $4 \times 10^{-4} < k_s < 2 \times 10^{-2}$ cm/sec. An experimental evaluation of the method for reduction of azobenzene is used to establish that the above upper limit for k_s is correct, and that this limit is set by double-layer charging. These experiments also were used to demonstrate that in practice application of the new method is simple and straightforward.

In an attempt to extend the range of the method to larger rate constants, the combined influence of double-layer

charging and electrode kinetics on chronopotentiometry also was examined. In this case theory could only be obtained by numerical solution of nonlinear integral equations, and therefore results are expressed as a family of working curves. The working curves relate observed overpotential to current density, concentration of depolarizer, and k_s . Each working curve depends on the value of the double-layer capacitance, and therefore to identify the proper working curve, double-layer capacitance must be evaluated independently. A procedure for doing this is described in detail. Reduction of cadmium was used to evaluate use of the working curves, and also to compare calculated and experimental chronopotentiograms. The agreement between theory and experiment is excellent, and it is estimated that values of k_s as large as 1.2 cm/sec can be determined with the working curves.

To perform the experiments two different instruments were constructed from operational amplifiers. One of these instruments provides for automatic current reversal at a pre-selected switching potential. The construction and operation of this instrument is described in detail.

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By
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INTRODUCTION

An important part of modern electrochemistry is the measurement of heterogeneous electron transfer kinetics. The usefulness of such measurements in electrochemistry exactly parallels those in classical chemical kinetics, and therefore need not be detailed here (20). Unfortunately, although the ultimate applications are the same, the actual measurement of electrochemical rate constants is considerably more difficult than the measurement of homogeneous rate constants. Consider, for example, ac polarography, which has been widely used in the past for measuring electrochemical rate constants (55). With this technique a small amplitude ac perturbation is superimposed on a slow dc potential scan. The frequency of the ac component is then progressively increased until the rate of electron transfer is no longer rapid enough to maintain electrochemical equilibrium at the electrode surface. When this happens the observed ac current begins to lag the applied ac voltage, and the resulting phase angle and frequency are a measure of the rate constant. Although relatively simple in principle, ac polarography is fairly complicated from both experimental and theoretical viewpoints. Experimentally, it requires

variable frequency ac and dc potential sources, a summing circuit and electronic potentiostat, and sophisticated phase angle detection circuits. To determine the rate constant it is necessary to measure the frequency dependence of the phase angle over a wide range of frequencies and at several different dc potentials. These experimental data then must be corrected for ohmic potential losses and double-layer charging by fairly involved vector calculations (55), or complex plane analysis (55). Diffusion coefficients and the transfer coefficient also must be known, and therefore evaluated independently.

Difficulties such as these in measuring heterogeneous rate constants no doubt have contributed to the as yet relatively limited number of applications of electrode kinetics. Thus, the major objective of this research was to attempt to develop a new method for measuring heterogeneous electron transfer rate constants. The criteria for selecting the method were that it be conceptually straightforward, simple to apply experimentally, and require minimal data analysis. Of several modern electrochemical techniques, chronopotentiometry appeared at the onset capable of satisfying the majority of these criteria. Since the reader may not be very familiar with chronopotentiometry, the remainder of this Introduction will consist of a brief description and review of the subject. This also will provide a logical format for describing the essential ideas of using chronopotentiometry

to measure electron transfer rate constants, which the remainder of this thesis attempts to develop and evaluate in detail.

Basically, chronopotentiometry is an experimental procedure which involves recording the potential of a stationary electrode as a function of time during polarization by constant current. The expected form of such a chronopotentiogram can be understood by considering the following hypothetical experiment. Suppose that during the constant current electrolysis it is possible to analyze the surface concentration of reactant (also called depolarizer) by removing samples from the electrode surface at fixed times during the electrolysis. Suppose also that it is possible to analyze these samples by conventional polarography. The results of this hypothetical experiment would be polarograms similar to those illustrated in Figure 1a, where the dashed line, i_{const} , represents the magnitude of the constant current used for the chronopotentiometric experiment. Each curve, going from top to bottom, represents a polarogram for the hypothetical samples taken at progressively longer times during the constant current electrolysis. Initially, before the constant current is imposed, the surface concentration of depolarizer will equal its bulk value (Curve 1) and the electrode potential will be at its equilibrium value (i.e., zero current value, Point A). As soon as the constant current is imposed, however, the electrode will be forced to assume a potential

Figure 1. (a) Polarograms for hypothetical solution samples removed from the electrode surface during constant current electrolysis. Time during electrolysis increases from Curve 1 to 3; (b) Chronopotentiogram.

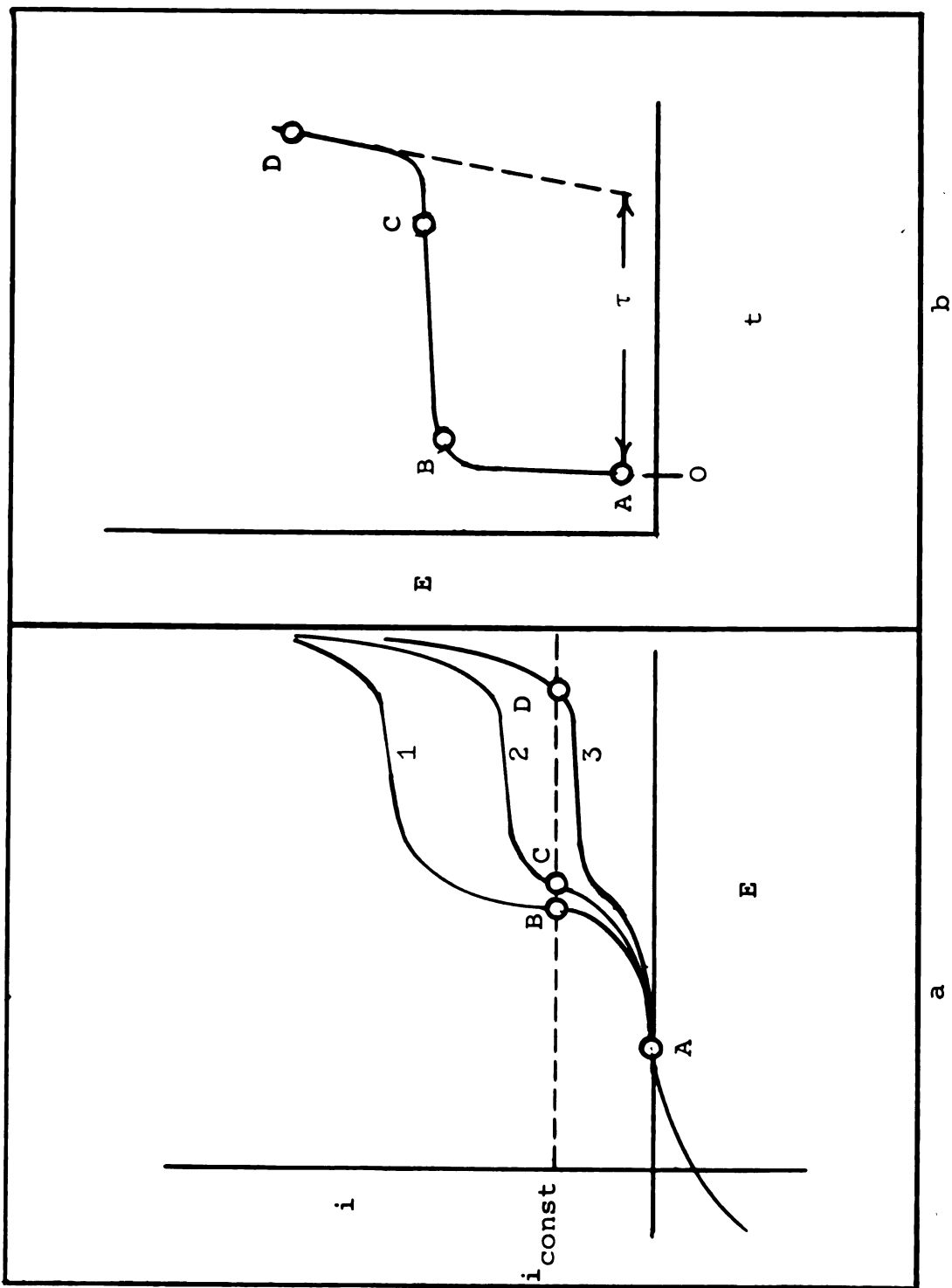


Figure 1

at which a faradaic reaction can proceed to consume the imposed current. Hence, as soon as the current is imposed, the electrode potential will jump abruptly from Point A to Point B, somewhere near the half-wave potential for the depolarizer. As the electrolysis proceeds the concentration of depolarizer at the electrode surface is continually decreased, so that at some later time the hypothetical polarogram will look like Curve 2. Here, the concentration of depolarizer is still large enough to sustain all of the constant current (i.e., there is still 100% current efficiency with respect to depolarizer), and the only effect has been a small cathodic displacement of potential (from Point B to Point C). As the constant current electrolysis proceeds, however, eventually a condition is reached, represented by Curve 3, where the surface concentration of depolarizer is no longer great enough to maintain, by itself, all of the constant current. Thus, in Curve 3 the hypothetical limiting current for depolarizer is less than $i_{\text{const.}}$, and therefore the electrode potential must shift to a point (Point D) where a new faradaic reaction (e.g., decomposition of the solvent or supporting electrolyte) can supply the additional faradaic reaction necessary to sustain the total constant current. Hence, at this particular time during constant current electrolysis there is an abrupt and rather large change of potential. It is important to note that since the new potential (Point D) corresponds to the limiting current region

for reduction of depolarizer, it follows that the surface concentration of depolarizer has gone to essentially zero.

If the potentials in Figure 1a (Points A, B, C and D) are now plotted vs. the times at which they were observed, the result is the chronopotentiogram shown in Figure 1b. Hence, in general a chronopotentiogram consists of an initially abrupt change of potential to a point near the polarographic half-wave potential, followed by a period of time where the potential is nearly constant. This period is then followed by another abrupt transition of potential, at which time the surface concentration of depolarizer also drops to zero. The time from the beginning of the experiment to the second sharp potential change is termed the transition time which is labeled τ in Figure 1b.

The first mathematical analysis of the chronopotentiometry experiment was published by Sand in 1901 (54). Sand derived an expression for the time dependence of surface concentration of depolarizer based on a semi-infinite linear diffusion model. By defining τ as the time at which surface concentration of depolarizer becomes zero, Sand obtained the following expression for transition time (now known as the Sand equation):

$$\tau^{\frac{1}{2}} = nFC_0^* \sqrt{\pi D_0} / 2i_0 \quad (1)$$

There n is the number of electrons transferred in the electrode reaction, F is the Faraday, C_0^* is the analytical

concentration of depolarizer, D_0 is the diffusion coefficient for the depolarizer, and i_0 is constant current density.

An interesting feature of the Sand equation is that it is derived without assuming a model for the electron transfer reaction. Thus, the transition time is the same for both reversible and totally irreversible electrode reactions. The shape of the entire potential-time curve does, of course, depend on reversibility of the electrode reaction. For example, for reversible electron transfer, the chronopotentiogram is described by substituting surface concentrations derived by Sand into the Nernst equation. In this case it is easily shown (16) that the potential at $t = \tau/4$ (the so-called quarter-wave potential) is identical with the classical polarographic half-wave potential.

Although theoretically the transition time is a well-defined quantity, experimentally it is frequently found that chronopotentiograms exhibit distortions which make measurement of τ ambiguous. As a result a number of empirical methods for measuring τ , usually based on some graphical construction, have been developed over the years (48). One of these methods, which will be referred to frequently in the remainder of this thesis, is due to Berzins and Delahay (3), and is illustrated in Figure 2. Their method is derived from a similar construction commonly used in the measurement of half-wave potentials on conventional polarograms. The method is applied in the following manner. Line AB is drawn tangent to the curve at

Figure 2. Method of Berzins and Delahay for determining transition time.

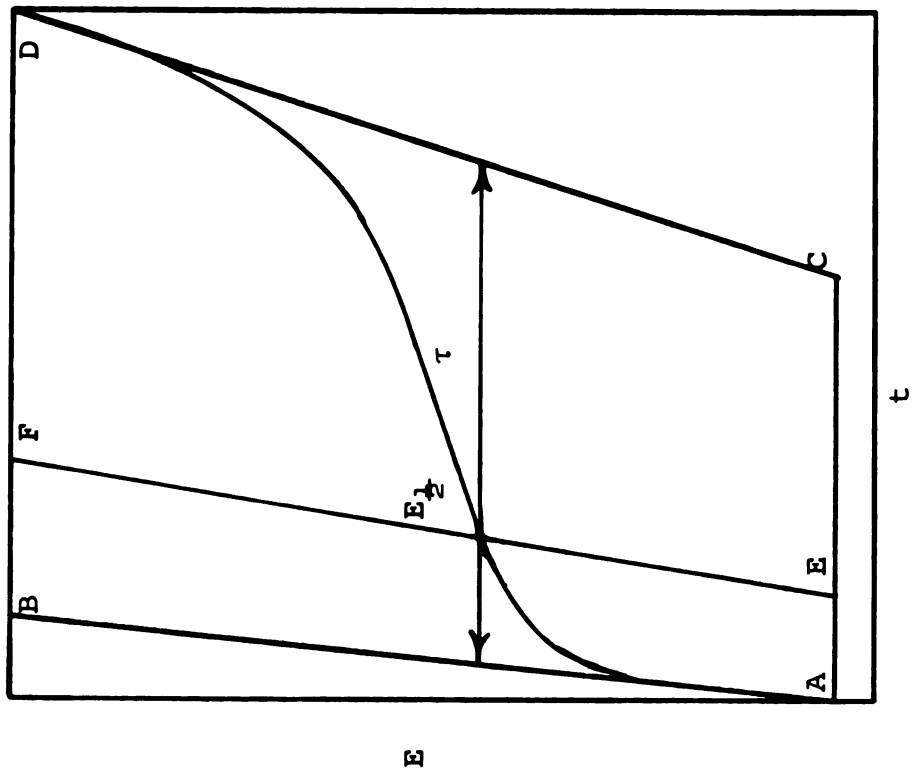


Figure 2

Point A and CD is drawn tangent to the curve at Point D. Since the polarographic half-wave potential is at $\underline{t} = \tau/4$, Points E and F are located at one-fourth of the distance between A and C, and B and D respectively. A line joining Points E and F intersects the curve at the half-wave potential, and the length of the line drawn through the point of intersection of Line EF with the curve, parallel to the time axis and bounded by Lines AB and CD, is taken as a measure of τ .

The instrumentation required for chronopotentiometry can be extremely simple, and is one of the virtues of the method. For example, many literature applications of chronopotentiometry are based on the use of simply a battery and large resistor as a source of the constant polarizing current. Of course, more sophisticated circuitry can be used and is necessary in applications such as current reversal (vide infra). Recording of potential-time curves is usually accomplished with a potentiometric recorder, or oscilloscope, depending on the time scale of the experiment.

The applications of chronopotentiometry are extensive, ranging from purely analytical to measurement of kinetics and transport properties (14). The analytical applications in general are straightforward, and based on the fact that τ is proportional to depolarizer concentration. Since τ varies as the square of depolarizer concentration, the method in principle is more sensitive than techniques like polarography.

Analytical applications have been reviewed by Everett, Johns, and Reilley (24).

The major applications of chronopotentiometry have been in the study of electrolysis mechanisms and the measurement of rates of chemical reactions coupled to the depolarizer or product of the electrode reaction. In these applications chronopotentiometry is especially useful diagnostically, since in the absence of kinetic complications $i\tau^{1/2}$ is a constant independent of current density (cf. discussion of Sand equation). For example, the presence of a chemical reaction preceding the electron transfer is easily detected by a decrease of $i\tau^{1/2}$ with increasing current density (28). In this case the test is especially useful because it is unaffected by reversibility of the electron transfer (vide supra). This is in sharp contrast with most other electrochemical techniques where preceding chemical reactions and slow electron transfer behave similarly.

Another important class of reactions where chronopotentiometry has been used very successfully are following chemical reactions, i.e., chemical reactions involving the initially formed product of the electron transfer. The advantage of chronopotentiometry in this case derives from the fact that a stationary electrode is used, and therefore products of the electrolysis accumulate near the electrode surface and can be studied by re-oxidation (in the case of an initial reduction). The re-oxidation is accomplished by

abruptly reversing the direction of current flow. With this approach, known as current reversal chronopotentiometry, chronopotentiometric waves are observed directly for both the reduction and oxidation processes. A typical example is shown in Figure 3 for reversible electron transfer, with current reversal at the first transition time. In this case the first transition, labeled τ_F , corresponds to reduction of depolarizer, and the second transition, τ_R , corresponds to oxidation of the reduced form of depolarizer. When the reduced form is chemically stable, it is easily shown (4) that the ratio of transition times, τ_R/τ_F , is one-third. Clearly, if the reduced form is chemically unstable, in general τ_R/τ_F will be less than one-third, since less of the reduced form will be available for oxidation. Moreover, the magnitude of the effect will be a function of current density, since, for example, if τ_R is small with respect to the life-time of the reduced form, then essentially all of the reduced form will still be oxidized. Thus, by observing the variation of τ_R/τ_F with current density the presence of this class of reactions is easily detected, and quantitatively correlated with the chemical lifetime of the reactant (22,56).

Two other areas in which chronopotentiometry has been extensively employed are adsorption studies and measurement of diffusion coefficients. In the former area the technique enjoyed considerable popularity in the early part of the last decade, until the advent of chronocoulometry (2). Since then

Figure 3. Chronopotentiogram illustrating the technique of current reversal.

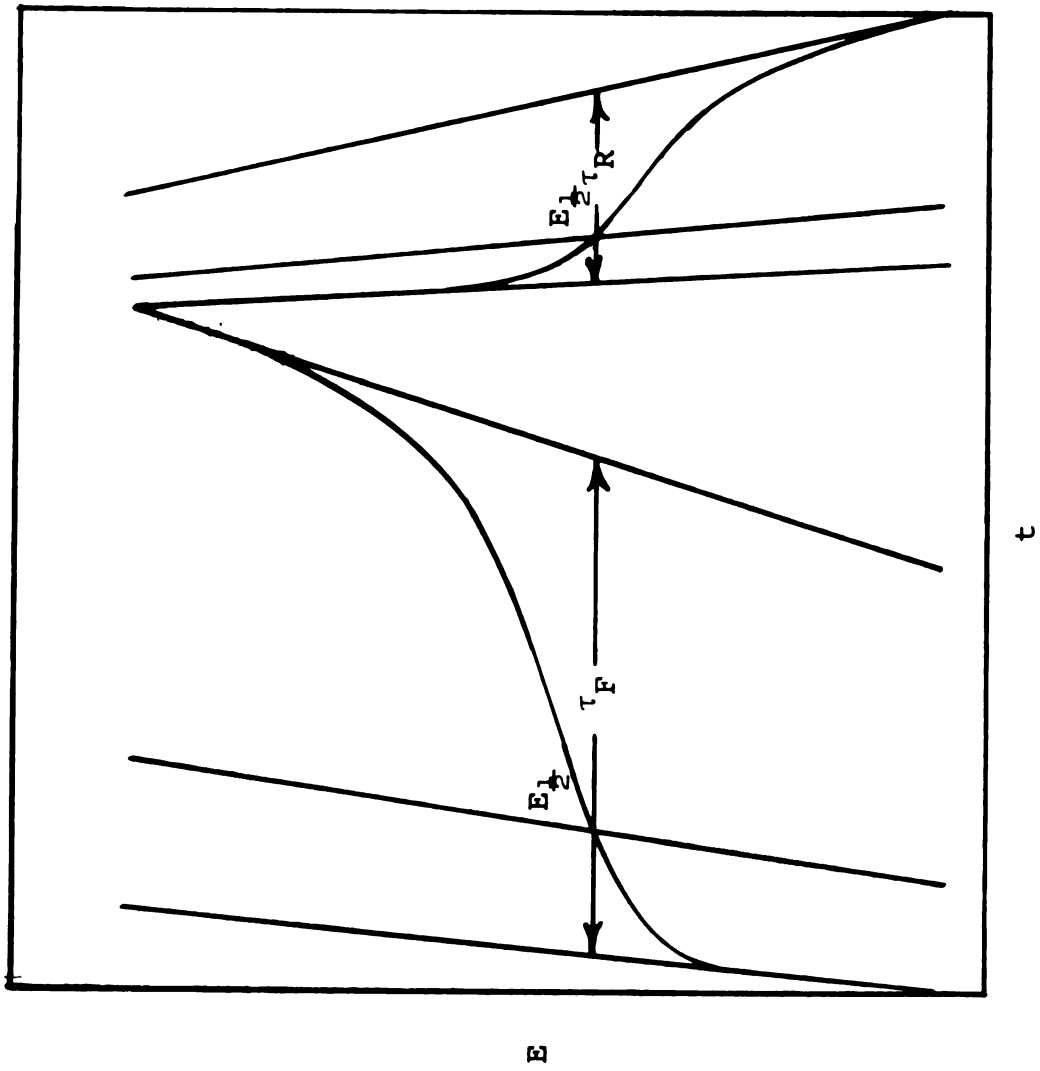


Figure 3

the use of chronopotentiometry for adsorption studies has been severely criticized (40), and presently has been essentially replaced by chronocoulometry. Measurement of diffusion coefficients usually has been based on direct application of the Sand equation, under conditions where all parameters in Equation 1 are known except the diffusion coefficient. The meaning of diffusion coefficients measured in this manner recently was analyzed in detail by Laity and McIntyre (39), who were interested primarily in measuring transport properties of fused salts.

Finally, chronopotentiometry has been used for measuring heterogeneous electron transfer rate constants, but these applications always involve data analysis and interpretation roughly as complicated (1) as those ascribed above to ac polarography. The approach to date is based on analysis of single cathodic (or anodic) polarization, so that the rate constant for the reverse reaction (anodic reaction in the case of cathodic polarization) must be estimated indirectly. It appeared, however, that by using current reversal, a more direct and conceptually simpler method could be devised, which apparently would satisfy the criteria stated at the beginning of this Introduction. The essential ideas of this new method for measuring standard electron transfer rate constants (or exchange currents) are as follows.

With current reversal chronopotentiometry, the potentials at which oxidation and reduction occur are observed directly

(cf. Figure 3). For a reversible electrode process, by definition oxidation and reduction occur at the same (equilibrium) potential--i.e., there is no so-called overpotential between the forward and reverse reactions. For example, the curve of Figure 3 corresponds to reversible electron transfer, since the forward and reverse quarter-wave potentials are identical and equal to the reversible half-wave potential. If the reaction were not perfectly reversible the activation energy associated with the electron transfer would appear as a finite overpotential between the reduction and oxidation reactions. Now consider the following hypothetical experiment involving some simple redox system characterized by its standard rate constant, k_s . For some given current density the rate of the electrochemical reaction will be large enough that even though electrode potential changes continually during the course of the chronopotentiometric experiment, essentially equilibrium conditions will be maintained at the electrode surface. Under these conditions there will be no apparent overpotential between the forward and reverse chronopotentiograms. Now consider the effect on this same system of progressively increasing the current density. As current density is increased the transition time decreases (cf. Equation 1), so that the rate at which the electrode potential changes increases. As this happens a point should be reached where the kinetics of the electron transfer are no longer rapid enough to maintain

electrochemical equilibrium at the electrode surface, and this condition should evidence itself as an overpotential between the forward and reverse chronopotentiograms. Thus, as current density is increased one would expect the difference between forward and reverse quarter-wave potentials to increase from zero. Hopefully, one should be able to correlate this directly measured overpotential with the associated current density and the standard electron transfer rate constant for the redox system. This correlation was accomplished successfully, and a description of that theory constitutes the next major section of this thesis.

As will be seen the theory proved to be as straightforward as the conceptual basis of the method. Thus, it appeared that a truly simple method had been developed which satisfied most of the criteria stated earlier. The scope and practicability of the new approach were next evaluated experimentally with some model chemical systems. In the course of this evaluation, the results of which are presented later in this thesis, it was concluded that the major limitation of the method was the interference of charging current, which set the upper limit of rate constants that could be measured. Charging current is a term used to indicate the fact that an electrode in an electrolyte solution behaves like a capacitor, and therefore current (charging current) is required to change the electrode potential. Thus, in an electrolyte considerable structuring occurs at the interface of a charged

electrode (45). For example, if the electrode is negatively charged then the solution adjacent to the electrode consists predominately of cations, a structure referred to as the electrical double-layer. If the charge on the electrode is changed by an external source, then a restructuring of the double-layer occurs, and this movement of ions results in a net flow of current. At high current densities with chronopotentiometry the relative importance of double-layer charging increases because the rate of change of electrode potential increases. Hence, since high current densities are required to measure large rate constants, it is apparent why the new method was limited by double-layer charging.

Under conditions where double-layer charging is negligible, chronopotentiometry theory is straightforward and results can be expressed in closed form, as mentioned above. Unfortunately, to include double-layer charging in the theoretical model makes the mathematics virtually intractable. Thus, prior to 1968 all attempts to account for double-layer charging in chronopotentiometry were empirical. In 1968 three groups independently published theoretical calculations for chronopotentiometry based on a rigorous mathematical model that included double-layer charging (21,50,53). These papers provided the first quantitative basis for evaluating the influence of double-layer charging on chronopotentiograms. Unfortunately, none of these papers treated the case of kinetically controlled electron transfer, and

therefore none of the results was directly applicable to the case being considered here. Indeed, because of the mathematical complexity, it seemed unlikely that any theory could be developed to include double-layer charging and still satisfy the criteria of simplicity set forth above. On the other hand, Olmstead and Nicholson (50) showed that the method of Berzins and Delahay gives accurate values of the quarter-wave potential even in the presence of extensive double-layer charging. Thus, the possibility presented itself that using the method of Berzins and Delahay, or some modification thereof, the simple theory could be used directly, thereby considerably extending the range of applicability of the new method. Based on this possibility, and the fact that a more detailed analysis of the influence of double-layer charging should be useful per se, it was decided to attempt the appropriate theoretical calculations. The last major section of this thesis presents this theory for a model which includes both kinetically controlled electron transfer and double-layer charging.

THEORY FOR THE CASE OF NEGLIGIBLE DOUBLE-LAYER CHARGING

Once again, the objective is to develop an expression for overpotential between the cathodic and anodic parts of a current reversal chronopotentiogram for a kinetically controlled redox reaction. Based on the conceptual idea of the proposed method, it is anticipated that the overpotential will be proportional to current density, and inversely proportional to the rate of the redox reaction.

The redox reaction can be symbolized as follows



where k_f and k_b are the heterogeneous rate constants for electron transfer, and hence are functions of potential. The potential dependence of k_f and k_b is given by the following well-known equations (38):

$$k_f = k_s \exp [(-\alpha nF/RT) (E-E^0)] \quad (2)$$

$$k_b = k_s \exp [(1-\alpha) nF/RT) (E-E^0)] \quad (3)$$

There k_s is the common value of k_f and k_b at the standard equilibrium potential (E^0), and is directly proportional to the standard exchange current density (38). α is the

transfer coefficient and other terms have their usual meaning.

The rate equation for Reaction I can be written in terms of the flux and surface concentration of O and R:

$$\text{FLUX} = k_f C_O(0,t) - k_b C_R(0,t) \quad (4)$$

where the first index on concentration represents distance from the electrode surface (zero in this case) and the second index represents time during electrolysis.

The problem now is to substitute in this rate law expressions for the temporal dependence of surface concentrations during the entire current reversal experiment, as well as expressions for potential dependence of k_f and k_b , and from the result obtain a (hopefully) simple expression for overpotential. Since the chronopotentiometry experiment is performed under conditions designed to make diffusion the only source of mass transport, the concentrations can be calculated by solving the appropriate Fick's law diffusion equations. These results already are available in the literature (1), and could provide the starting point for the present treatment. However, to make the discussion more lucid and cohesive, the entire derivation starting with the Fick's law boundary value problem will be presented.

Boundary Value Problem

To account for concentration polarization, linear diffusion is assumed to be the only source of mass transport.

The appropriate diffusion equations are

$$\frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial x^2} \quad (5)$$

for the oxidized form of the couple, O, and

$$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2} \quad (6)$$

for the reduced form, R. These partial differential equations are to be solved for the concentration of O and R as a function of distance from the electrode surface, x , and time during the electrolysis, t . To obtain explicit solutions the following initial and boundary conditions will be assumed.

Initially, the concentration of depolarizer at any point in solution is given by the bulk concentration value, which will be represented as C_O^* . It will be further assumed that substance R is generated in situ, and is therefore initially absent from the solution. Thus, stated mathematically, the initial conditions are

$$t=0; x \geq 0 \quad C_O = C_O^*; C_R = 0 \quad (7)$$

For the first boundary condition it will be assumed that conditions of so-called semi-infinite diffusion prevail. In other words, it will be assumed that the thickness of the diffusion layer developed during electrolysis is much less than the dimensions of the entire solution. It is easily shown that this condition is satisfied whenever the walls of

the electrolysis cell are greater than a few millimeters from the electrode surface (52). Stated mathematically, this boundary condition is

$$t \geq 0; x \rightarrow \infty \quad C_0 \rightarrow C_0^*; C_R \rightarrow 0 \quad (8)$$

The second boundary condition is a statement of mass balance for O and R at the electrode surface. The quantity of electroactive species diffusing to the electrode can be expressed in terms of the surface flux, defined by the following expression

$$\text{FLUX} = D \left[\frac{\partial C}{\partial x} \right]_{x=0} \quad (9)$$

Thus, the final boundary condition is simply

$$t \geq 0; x = 0 \quad D_0 \frac{\partial C_0}{\partial x} = -D_R \frac{\partial C_R}{\partial x} \quad (10)$$

Since it has been assumed that only substance O is initially present, the forward part of the chronopotentiogram consists of the reduction of O at a constant current density, $\underline{i}_F$. Arbitrarily, current reversal will be introduced when the forward transition time, τ_F , is reached. The current density after reversal will be labeled $\underline{i}_R$, and the resulting anodic transition time will be designated τ_R . By convention τ_R will be measured from the forward transition time, rather than from $\underline{t}$ equal zero.

The flux is related to current density by Fick's first law, which for the present case takes the following form

$$0 \leq t \leq \tau_F; \quad x=0$$

$$D_0 \frac{\partial C_0}{\partial x} = i_F / nF \quad (11)$$

$$\tau_F \leq t \leq \tau_R; \quad x=0$$

$$D_R \frac{\partial C_R}{\partial x} = - i_R / nF \quad (12)$$

or written in terms of the flux of O

$$\tau_F \leq t \leq \tau_R; \quad x=0$$

$$D_R \frac{\partial C_R}{\partial x} = - D_0 \frac{\partial C_0}{\partial x} = R_i i_F / nF \quad (13)$$

where

$$R_i = i_R / i_F \quad (14)$$

The above boundary value problem must now be solved for the surface concentration of O and R as a function of time. The only potential difficulties might come from the fact that the last boundary condition (Equations 11 and 12) is discontinuous, but as shown in the next section this problem is easily handled with the Laplace transform operator.

Solution of the Boundary Value Problem

The discontinuous boundary condition is easily handled by first transforming Equations 5 and 6 into integral form, and then incorporating the boundary condition. Laplace transformation of Equations 5 and 6 leads directly to the following expressions (52):

$$c_0(t) = c_0^* - \frac{1}{\sqrt{\pi D_0}} \int_0^t \frac{f_0(x) dx}{\sqrt{t-x}} \quad (15)$$

$$c_R(t) = \frac{1}{\sqrt{\pi D_R}} \int_0^t \frac{f_0(x) dx}{\sqrt{t-x}} \quad (16)$$

where the symbol $f_0(t)$ is used to represent the surface flux of substance 0. Prior to current reversal the expression for flux is given by Equation 11, and after current reversal by Equation 13. Thus, substituting Equations 11 and 13 in Equations 15 and 16, and performing the indicated integrations leads to the following expressions for surface concentration

$$0 \leq t \leq \tau_F$$

$$c_0(t) = c_0^* - \frac{2i_F t^{\frac{1}{2}}}{nF\sqrt{\pi D_0}} \quad (17)$$

$$c_R(t) = \frac{2i_F \gamma t^{\frac{1}{2}}}{nF\sqrt{\pi D_0}} \quad (18)$$

$$\tau_F \leq t \leq \tau_R$$

$$c_0(t) = c_0^* - \frac{2i_F t^{\frac{1}{2}}}{nF\sqrt{\pi D_0}} + \frac{2i_F(1-R_i)(t-\tau_F)^{\frac{1}{2}}}{nF\sqrt{\pi D_0}} \quad (19)$$

$$c_R(t) = \frac{2i_F \gamma t^{\frac{1}{2}}}{nF\sqrt{\pi D_0}} - \frac{2i_F \gamma (1-R_i)(t-\tau_F)^{\frac{1}{2}}}{nF\sqrt{\pi D_0}} \quad (20)$$

where

$$\gamma = \sqrt{D_0/D_R} \quad (21)$$

By introducing the above expressions into the rate equation (Equation 4) together with expressions for k_f and k_b (Equations 2 and 3), the following equations for the potential-time curves are obtained

$$0 \leq t \leq \tau_F$$

$$\rho \exp[\alpha g(E)] = 1 - y^{\frac{1}{2}} - y^{\frac{1}{2}} \exp[g(E)] \quad (22)$$

$$\tau_F \leq t \leq \tau_R$$

$$\begin{aligned} \rho R_i \exp[\alpha g(E)] = 1 + (1-R_i)(y-1)^{\frac{1}{2}} - y^{\frac{1}{2}} + \\ [(1-R_i)(y-1)^{\frac{1}{2}} - y^{\frac{1}{2}}] \exp[g(E)] \end{aligned} \quad (23)$$

Terms in Equations 22 and 23 not previously defined have the following definitions

$$\rho = i_F(D_R)^{\alpha/2} / nFk_s C_0^*(D_0)^{\alpha/2} \quad (24)$$

$$y = t/\tau_F \quad (25)$$

$$g(E) = (nF/RT)(E-E_{\frac{1}{2}}) \quad (26)$$

where $E_{\frac{1}{2}}$ is the conventional polarographic half-wave potential.

Calculation of Potential-Time Curves

Equations 22 and 23 describe the potential-time behavior for the entire chronopotentiometric experiment. Unfortunately, because these equations are nonlinear, in general, they cannot

be solved explicitly for $g(\underline{E})$, and therefore to calculate $g(\underline{E})$ as a function of $\underline{y}$ (dimensionless time, see Equation 25) would require numerical solution of Equations 22 and 23. Of course, if the only objective is to construct theoretical potential-time curves, then it is simpler to consider $\underline{y}$ as the dependent variable, because Equations 22 and 23 can be solved explicitly for $\underline{y}$. Thus, prior to current reversal, one obtains from Equation 22 the following expression for $\underline{y}$:

$$0 \leq t \leq \tau_F$$

$$\underline{y}^{\frac{1}{2}} = 1 - \rho \exp[\alpha g(E)] / 1 + \exp[g(E)] \quad (27)$$

The explicit solution for $\underline{y}$ in Equation 23 is less obvious, but can be obtained as follows. After expanding the last term on the right hand side of Equation 23, and collecting similar terms and factoring, the following expression is obtained

$$(1-R_i)(\underline{y}-1)^{\frac{1}{2}} - \underline{y}^{\frac{1}{2}} = K(E) \quad (28)$$

where

$$K(E) = \frac{\rho R_i \exp[\alpha g(E)] - 1}{1 + \exp[g(E)]} \quad (29)$$

Equation 28 is of the form of a quadratic in the $\underline{y}^{\frac{1}{2}}$, as can be seen by squaring both sides and transposing all terms to one side of the equality. The result is

$$\underline{y}[(1-R_i)^2 - 1] - 2K(E)\underline{y}^{\frac{1}{2}} - [(1-R_i)^2 + K^2(E)] = 0 \quad (30)$$

An expression for $y^{\frac{1}{2}}$ is obtained directly by applying the quadratic equation to Equation 30. Only the positive root is retained, because the negative root does not give values of y which correspond to those calculated from Equation 23 for the same value of $g(E)$. Thus, after current reversal the expression for time as a function of potential is

$$\tau_F \leq t \leq \tau_R$$

$$y^{\frac{1}{2}} = \frac{K(E) + \{K^2(E) + [(1-R_i)^2 - 1][(1-R_i)^2 + K^2(E)]\}^{\frac{1}{2}}}{(1-R_i)^2 - 1} \quad (31)$$

Equations 27 and 31 can be used to construct theoretical potential-time curves without performing extensive numerical calculations. Potential-time curves calculated in this manner for three values of ρ are shown in Figure 4. These potential-time curves clearly illustrate the anticipated effect of current density and kinetically controlled electron transfer. Thus, from Figure 4 it is apparent that increases in current density (increases in ρ) do lead to the introduction of an overpotential between the cathodic and anodic reactions. Curves like those of Figure 4 also depend on two other parameters, α and R_i , and therefore the influence of these parameters on potential-time curves also must be considered.

Effect of R_i . R_i is the ratio of reverse to forward current densities and as such determines the relative size of transition times. Most often R_i is -1--i.e., current

Figure 4. Theoretical chronopotentiogram showing effect of kinetic parameter, ρ , when $\alpha = 0.5$ and $R_1 = -1.0$.

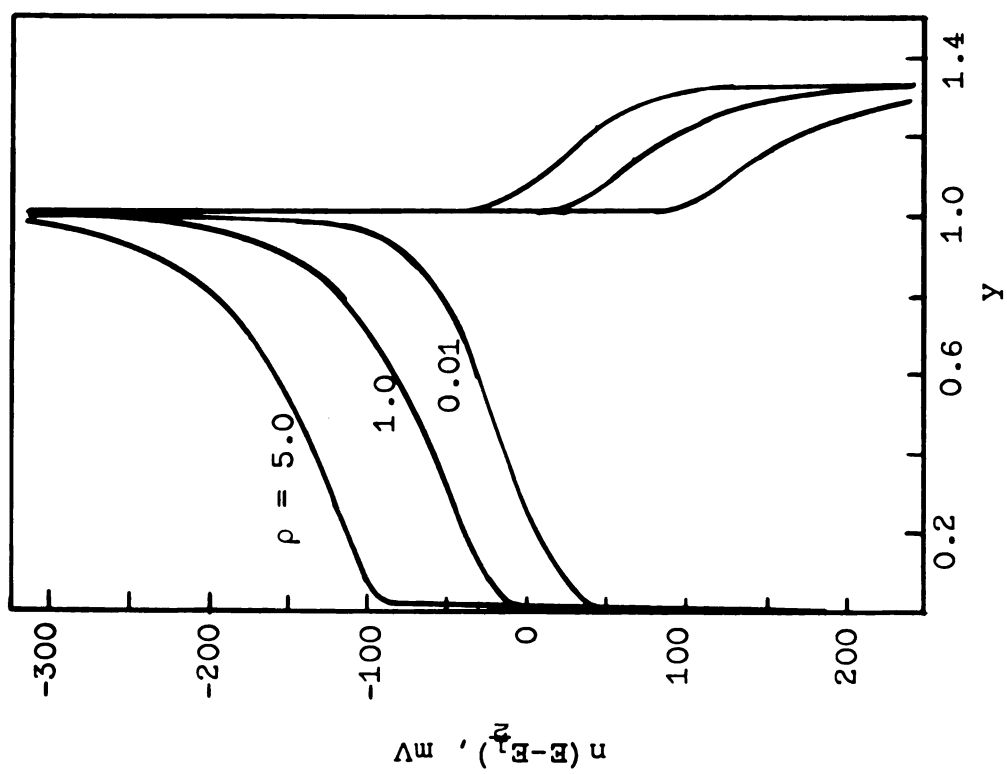


Figure 4

densities of equal absolute magnitude are used before and after current reversal--and as mentioned earlier the ratio τ_F/τ_R in this case is 3. If values of $\underline{R}_i$ less than one are employed, then the ratio τ_F/τ_R can be made close to unity, which has obvious advantages in terms of the precision of experimental measurements. This fact, and the effect of $\underline{R}_i$ in general, are illustrated by the curves of Figure 5.

To select optimal values of $\underline{R}_i$ for experimental purposes, it would be useful to have a relationship between $\underline{R}_i$, τ_F , and τ_R . Such a relationship can be obtained by evaluating Equation 20 at $\underline{t} = \tau_R$, and recognizing that at this time the surface concentration of R will be zero. The result, after rearranging to solve for τ_F/τ_R , is simply

$$\tau_F/\tau_R = (1-\underline{R}_i)^2 - 1 \quad (32)$$

Thus, for example, to have exactly equal transition times, one would use a value of $\underline{R}_i$ equal - 0.414.

Effects of ρ and α . Both ρ and α affect the potential-time curves of Figure 4, and in general these effects cannot be separated. However, some limiting cases exist where the relationship between $g(\underline{E})$, $\underline{R}_i$, ρ , and α can be stated explicitly. For example, as ρ approaches zero (small $\underline{i}_F$ and/or large $\underline{k}_g$), the redox reaction always is in equilibrium, and Equations 27 and 31 reduce to the following well-known relationships which are independent of kinetic parameters (17)

Figure 5. Effect of ratio of current densities, R_i , on theoretical chronopotentiograms when $\rho = 0.3$ and $\alpha \approx 0.5$. Curve A, $R_i = -1.0$; Curve B, $R_i = -0.414$.

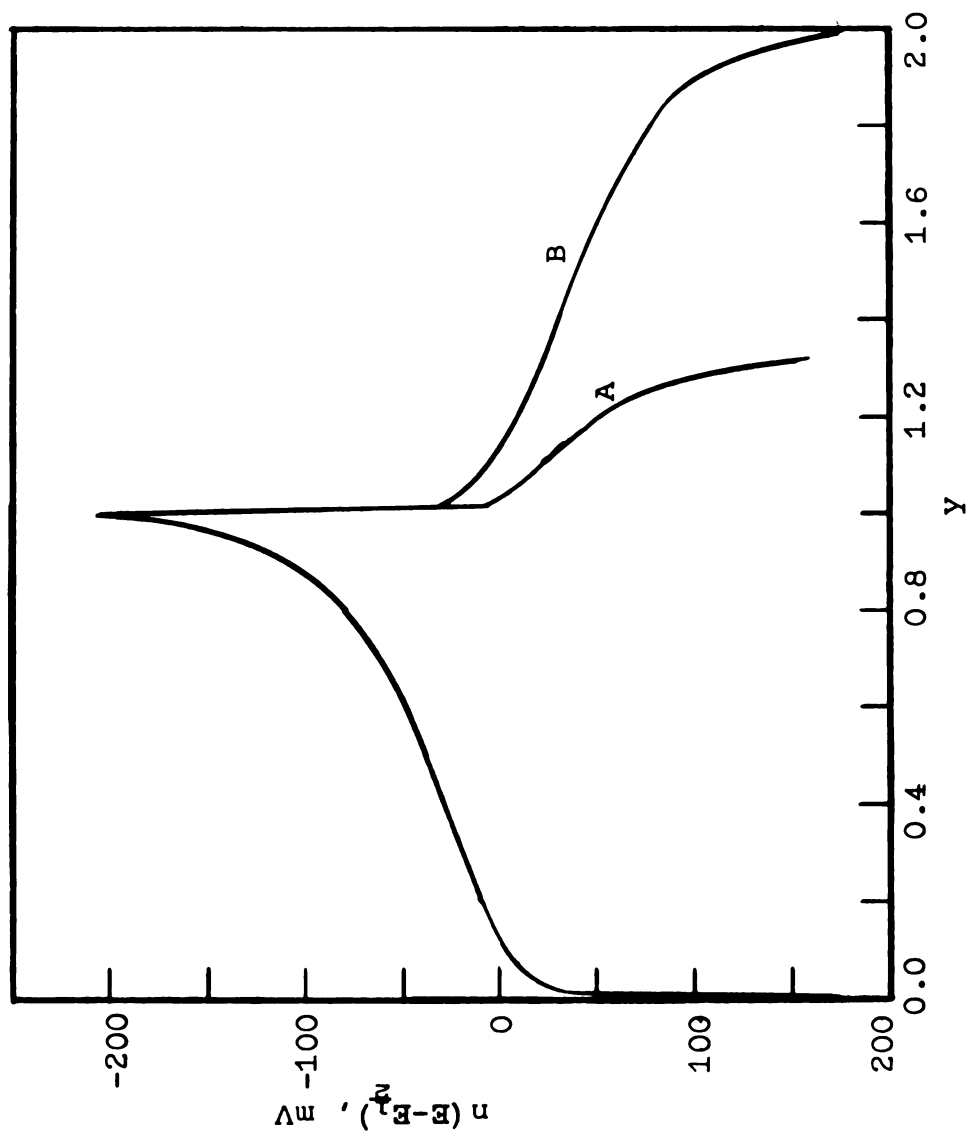


Figure 5

$$0 \leq t \leq \tau_F$$

$$g(E) = \ln [(1-y^{\frac{1}{2}})/y^{\frac{1}{2}}] \quad (33)$$

$$\tau_F \leq t \leq \tau_R$$

$$g(E) = \ln \left[\frac{1 + (1-R_i)(y-1)^{\frac{1}{2}} - y^{\frac{1}{2}}}{y^{\frac{1}{2}} - (1-R_i)(y-1)^{\frac{1}{2}}} \right] \quad (34)$$

It was found that potential-time curves are described by Equations 33 and 34 within 2-3mV whenever ρ is less than 0.01.

A second limiting case arises when ρ is sufficiently large (large i_F and/or small k_s) that the processes of oxidation and reduction can be treated separately as the totally irreversible case (large overpotentials) (15). This is equivalent to neglecting the back reaction [*i.e.*, the term $k_D C_R(0,t)$] in the original rate expression. Results can be derived from that formalism, or more directly by taking the limit of Equations 27 and 31 as ρ becomes large. With the latter approach it also is necessary to recognize that terms like $\exp[g(E)]$ approach zero as ρ increases, because of the large overpotential. With either approach the final results take the following form (18)

$$0 \leq t \leq \tau_F$$

$$\alpha g(E) = \ln [(1-y^{\frac{1}{2}})/\rho] \quad (35)$$

$$\tau_F \leq t \leq \tau_R$$

$$-(1-\alpha)g(E) = \ln \left[\frac{(1-R_i)(y-1)^{\frac{1}{2}} - y^{\frac{1}{2}}}{R_i \rho} \right] \quad (36)$$

It was found by calculation that potential-time curves are described within 2-3mV by Equations 35 and 36 whenever ρ is greater than 2.5.

Generally α affects potential-time curves in the expected manner. Thus, for $\rho < 0.01$, curves are independent of α (cf. Equations 33 and 34). For $\rho > 2.5$, the effect of α is given explicitly by Equations 35 and 36. For values of ρ between these limits, α affects both the symmetry of potential-time curves, and their position on the potential axis. These effects are illustrated in Figure 6 where theoretical chronopotentiograms are plotted for three values of α .

Overpotential, ΔE , as a Measure of k_s . With current reversal chronopotentiometry the potentials at which oxidation and reduction occur are observed directly, and it is clear that the effect is the same as anticipated in the Introduction. Of course, to obtain a quantitative correlation between overpotential and the standard rate constant it is necessary to select a fixed reference time during the forward and reverse parts of the potential-time curves from which to calculate overpotential. An obvious choice for this reference point is the time at which the potential is equal to the reversible half-wave potential in the zero overpotential case--i.e., the so-called quarter-wave potential defined earlier. To do this it is necessary to determine precisely the times relative to the respective transition times (τ_F and τ_R) where the potential is equal to the half-wave

Figure 6. Theoretical chronopotentiograms showing effect of transfer coefficient, α , when $\rho = 1.0$ and $R_i = -1.0$.

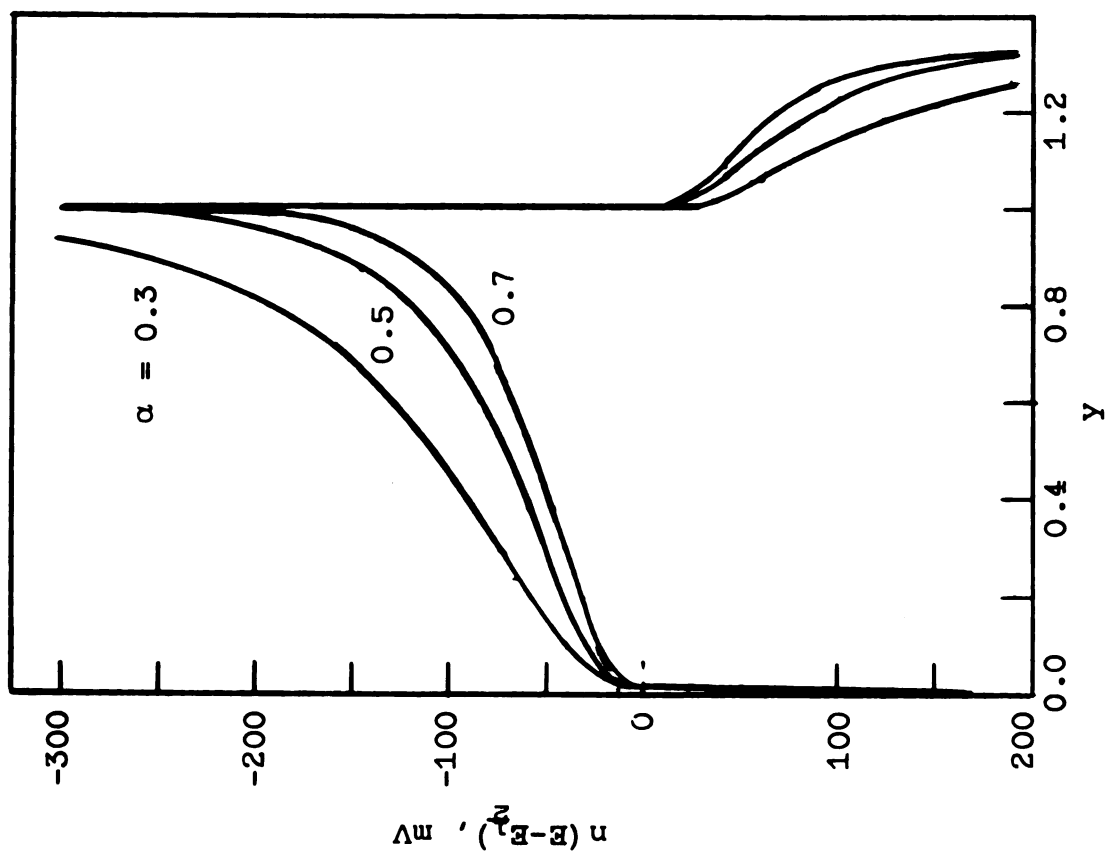


Figure 6

potential. Once this is known overpotential can be calculated as the difference of potential at these two times. Although the choice of reference is essentially arbitrary, this E_2 reference has the advantage that overpotential will be zero in the reversible case, so results will not be complicated by concentration overpotential.

The times at which the potential is equal to the reversible half-wave potential can be obtained from Equations 33 and 34 for the forward and reverse parts of the potential-time curve respectively. To evaluate these times it is necessary to recall that $g(E)$ is zero at the half-wave potential (see Equation 26), which is equivalent to the argument of the logarithmic terms being unity. Thus, by setting the argument of the logarithm in Equation 33 equal to unity and solving for y , it is found that the half-wave potential occurs when $y = 0.25$ (hence the name quarter-wave potential). The corresponding time for the reverse part of the curve is obtained as follows. After setting the argument of the logarithm term in Equation 34 equal to unity and collecting like terms the following equation is obtained

$$1 + 2K(y-1)^{\frac{1}{2}} - 2y^{\frac{1}{2}} = 0 \quad (37)$$

where

$$K = (1-R_i) \quad (38)$$

Equation 37 can be written in the form of a quadratic by transposing the $(y-1)^{\frac{1}{2}}$ term to the right hand side of the

equality and squaring both sides of the expression to obtain

$$4(K^2-1)y + 4y^{\frac{1}{2}} - (4K^2 + 1) = 0 \quad (39)$$

After solving for y by application of the quadratic equation, and retaining only the positive root, the following expression for the value of y at which $\underline{E}_2$ occurs is obtained

$$y_{g(E)=0} = \left[\frac{-1 + \{1 + [(1-R_i)^2 - 1][4(1-R_i)^2 + 1]\}^{\frac{1}{2}}}{2[(1-R_i)^2 - 1]} \right] \quad (40)$$

Thus, for example when $\underline{R}_i$ equals -1 , from Equation 40 $\underline{E}_2$ occurs at $y = 1.0716$. Since τ_R is to be measured from τ_F (where y equals 1) this corresponds to y equal 0.0716 relative to τ_F . Or, since with $\underline{R}_i = -1$, τ_F/τ_R is 3, the time on the reverse part of the potential-time curve corresponding to $\underline{E}_2$ is $0.215 \tau_R$. Interestingly, this time is not precisely a "quarter-wave" potential for the reverse part of the chronopotentiogram. Potentials corresponding to these two times (0.25 and $y_{g(E)=0}$) hereafter are referred to as $\underline{E}_F$ and $\underline{E}_R$ respectively. $\Delta \underline{E}$ will then be the difference between $\underline{E}_R$ and $\underline{E}_F$ ($=\underline{E}_R - \underline{E}_F$).

The effect of α on $\Delta \underline{E}$ is shown in Figure 7. Because for the mechanism being considered here α is typically about 0.5, and rarely outside the range 0.3-0.7, these data of Figure 7 show that for reasonable values of α , the parameter $\Delta \underline{E}$ tends to be independent of α , the dependence becoming less as ρ decreases. The explanation of this fact is that as α

Figure 7. Dependence of ΔE on charge transfer coefficient, α .

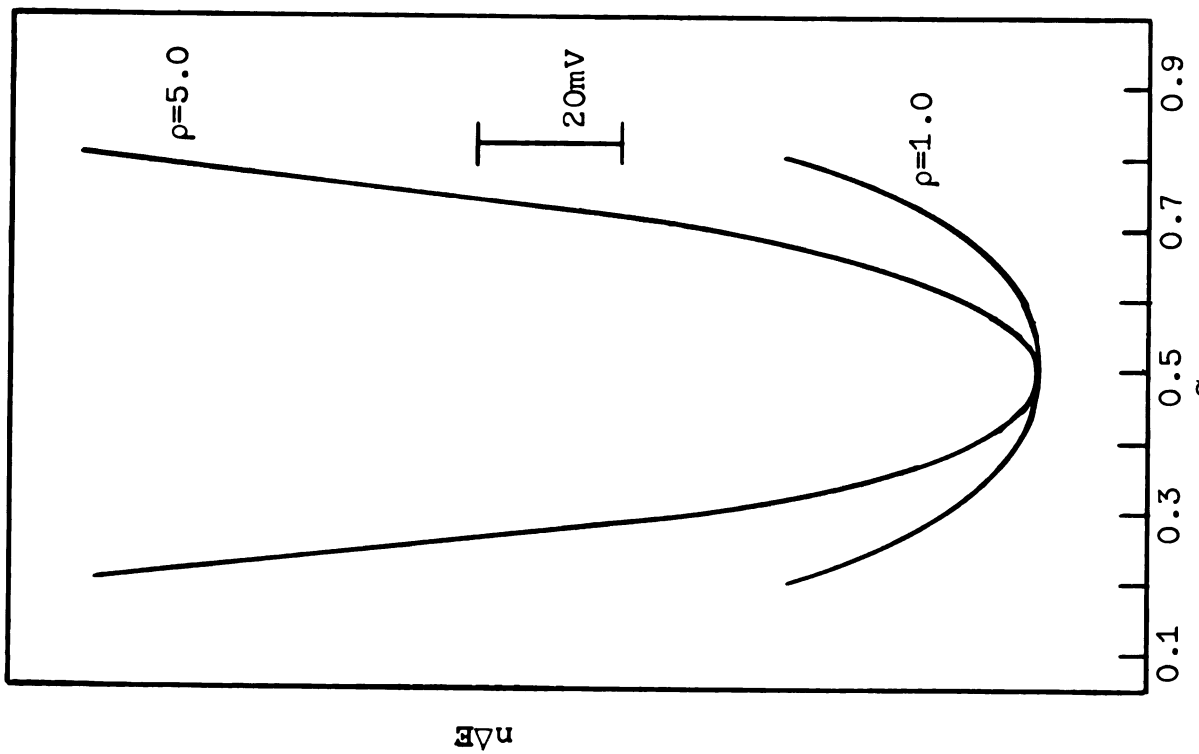


Figure 7

varies both $\underline{E}_F$ and $\underline{E}_R$ shift in the same direction, and these shifts tend to cancel in terms of $\Delta\underline{E}$. Nevertheless, for extreme values of α near 0 or 1, $\Delta\underline{E}$ is markedly dependent on α . The reason for this fact is that, for example, as α approaches 1, $\underline{E}_F$ tends to be independent of α (see Equation 35), whereas $\underline{E}_R$ tends to vary exponentially with α (see Equation 36).

The fact that for small values of ρ and reasonable values of α , $\Delta\underline{E}$ is independent of α is important for two reasons. First, when $\Delta\underline{E}$ is independent of α , $\Delta\underline{E}$ is determined uniquely by ρ , and therefore $\Delta\underline{E}$ is a simple measure of ρ , and hence $\underline{k}_s$ (see Equation 24). Second, for the special case of α equal 0.5, Equations 27 and 31 take the form of a quadratic equation and both can be solved explicitly for $g(\underline{E})$. This means that an equation can be derived for $\Delta\underline{E}$ which always is valid when α equals 0.5, and which, depending on ρ , may be exact for any α between 0.3 and 0.7.

Thus, by restricting the discussion of the case of α equal 0.5, it should be possible to derive an explicit expression for overpotential. Introducing α of 0.5 into Equations 27 and 31 leads to the following equations

$$0 \leq t \leq \tau_F$$

$$y^{\frac{1}{2}} x^2 + \rho x + y^{\frac{1}{2}} - 1 = 0 \quad (41)$$

$$\tau_F \leq t \leq \tau_R$$

$$[(1-R_i)(y-1)^{\frac{1}{2}} - y^{\frac{1}{2}}]x^2 - \rho R_i x + (1-R_i)(y-1)^{\frac{1}{2}} - y^{\frac{1}{2}} + 1 = 0 \quad (42)$$

where

$$x = \exp [0.5 g(E)] \quad (43)$$

Equations 41 and 42 can be solved directly for $g(E)$ by use of the quadratic equation. The positive roots are retained in both instances, since negative roots lead to undefined values of $g(E)$. Thus, the pertinent solutions of Equations 41 and 42 are

$$0 \leq t \leq \tau_F \quad g(E) = 2 \ln \left[\frac{-\rho + \{\rho^2 + 4y^{\frac{1}{2}}(1-y^{\frac{1}{2}})\}^{\frac{1}{2}}}{2y^{\frac{1}{2}}} \right] \quad (44)$$

$$\tau_F \leq t \leq \tau_R \quad g(E) = 2 \ln \left[\frac{-\rho R_i + \{\rho^2 R_i^2 - 4[y^{\frac{1}{2}} - (1-R_i)(y-1)^{\frac{1}{2}}][y^{\frac{1}{2}} - 1 - \frac{(1-R_i)(y-1)^{\frac{1}{2}}]}{2[y^{\frac{1}{2}} - (1-R_i)(y-1)^{\frac{1}{2}}]}\}^{\frac{1}{2}}}{2[y^{\frac{1}{2}} - (1-R_i)(y-1)^{\frac{1}{2}}]} \right] \quad (45)$$

To calculate the overpotential, ΔE , values of E_F and E_R are first determined by evaluating Equation 44 at $y = 0.25$, and Equation 45 at $y_{g(E)=0}$ given by Equation 40. The results when combined with the definition of $g(E)$ (cf. Equation 26) are

$$0 \leq t \leq \tau_F \quad E_F = (2RT/nF) \ln [-\rho + (\rho^2 + 1)^{\frac{1}{2}}] \quad (46)$$

$$\tau_F \leq t \leq \tau_R \quad E_R = (2RT/nF) \ln [-\rho R_i + (\rho^2 R_i^2 + 1)^{\frac{1}{2}}] \quad (47)$$

Finally, the expression for overpotential is obtained as the difference of Equation 46 and 47

$$\Delta E = (2RT/nF) \ln \left(\frac{-\rho R_i + (\rho^2 R_i^2 + 1)^{\frac{1}{2}}}{-\rho + (\rho^2 + 1)^{\frac{1}{2}}} \right) \quad (48)$$

Equation 48 is the final result of the derivation and represents the desired relationship between overpotential, current density, and the standard rate constant for electron transfer (recall definition of ρ , Equation 24). In view of some of the preceding relationships, the final equation is surprisingly simple. Ideally, of course, it would be desirable to consider ρ as the independent variable and solve Equation 48 directly for ρ as a function of ΔE . In that case experimentally determined values of ΔE could quickly be related to corresponding values of ρ from which the value of k_s could be directly calculated. Although Equation 48 can be solved explicitly for ρ , the resulting expression is cumbersome, and therefore an alternate approach actually appears to be more useful. This alternate approach consists of generating a working curve by plotting Equation 48 as ΔE vs. ρ . From this working curve experimental values of ΔE can quickly be converted to the corresponding ρ . If concentration, current density, etc., are known, then k_s can easily be calculated from Equation 24. Figure 8 illustrates these working curves for two values of R_i .

Figure 8. Working curves showing variation of ΔE with ρ for two values of B_i .

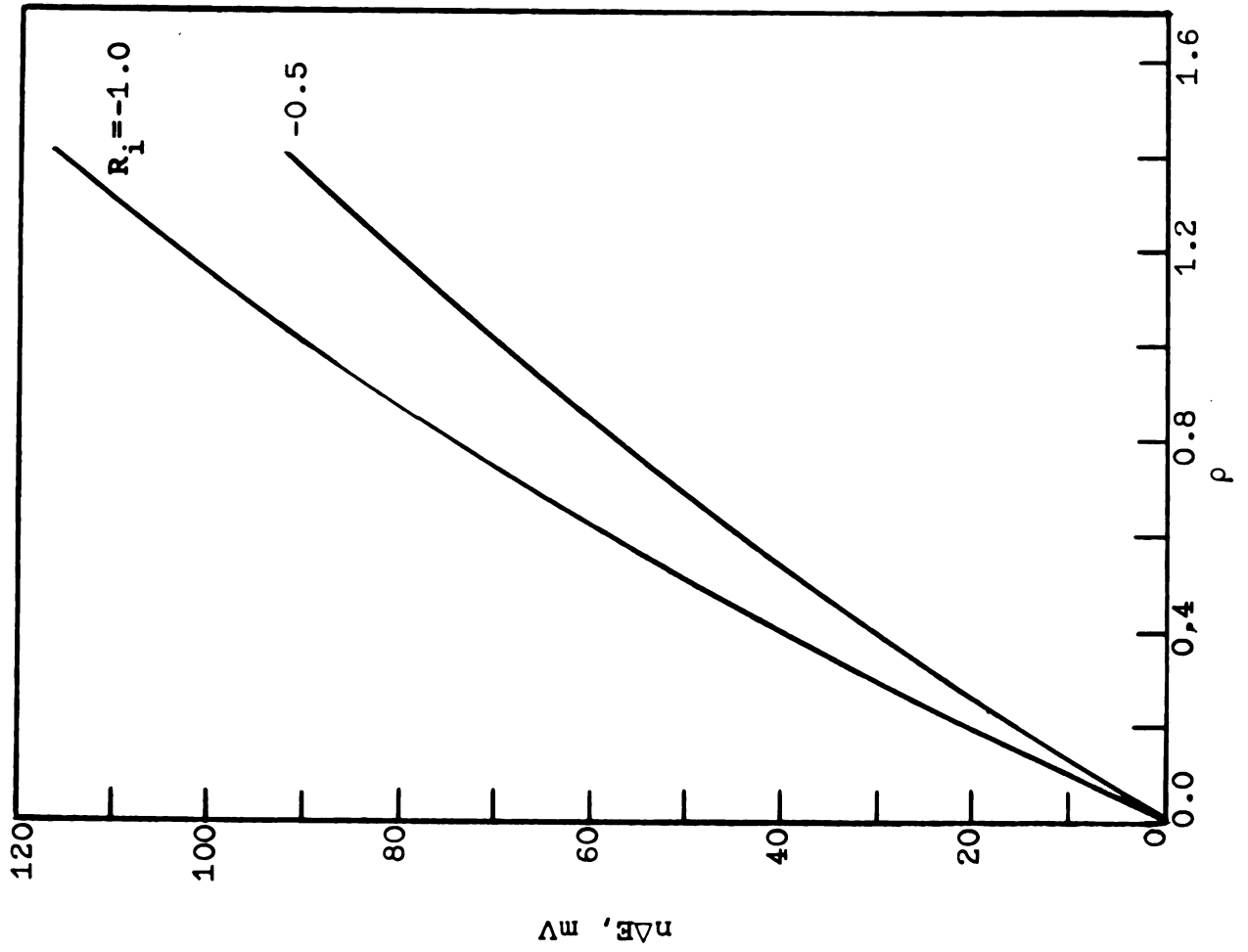


Figure 8

The only assumption incorporated in the derivation of the equation for ΔE is that α is 0.5. For Equation 48 to be generally useful, it is important to attempt to evaluate the errors that will result if Equation 48 is applied to a system where α is different from 0.5. By using the exact expressions it was found that for ΔE of about $95/\underline{n}$ mV ($\rho \approx 1.0$), a value of ρ calculated on the basis of Equation 48 always is too small by about 10% if α is 0.3 or 0.7. For ΔE about $50/\underline{n}$ mV ($\rho \approx 0.5$) the error is reduced to about 6%. Because in terms of rate constants an error of 10% is not large, and often within experimental error, it is concluded that Equation 48 can be applied whenever ΔE is less than $95/\underline{n}$ mV. Thus, to apply Equation 48 experimentally, conditions (current density, etc.) are selected which give ΔE less than $95/\underline{n}$ mV, and then from this experimental ΔE , and Figure 8, ρ is determined. The method due to Berzins and Delahay can be applied to the forward and reverse parts of the potential-time curve to determine the experimental value of ΔE . If current density and concentration are known, $\underline{k}_s$ can be calculated from Equation 24. Actually, to apply Equation 24 rigorously, $(\underline{D}_R/\underline{D}_O)^{\alpha/2}$ must be known, implying that α must be known. However, except for the unusual case of very large differences between $\underline{D}_O$ and $\underline{D}_R$, the quantity $(\underline{D}_R/\underline{D}_O)^{\alpha/2}$ is very nearly unity, regardless of α .

Limits of Applicability of Equation 48. It also is useful to estimate the range of rate constants that can be

measured by the above approach. The smallest values of $\underline{k}_s$ that are measurable will be determined by the onset of convection and the fact that ρ must be less than 1.0 for $\underline{\Delta E}$ to be independent of α . The largest measurable value of $\underline{k}_s$ presumably will be determined by interferences of double-layer charging at high current densities and the fact that ρ must be greater than 0.1 to obtain an experimentally measurable $\underline{\Delta E}$. The quantitative extent of these limitations is discussed next.

The smallest value of $\underline{k}_s$ that can be determined is set by the restriction $\rho \leq 1.0$, that is (see Equation 24)

$$1.0 \geq i_F(D_R)^{\alpha/2} / nFk_s C_0^*(D_0)^{\alpha/2} \quad (49)$$

Combining this inequality with the Sand equation (Equation 1) gives

$$k_s \geq \sqrt{\pi D_0}(D_R)^{\alpha/2} / 2\sqrt{\tau_F} (D_0)^{\alpha/2} \quad (50)$$

Assuming the ratio $(D_R/D_0)^{\alpha/2}$ is unity and τ_F cannot be greater than 50 seconds to avoid convection, and assuming a value of 1×10^{-5} cm²/sec for D_0 , the smallest $\underline{k}_s$ is approximately 4×10^{-4} cm/sec.

The maximum value of $\underline{k}_s$ that can be determined is set by the restriction that ρ must be greater than about 0.1 ($\underline{\Delta E} \geq 10$ mV), and the fact that to fit the theoretical model it is necessary for charging current to be less than about 1% of the total constant current. The latter restriction sets the

minimum transition time that can be measured and still have the charging current be less than 1% of the faradaic current. The condition $\rho \geq 0.1$ is equivalent to

$$k_s \leq \sqrt{\pi D_0} / 0.2 \sqrt{\tau_F} \quad (51)$$

where $(D_R/D_0)^{a/2}$ has been set equal to one. Based on Gierst's (19) discussion of double-layer charging, one can estimate the minimum value of τ_F that can be measured experimentally and still satisfy the condition that charging current be less than 1% of the faradaic current. This can be accomplished by calculating the number of coulombs involved in the charging process compared to the number of coulombs consumed by the faradaic process. The number of coulombs used for the charging process can be estimated from the following definition of the differential double-layer capacitance

$$C_1 = -dQ_c/dE \quad (52)$$

where E is the electrode potential and Q_c is the surface charge density (coulombs per unit area) of electricity on the electrode. Rewriting Equation 52 in terms of differences and rearranging yields

$$Q_c = C_1 \Delta E \quad (53)$$

The quantity of electricity involved in the electrochemical reaction for a current density i_0 and over the time τ is simply

$$Q_f = i_0 \tau \quad (54)$$

Of course, in general Equation 54 is only approximate because the faradaic current is less than the constant current by the amount used for the charging process. In the present case this error will be negligible, since it is being assumed that double-layer charging is only 1% of the faradaic reaction. The extent of double-layer charging can now be estimated from the ratio Q_c/Q_f

$$Q_c/Q_f = C_1 \Delta E / i_0 \tau \quad (55)$$

If τ is taken as the transition time, then one can replace τ in Equation 55 by the Sand equation and obtain the following relationship

$$Q_c/Q_f = 4i_0 C_1 \Delta E / \pi D_0 (nFC_0^*)^2 \quad (56)$$

From Equation 56 and the restriction that charging current interferences are to be no more than 1% ($Q_c/Q_f \leq 0.01$) the following inequality must be satisfied

$$n^2 C_0^{*2} \geq 1.3 \times 10^{-8} i_0 \quad (57)$$

The following representative values given by Delahay (19) can be used to estimate the numerical constant in Equation 57: $C_1 = 20 \text{ uf/cm}^2$, $\Delta E = 0.5 \text{ V}$, and $D_0 = 1 \times 10^{-5} \text{ cm}^2/\text{sec}$. The above inequality substituted in the Sand equation yields

$$\sqrt{\tau} \geq 1.3 \times 10^{-8} \sqrt{\pi D_0} / 2nC_0^* \quad (58)$$

For typical values of $\underline{n}$ equal 2 and $\underline{C}_0^*$ equal 1×10^{-6} mole/ cm^3 , it follows from Equation 58 that transition times of the order of 3 seconds can be measured without interference from double-layer charging. By combining this fact with Equation 58, it is estimated that values of $\underline{k}_s \leq 2 \times 10^{-2}$ cm/sec can be determined by direct application of the equation for ΔE .

The range calculated above is based on the assumption that essentially no double-layer charging can be tolerated in the application of the expression for ΔE . As pointed out in the Introduction, however, it has been shown that the method of Berzins and Delahay for locating quarter-wave potentials is accurate even when 50% of the total charge is used for double-layer charging. Hence, it seemed that the estimated range may be unrealistically small, and therefore it appeared profitable to determine unambiguously the influence of double-layer charging with kinetically controlled electron transfer.

THEORY FOR THE CASE OF SIGNIFICANT DOUBLE-LAYER CHARGING

The objective of this section is to attempt to determine quantitatively the effects of double-layer charging on kinetically controlled electron transfer. Specifically, a relationship will be developed between observed overpotential for the cathodic and anodic parts of a current reversal chronopotentiogram and the rate of electron transfer. As pointed out in the Introduction previous studies have shown that the method of Berzins and Delahay for measuring quarter-wave potentials gives accurate values even in cases of appreciable double-layer charging, and therefore this technique will be applied to theoretical chronopotentiograms. By determining ΔE with this method for a range of electron transfer rate constants, working curves similar to those in Figure 8, but applicable in the presence of double-layer charging, will be obtained. The following model was assumed as a basis for these calculations.

Model

The basis of the present treatment is a simple model, which consists of the following main points: (1) mass transport occurs by semi-infinite linear diffusion; (2) charging

of the electrical double-layer is as though the electrode were ideally polarized (29); (3) the differential double-layer capacitance is independent of potential; and (4) the potential dependence of the electron transfer rate constants is given by Equations 2 and 3.

Each point in this model can be restated mathematically in the form of the boundary value problem described next.

Boundary Value Problem

Based on Point 1 of the model the surface concentrations of O and R as a function of time can be obtained by solving the following equations

$$\frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial x^2} \quad (59)$$

$$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2} \quad (60)$$

The following initial and boundary conditions will be assumed in order to solve the above differential equations explicitly for concentration

$$t = 0; x \geq 0 \quad C_O = C_O^*; C_R = C_R^* \quad (61)$$

$$t \geq 0; x \rightarrow \infty \quad C_O \rightarrow C_O^*; C_R \rightarrow C_R^* \quad (62)$$

$$t \geq 0; x = 0 \quad D_O \frac{\partial C_O}{\partial x} = - D_R \frac{\partial C_R}{\partial x} \quad (63)$$

These conditions are similar to those presented and discussed

previously (cf. the discussion of Equations 7, 8, and 10). The only difference between the two sets of conditions is that to preserve generality the analytical concentration of R, $\bar{C}_R^*$, is assumed to be finite in the present case (see Equations 61 and 62).

As before, it will be assumed that the forward part of the chronopotentiogram consists of the reduction of O at a constant current density, $\underline{i}_{T_F}$, and that current reversal is introduced when the forward transition time, τ_F , is reached. The current density after reversal will be labeled $\underline{i}_{T_R}$, and the resulting anodic transition time will be designated τ_R . Again, by convention, τ_R will be measured from the forward transition time.

The major difference between the calculations presented here and those of the previous section is that previously it was assumed that the constant current was consumed entirely by the faradaic reaction, whereas in the present case the assumption will be made that the total current is partitioned between the faradaic and double-layer charging processes. Thus, rather than being a constant, the faradaic current density is actually some (unknown) function of time. The total current density, $\underline{i}_T(t)$, can be written as the algebraic sum of the faradaic, $\underline{i}_f(t)$, and charging current, $\underline{i}_c(t)$, densities (Point 2 of model)

$$\underline{i}_T(t) = \underline{i}_f(t) + \underline{i}_c(t) \quad (64)$$

where $i_T(t)$ is written as time dependent to account for current reversal.

The double-layer current in Equation 64 is given by

$$i_c(t) = - C_1 \frac{dE(t)}{dt} \quad (65)$$

where C_1 is the potential-independent differential double-layer capacitance referred to in Point 3. The negative sign is included so cathodic potential excursions correspond to positive current densities according to the usual sign convention. Thus, for the case of current reversal at the forward transition time, $i_T(t)$ is given by the following expression

$$i_T(t) = \begin{cases} i_{T_F} = i_f(t) + i_c(t) & 0 \leq t \leq \tau_F \\ i_{T_R} = R_i i_{T_F} = i_f(t) + i_c(t) & \tau_F \leq t \leq \tau_R \end{cases} \quad (66)$$

where

$$R_i = i_{T_R} / i_{T_F} \quad (67)$$

The flux is related to current density by Fick's first law which for the present case takes the following form

$$0 \leq t \leq \tau_F; \quad x=0$$

$$D_0 \frac{\partial C_0}{\partial x} = i_f(t) / nF = (i_{T_F} - i_c(t)) / nF \quad (68)$$

$$\tau_F \leq t \leq \tau_R; \quad x=0$$

$$D_R \frac{\partial C_R}{\partial x} = i_f(t) / nF = (i_{T_R} - i_c(t)) / nF = (R_i i_{T_F} - i_c(t)) / nF \quad (69)$$

or written in terms of the flux of O

$$\tau_F \leq t \leq \tau_R; \quad x=0$$

$$-D_0 \frac{\partial C_0}{\partial x} = (R_i i_{T_F} - i_c(t))/nF \quad (70)$$

The objective, now, is to solve this boundary value problem for the time dependence of surface concentrations of O and R, and then to combine these surface concentrations with the expressions for the potential dependence of k_f and k_b (Point 4 of the model), and the rate law expression (Equation 4). The results will define, within the framework of the model, the effects of double-layer charging on kinetically controlled electron transfer.

Unfortunately, this boundary value problem cannot be solved analytically because of the nonlinearity associated with Equations 2, 3, 4, 68, and 69. The problem can, of course, be solved numerically. Numerical calculations are simplified by first transforming the problem to an integral equation, which can be solved without loss of generality by proper dimensional analysis. These two topics are discussed next.

Integral Equation Form of Boundary Value Problem

An approach that has proved very successful in solving nonlinear boundary value problems is transformation to an integral equation (22). This approach has two major advantages. First, the problem usually can be reduced to a

single equation involving a single unknown, rather than a set of partial differential equations and boundary conditions that must be solved simultaneously. And second, the numerical solution of integral equations is considerably more straightforward and accurate than the numerical solution of partial differential equations.

In the present case the problem can be transformed to two integral equations, one applicable prior to current reversal and the other applicable after current reversal. Of course, these integral equations are necessarily nonlinear, and therefore they also cannot be solved analytically. The transformation to integral equations is readily accomplished with the Laplace transform operator and is developed in Appendix A. The resulting equations are (Equations A15 and A16):

$$0 \leq t \leq \tau_F$$

$$\frac{i_{T_F} (D_R)^{\alpha/2}}{nFC_0^* (D_0)^{\alpha/2} k_s} - \frac{i_c(t) (D_R)^{\alpha/2}}{nFC_0^* (D_0)^{\alpha/2} k_s} = \exp(-\alpha \sqrt{D_0} C_Q^* / \sqrt{D_R} C_R^*) \exp$$

$$(\alpha nF / RTC_1 \int_0^t i_c(\tau) d\tau)$$

$$\left[1 - 2i_{T_F} \sqrt{t} / nFC_0^* \sqrt{\pi D_0} + 1 / nFC_0^* \sqrt{\pi D_0} \int_0^t \frac{i_c(\tau) d\tau}{\sqrt{t - \tau}} - \exp(-nF / RTC_1 \int_0^t i_c(\tau) d\tau) \right.$$

$$\left. - (2i_{T_F} \sqrt{t} / nFC_0^* \sqrt{\pi D_0}) \exp(\sqrt{D_0} C_Q^* / \sqrt{D_R} C_R^*) \exp(nF / RTC_1 \int_0^t i_c(\tau) d\tau) \right.$$

$$\left. + (\exp(\sqrt{D_0} C_Q^* / \sqrt{D_R} C_R^*) / nFC_0^* \sqrt{\pi D_0}) \exp(-nF / RTC_1 \int_0^t i_c(\tau) d\tau) \int_0^t \frac{i_c(\tau) d\tau}{\sqrt{t - \tau}} \right]$$

(71)

$$\tau_F \leq t \leq \tau_R$$

$$\begin{aligned} & \frac{R_i i_{T_F} (D_R)^{\alpha/2}}{nFC_0^* (D_0)^{\alpha/2} k_s} - \frac{R_i i_c(t) (D_R)^{\alpha/2}}{nFC_0^* (D_0)^{\alpha/2} k_s} = \exp(-\sqrt{D_0} C_0^* / \sqrt{D_R} C_R^*) \exp \\ & \left[(anF/RTC_1) \left(\int_0^{\tau_F} i_c(\tau) d\tau + 1/C_1 \int_{\tau_F}^t i_c(\tau) d\tau \right) \right] \left\{ 1 + (2i_{T_F} \sqrt{t} / nFC_0^* \sqrt{\pi D_0} \right. \\ & - 2i_{T_F} \sqrt{\tau_F} / nFC_0^* \sqrt{\pi D_0})^{\frac{1}{2}} (1 - R_i) - 2i_{T_F} \sqrt{t} / nFC_0^* \sqrt{\pi D_0} + 1/nFC_0^* \sqrt{\pi D_0} \\ & \int_0^{\tau_F} \frac{i_c(\tau) d\tau}{\sqrt{t - \tau}} + 1/nFC_0^* \sqrt{\pi D_0} \int_{\tau_F}^t \frac{i_c(\tau) d\tau}{\sqrt{t - \tau}} - (\exp[-nF/RTC_1] \\ & \left. (\int_0^{\tau_F} i_c(\tau) d\tau + 1/C_1 \int_{\tau_F}^t i_c(\tau) d\tau) \right) \left[1 - (\exp(\sqrt{D_0} C_0^* / \sqrt{D_R} C_R^*) \right. \\ & (2i_{T_F} \sqrt{t} / nFC_0^* \sqrt{\pi D_0} - 2i_{T_F} \sqrt{\tau_F} / nFC_0^* \sqrt{\pi D_0})^{\frac{1}{2}} (1 - R_i)) + \exp(\sqrt{D_0} C_0^* / \\ & \sqrt{D_R} C_R^*) (2i_{T_F} \sqrt{t} / nFC_0^* \sqrt{\pi D_0}) - \exp(\sqrt{D_0} C_0^* / \sqrt{D_R} C_R^*) / nFC_0^* \sqrt{\pi D_0} \int_0^{\tau_F} \\ & \left. \frac{i_c(\tau) d\tau}{\sqrt{t - \tau}} - \exp(\sqrt{D_0} C_0^* / \sqrt{D_R} C_R^*) / nFC_0^* \sqrt{\pi D_0} \int_{\tau_F}^t \frac{i_c(\tau) d\tau}{\sqrt{t - \tau}} \right] \left. \right\} \end{aligned} \quad (72)$$

Numerical Solution of Integral Equations

To solve Equations 71 and 72 numerically without loss of generality it is essential to have the equations in dimensionless form so that results are described by the minimum number of independent parameters. Equations 71 and 72 can be made dimensionless with the following changes of variable

$$t = (nFC_0^* \sqrt{\pi D_0})^2 y / 4i_{T_F}^2 \quad (73)$$

$$\tau = (nFC_0^* \sqrt{\pi D_0})^2 x / 4i_{TF}^2 \quad (74)$$

and the following definitions

$$h(y) = i_c(y) / i_T(y) \quad (75)$$

$$\exp(b) = \gamma C_0^* / C_R^* \quad (76)$$

$$\Psi = (RT/nF) \frac{4i_{TF} C_1}{(nFC_0^* \sqrt{\pi D_0})^2} \quad (77)$$

$$\rho = i_{TF} / nFC_0^* \gamma^\alpha k_s \quad (78)$$

$$y_f = \frac{4i_{TF}^2 \tau_F}{(nFC_0^* \sqrt{\pi D_0})^2} \quad (79)$$

Equations 71 and 72 now become

$$\begin{aligned} & 0 \leq t \leq \tau_F \\ & \frac{\rho(1 - h(y)) - e^{-\alpha(b - 1/\Psi \int_0^y h(x) dx)} (1 - e^{-1/\Psi \int_0^y h(x) dx})}{e^{-\alpha(b - 1/\Psi \int_0^y h(x) dx)} (1 + e^{b - 1/\Psi \int_0^y h(x) dx})} \\ & = -\sqrt{y} + 1/2 \int_0^y \frac{h(x) dx}{\sqrt{y - x}} \end{aligned} \quad (80)$$

$$\begin{aligned} & \tau_F \leq t \leq \tau_R \\ & \frac{R_i \rho(1 - h(y)) - e^{-\alpha(b - 1/\Psi \int_0^{y_f} h(x) dx) - \frac{R_i}{\Psi} \int_{y_f}^y h(x) dx} (1 - e^{-1/\Psi \int_0^{y_f} h(x) dx})}{e^{-\alpha(b - 1/\Psi \int_0^{y_f} h(x) dx) - \frac{R_i}{\Psi} \int_{y_f}^y h(x) dx} (1 + e^{b - 1/\Psi \int_0^{y_f} h(x) dx - \frac{R_i}{\Psi} \int_{y_f}^y h(x) dx})} \\ & \frac{h(x) dx - \frac{R_i}{\Psi} \int_{y_f}^y h(x) dx}{\int_{y_f}^y h(x) dx} = (y - y_f)^{\frac{1}{2}} (1 - R_i) - y^{\frac{1}{2}} + \\ & \frac{1}{2} \int_0^{y_f} \frac{h(x) dx}{\sqrt{y - x}} + \frac{R_i}{2} \int_{y_f}^y \frac{h(x) dx}{\sqrt{y - x}} \end{aligned} \quad (81)$$

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The only unknown in these equations is the function $h(y)$. Once $h(y)$ has been calculated it can be related to potential through the following expressions which are derived in Appendix B (Equations B5 and B6):

$$0 \leq t \leq \tau_F$$

$$n[E(y) - E_z] = RT/F [b - 1/\psi \int_0^y h(x) dx] \quad (82)$$

$$\tau_F \leq t \leq \tau_R$$

$$n[E(y) - E_z] = RT/F [b - 1/\psi \int_0^{y_f} h(x) dx - R_i/\psi \int_{y_f}^y h(x) dx] \quad (83)$$

Equations 80 and 81 were solved numerically by a step functional method (47). To make a description of this method applicable to all of the integrals appearing in Equations 80 and 81, it is useful to employ the following general representation for these integrals

$$\int_0^y h(z) K(y-z) dz \quad (84)$$

where $h(z)$ represents the unknown function, and $K(y-z)$ is the kernel function, which is defined explicitly. To approximate this integral the range of integration from $y = 0$ to $y = M$ is first divided into N equally spaced subintervals by the following change of variable

$$n = y/\delta \quad (85)$$

where δ is the length of the subinterval ($\delta = \underline{M}/\underline{N}$), and $\underline{n}$ is a serial number of the subinterval. Thus, Integral 84 becomes

$$\int_0^{n\delta} h(z)K(n\delta - z)dz \quad (86)$$

This integral can now be replaced by a finite sum of integrals which are integrated over each of the subintervals

$$\sum_{i=1}^n \int_{(i-1)\delta}^{i\delta} h(i)K(n\delta - z)dz \quad (87)$$

At this point the unknown function can be approximated in several ways (57). The simplest of these is to assume that it is a constant over the i th subinterval. With this approximation, Integral 87 becomes

$$\sum_{i=1}^n h(i) \int_{(i-1)\delta}^{i\delta} K(n\delta - z)dz \quad (88)$$

The notation can now be simplified by introducing the following change of variable

$$w = n\delta - z \quad (89)$$

which leads to

$$\sum_{i=1}^n h(i) \int_{(n-i)\delta}^{(n-i+1)\delta} K(w)dw = \sum_{i=1}^n h(i)A(n-i+1) \quad (90)$$

Thus, to approximate the integrals of Equations 80 and 81 it is simply necessary to evaluate $A(\underline{n}-\underline{i}+1)$ by integration

of the respective kernel functions, $K(\underline{w})$. For the kernel

$$K(w) = \frac{1}{\sqrt{w}} \quad (91)$$

one obtains

$$A(n-i+1) = 2 [\sqrt{(n-i+1)\delta} - \sqrt{(n-i)\delta}] \quad (92)$$

whereas for

$$k(w) = 1 \quad (93)$$

one obtains

$$A(n-i+1) = \delta \quad (94)$$

Thus, Integral 91 can be approximated as

$$\int_0^y \frac{h(x) dx}{\sqrt{y-x}} \cong 2 \sum_{i=1}^n h(i) [\sqrt{(n-i+1)\delta} - \sqrt{(n-i)\delta}] \quad (95)$$

and Integral 93 as

$$\int_0^y h(x) dx \cong \delta \sum_{i=1}^n h(i) \quad (96)$$

Replacing the respective integrals in Equations 80 and 81 by these finite sums yields

$$\begin{aligned} 0 \leq t \leq \tau_F \\ \rho = \frac{\rho h(n)}{\exp[-a(b - \delta h(n)/\Psi - \delta/\Psi \sum_{i=1}^{n-1} h(i))]} - 1 + \exp(-\delta h(n)/\Psi - \delta/\Psi \sum_{i=1}^{n-1} h(i)) \\ \frac{1 + \exp(b - \delta h(n)/\Psi - \delta/\Psi \sum_{i=1}^{n-1} h(i))}{1 + \exp(b - \delta h(n)/\Psi - \delta/\Psi \sum_{i=1}^{n-1} h(i))} \\ = -(n\delta)^{\frac{1}{2}} + (\delta)^{\frac{1}{2}} h(n) + (\delta)^{\frac{1}{2}} \sum_{i=1}^{n-1} h(i) [(n-i+1)^{\frac{1}{2}} - (n-i)^{\frac{1}{2}}] \quad (97) \end{aligned}$$

$$\begin{aligned}
& \tau_F \leq t \leq \tau_R \\
& \left\{ 1 + \exp(b - \delta/\Psi \sum_{i=1}^{n_1} h(i) - R_i \delta h(n)/\Psi - R_i \delta/\Psi \sum_{i=n_1+1}^{n-1} h(i)) \right\} \\
& \left\{ (n\delta - n_1 \delta)^{\frac{1}{2}} (1-R_i) - (n\delta)^{\frac{1}{2}} + (\delta)^{\frac{1}{2}} \sum_{i=1}^{n_1} h(i) [(n-i+1)^{\frac{1}{2}} - (n-i)^{\frac{1}{2}}] \right. \\
& \left. + R_i (\delta)^{\frac{1}{2}} \sum_{i=n_1+1}^{n-1} h(i) [(n-i+1)^{\frac{1}{2}} - (n-i)^{\frac{1}{2}}] + R_i (\delta)^{\frac{1}{2}} h(n) \right\} \\
& = \frac{R_i \rho - R_i \rho h(n)}{\exp[-\alpha(b - \delta/\Psi \sum_{i=1}^{n_1} h(i) - R_i \delta h(n)/\Psi - R_i \delta/\Psi \sum_{i=n_1+1}^{n-1} h(i))] - 1} \\
& + \exp(-\delta/\Psi \sum_{i=1}^{n_1} h(i) - R_i \delta h(n)/\Psi - R_i \delta/\Psi \sum_{i=n_1+1}^{n-1} h(i)) \quad (98)
\end{aligned}$$

Equations 97 and 98 are a system of equations in the function $h(\underline{n})$. Unfortunately, these equations are nonlinear and therefore cannot be solved directly for $h(\underline{n})$, but rather must be solved numerically. There are several methods suitable for solving equations of this type, such as the Newton-Raphson technique (58). The Newton-Raphson method is an iterative procedure which is ideally handled by a digital computer. Iterations are performed according to the following equation

$$X_{p+1} = X_p - f(X_p)/f'(X_p) \quad (99)$$

where $f(\underline{X}_p)$ is the function evaluated at $\underline{X}_p$, $f'(\underline{X}_p)$ is the derivative of $f(\underline{X})$ evaluated at $\underline{X}_p$, $\underline{X}_p$ is an approximate solution, and $\underline{X}_{p+1}$ is an improved solution. The iteration

is continued (replacing $\underline{X}_p$ by $\underline{X}_{p+1}$) to any desired degree of self-consistency between $\underline{X}_p$ and $\underline{X}_{p+1}$. Equations 97 and 98 written in the form of Equation 99 are

$$0 \leq t \leq \tau_F$$

$$\begin{aligned} h_{p+1}(n) = & h_p(n) - [-(n\delta)^{\frac{1}{2}} + (\delta)^{\frac{1}{2}}h_p(n) + A - D(n\delta)^{\frac{1}{2}}\exp(-Eh_p(n)) \\ & + D(\delta)^{\frac{1}{2}}h_p(n)\exp(-Eh_p(n)) + AD\exp(-Eh_p(n)) - \frac{\rho - \rho h_p(n)}{B\exp(\alpha Eh_p(n))} + 1 \\ & - C\exp(-Eh_p(n))] / [(\delta)^{\frac{1}{2}} + ED(n\delta)^{\frac{1}{2}}\exp(-Eh_p(n)) - DE(\delta)^{\frac{1}{2}}h_p(n) \\ & \exp(-Eh_p(n)) + D(\delta)^{\frac{1}{2}}\exp(-Eh_p(n)) - ADE\exp(-Eh_p(n)) + \\ & \frac{\rho + \rho \alpha E - \rho \alpha Eh_p(n)}{B\exp(\alpha Eh_p(n))} + CE\exp(-Eh_p(n))] \end{aligned} \quad (100)$$

$$\tau_F \leq t \leq \tau_R$$

$$\begin{aligned} h_{p+1}(n) = & h_p(n) - [V + GV\exp(-R_i Eh_p(n)) + W + GW\exp(-R_i Eh_p(n)) \\ & + R_i(\delta)^{\frac{1}{2}}h_p(n) + GR_i(\delta)^{\frac{1}{2}}h_p(n)\exp(-R_i Eh_p(n)) - \frac{R_i \rho - R_i \rho h_p(n)}{T\exp(\alpha R_i Eh_p(n))} \\ & + 1 - Z\exp(-R_i Eh_p(n))] / [-GVR_i E\exp(-R_i Eh_p(n)) - R_i EGW\exp(-R_i Eh_p(n)) \\ & + R_i(\delta)^{\frac{1}{2}} - R_i^2 EG(\delta)^{\frac{1}{2}}h_p(n)\exp(-R_i Eh_p(n)) + GR_i(\delta)^{\frac{1}{2}}\exp(-R_i Eh_p(n)) \\ & + \frac{R_i \rho + \alpha R_i^2 \rho E - \alpha R_i^2 E \rho h_p(n)}{T\exp(\alpha R_i Eh_p(n))} + R_i EZ\exp(-R_i Eh_p(n))] \end{aligned} \quad (101)$$

where

$$A = (\delta)^{\frac{1}{2}} \sum_{i=1}^{n-1} h(i) [(n-i+1)^{\frac{1}{2}} - (n-i)^{\frac{1}{2}}] \quad (102)$$

$$B = \exp[-\alpha(b - \delta/\psi \sum_{i=1}^{n-1} h(i))] \quad (103)$$

$$C = \exp(-\delta/\psi \sum_{i=1}^{n-1} h(i)) \quad (104)$$

$$D = \exp(b - \delta/\psi \sum_{i=1}^{n-1} h(i)) \quad (105)$$

$$E = \delta/\psi \quad (106)$$

$$G = \exp(b - \delta/\psi \sum_{i=1}^{n_1} h(i) - R_i \delta/\psi \sum_{i=n_1+1}^{n-1} h(i)) \quad (107)$$

$$V = (n\delta - n_1\delta)^{\frac{1}{2}}(1 - R_i) - (n\delta)^{\frac{1}{2}} \quad (108)$$

$$W = (\delta)^{\frac{1}{2}} \sum_{i=1}^{n_1} h(i) [(n-i+1)^{\frac{1}{2}} - (n-i)^{\frac{1}{2}}] + R_i (\delta)^{\frac{1}{2}}$$

$$\sum_{i=n_1+1}^{n-1} h(i) [(n-i+1)^{\frac{1}{2}} - (n-i)^{\frac{1}{2}}] \quad (109)$$

$$T = \exp[-\alpha(b - \delta/\psi \sum_{i=1}^{n_1} h(i) - R_i \delta/\psi \sum_{i=n_1+1}^{n-1} h(i))] \quad (110)$$

$$Z = \exp(-\delta/\psi \sum_{i=1}^{n_1} h(i) - R_i \delta/\psi \sum_{i=n_1+1}^{n-1} h(i)) \quad (111)$$

To start the iterative procedure an arbitrary value of $h(n)$ equal 0.0004 was always used as the initial guess from which $h(y)$ was evaluated with y equal zero. Subsequent

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calculations were performed with the most recently calculated solution as an initial guess in the Newton-Raphson iteration. The iteration was continued until successive answers differed by a relative error less than 10^{-7} . Calculations were performed on the Michigan State University Control Data 3600 digital computer, and the FORTRAN program is listed in Appendix C.

Results of Calculations

The numerical solution of Equations 80 and 81 provides values of $h(y)$ (ratio of faradaic current to total current, Equation 75) as a function of y (dimensionless variable proportional to real time, see Equation 73). Alternatively, values of $h(y)$ are directly related to potential (Equations 82 and 83) so that theoretical potential-time curves also result from the solution of Equations 80 and 81. Both $h(y)$ and $n(\underline{E} - \underline{E}_2)$ are tabulated by the computer program given in Appendix C. Theoretical $\underline{E}-y$ curves calculated in this way depend on several parameters, but most predominantly on Ψ and ρ . The parameter Ψ is directly proportional to the double-layer capacitance (see Equation 77) and therefore its magnitude determines the extent to which double-layer charging affects chronopotentiograms. The parameter ρ (Equation 78) has the same definition used previously (Equation 24), and therefore its magnitude determines the effect of electron transfer kinetics on chronopotentiograms. Although these two parameters interact, their effect in general is readily

apparent from the theoretical chronopotentiograms of Figures 9 and 10. In Figure 9 curves were calculated for three values of Ψ and fixed ρ , whereas the curves of Figure 10 are for three values of ρ and fixed Ψ . In particular the curves of Figure 9 illustrate the dramatic effect of increased double-layer charging on chronopotentiograms. When it is recalled that $\underline{y} = 1$ corresponds to the Sand equation transition time, it is apparent that transition time becomes ill-defined in the presence of appreciable charging current. Among other things, this effect obviously makes unambiguous definition of $\underline{E}_F$ and $\underline{E}_R$ impossible.

Although the chronopotentiograms are determined largely by Ψ and ρ , they also depend to a lesser extent on the values of α , δ , $\underline{b}$, $\underline{R}_i$, and switching potential (potential where current reversal occurs). Thus, to interpret quantitatively the effect of Ψ and ρ , which is the primary goal, the effect of these other parameters also must be understood, and therefore they are discussed individually in the following paragraphs.

Effect of δ . It will be recalled that δ is the width of the subintervals over which the unknown function is approximated in the numerical integrations. Since this is a fairly crude approximation, it is important to evaluate the effect of δ , and select a value which provides satisfactory accuracy. Obviously, as δ approaches zero, the accuracy will improve, but at the same time the number of calculations involved will

Figure 9. Calculated chronopotentiograms showing the effect of double-layer parameter, ψ , when $\rho = 0.0$, $\alpha = 0.5$, and $R_i = -0.5$. Curve A, $\psi = 0.01$; Curve B, $\psi = 0.03$; Curve C, $\psi = 0.06$.

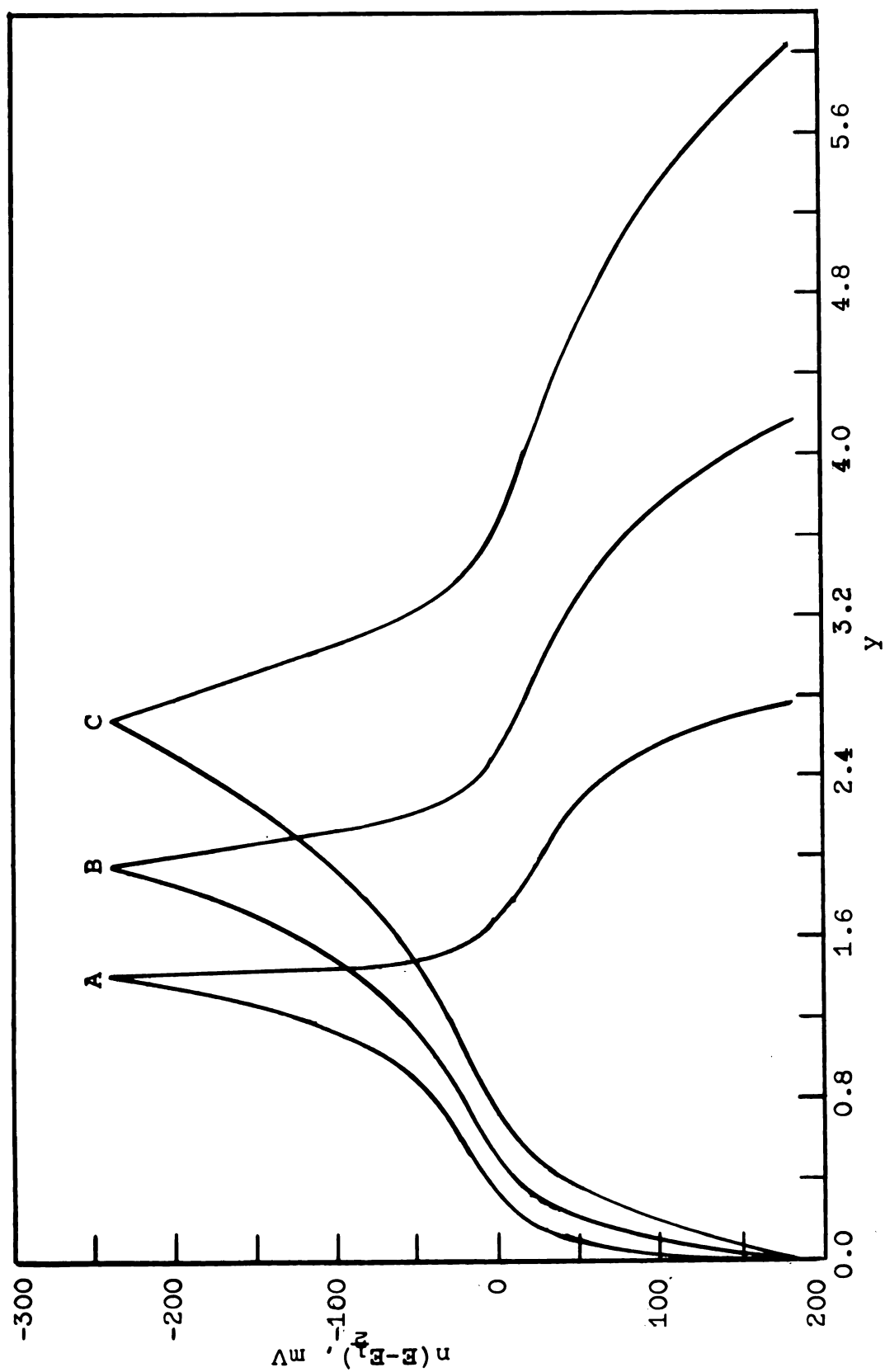


Figure 9

Figure 10. Calculated chronopotentiograms showing effect of kinetic parameter, ρ , when $\psi = 0.03$, $\alpha = 0.5$, and $R_i = -0.5$.
Curve A, $\rho = 0.0$; Curve B, $\rho = 1.0$; Curve C, $\rho = 2.5$.

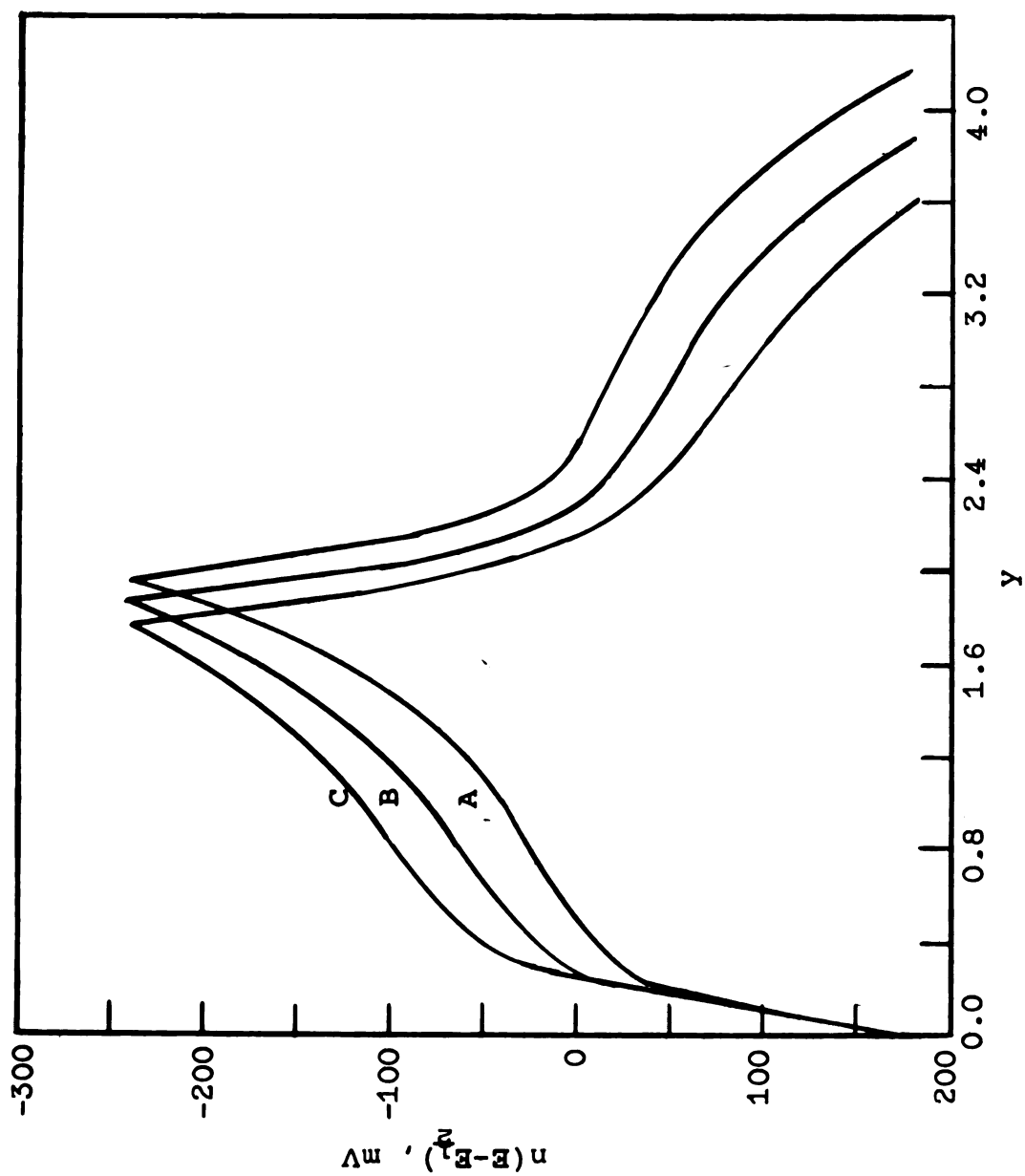


Figure 10

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increase. The optimum value of δ is one that provides acceptable accuracy without requiring inordinate amounts of computer time. This value of δ was determined by varying δ over the range 0.1 to 0.001. The value of δ equal 0.01 was found to satisfy the above requirements, so that results are accurate to ± 0.5 mV, except for very small values of Ψ (≤ 0.005) and finite ρ . For $\Psi \leq 0.005$, a value of δ equal 0.001 was found to give results to the same degree of accuracy mentioned above.

Effect of b . From its definition in Equation 76 parameter b simply defines the initial equilibrium potential for the experiment. Normally, in a chronopotentiometric experiment only one oxidation state of the depolarizer is present, for example the oxidized form in the case of an initial reduction. In this case the system is poised initially at an equilibrium potential very anodic of E_2 . It is observed experimentally that under these conditions chronopotentiograms are essentially independent of this initial potential. This experimental fact was verified in the theoretical calculations by observing that E - y curves are independent of b , except for very small shifts along the time axis, provided b is greater than 6.5, (E_1 more than 165 mV positive of E_2). Thus, all calculations reported in this thesis were calculated for $b = 7.0$, and results are independent of b within the accuracy of the calculations.

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Effect of R_i . R_i is the ratio of forward to reverse current densities, and its effect on $\underline{E}$ - $\underline{y}$ curves in the present case is identical to that discussed earlier in this thesis (cf. discussion of Figure 5). As pointed out in that discussion, the optimum value from an experimental point of view is about -0.5, and therefore, except where indicated, calculations reported here are for $R_i = -0.5$.

Effect of α . The transfer coefficient, α , affects the symmetry of $\underline{E}$ - $\underline{y}$ curves as illustrated by Figure 11, where theoretical chronopotentiograms are shown for three values of α at fixed Ψ and ρ . The effect is essentially the same as discussed earlier, and the limiting cases discussed there transpose directly to the present case. As shown by Figure 11 the overall influence of α is fairly small, the effect decreasing as ρ decreases. Since the curves become less dependent on α for smaller values of ρ , differences of potential (e.g., $\Delta \underline{E}$) on the forward and reverse parts of the $\underline{E}$ - $\underline{y}$ curve tend to be independent of α . This fact will be used below in developing a relationship between $\Delta \underline{E}$ and ρ for the case of finite Ψ .

Effect of Switching Potential. The effect of current reversal potentials on $\underline{E}$ - $\underline{y}$ curves is illustrated in Figure 12, where theoretical curves are shown for two values of switching potential at fixed Ψ and ρ . The overall effect of current reversal potential is to shift the anodic portion of the

Figure 11. Effect of charge transfer coefficient, α , on calculated chronopotentiograms when $\psi = 0.03$, $\rho = 0.5$, and $R_i = -0.5$. Curve A, $\alpha = 0.3$; Curve B, $\alpha = 0.5$; Curve C, $\alpha = 0.7$.

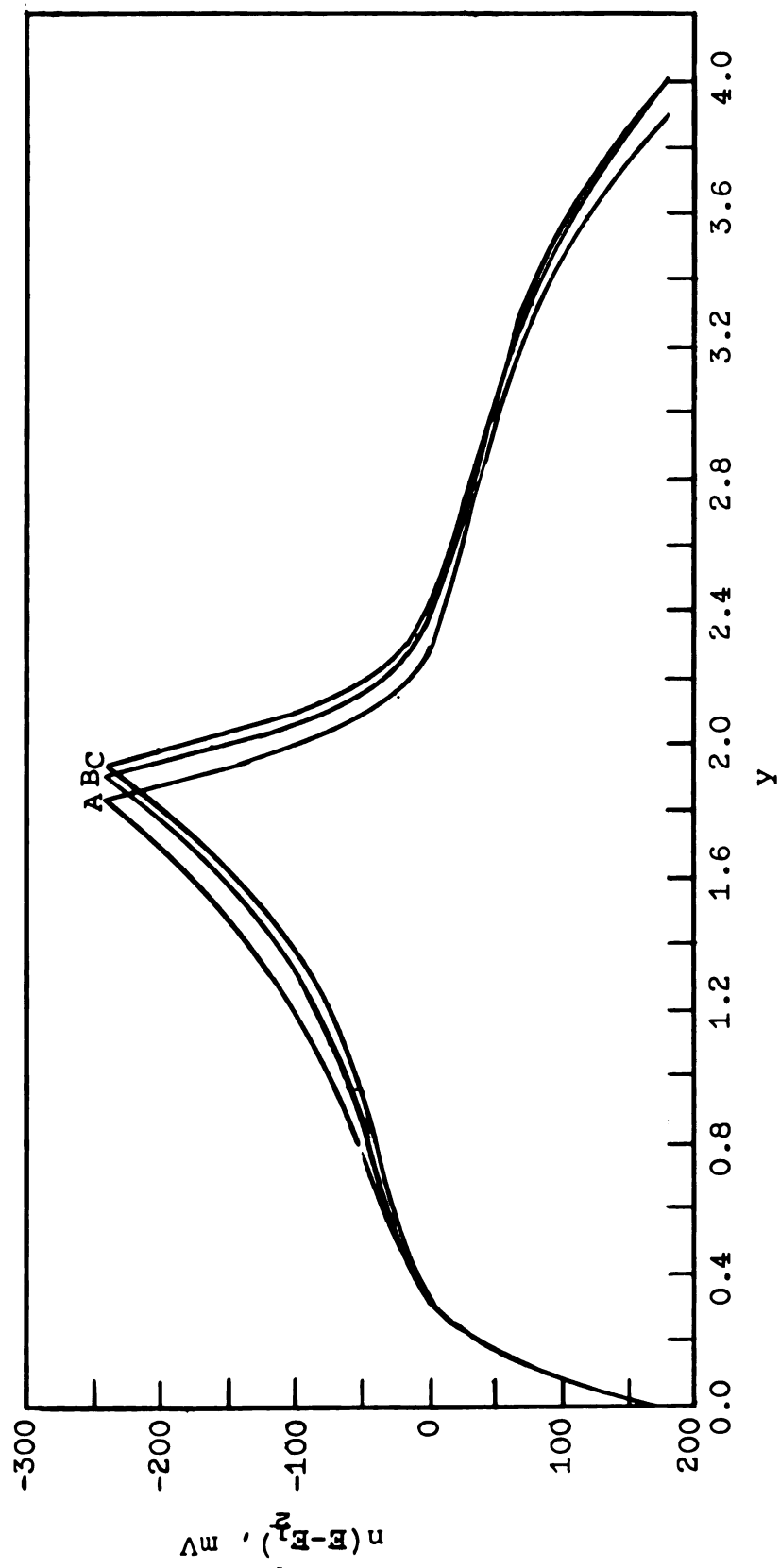


Figure 11

Figure 12. Calculated chronopotentiograms showing effect of current reversal potential when $\bar{y} = 0.03$, $\rho = 0.5$, $\alpha = 0.5$, and $R_i = -0.5$. Curve A, switching potential = -210 mV vs. E_1 ; Curve B, switching potential = -210 mV vs. E_2 .

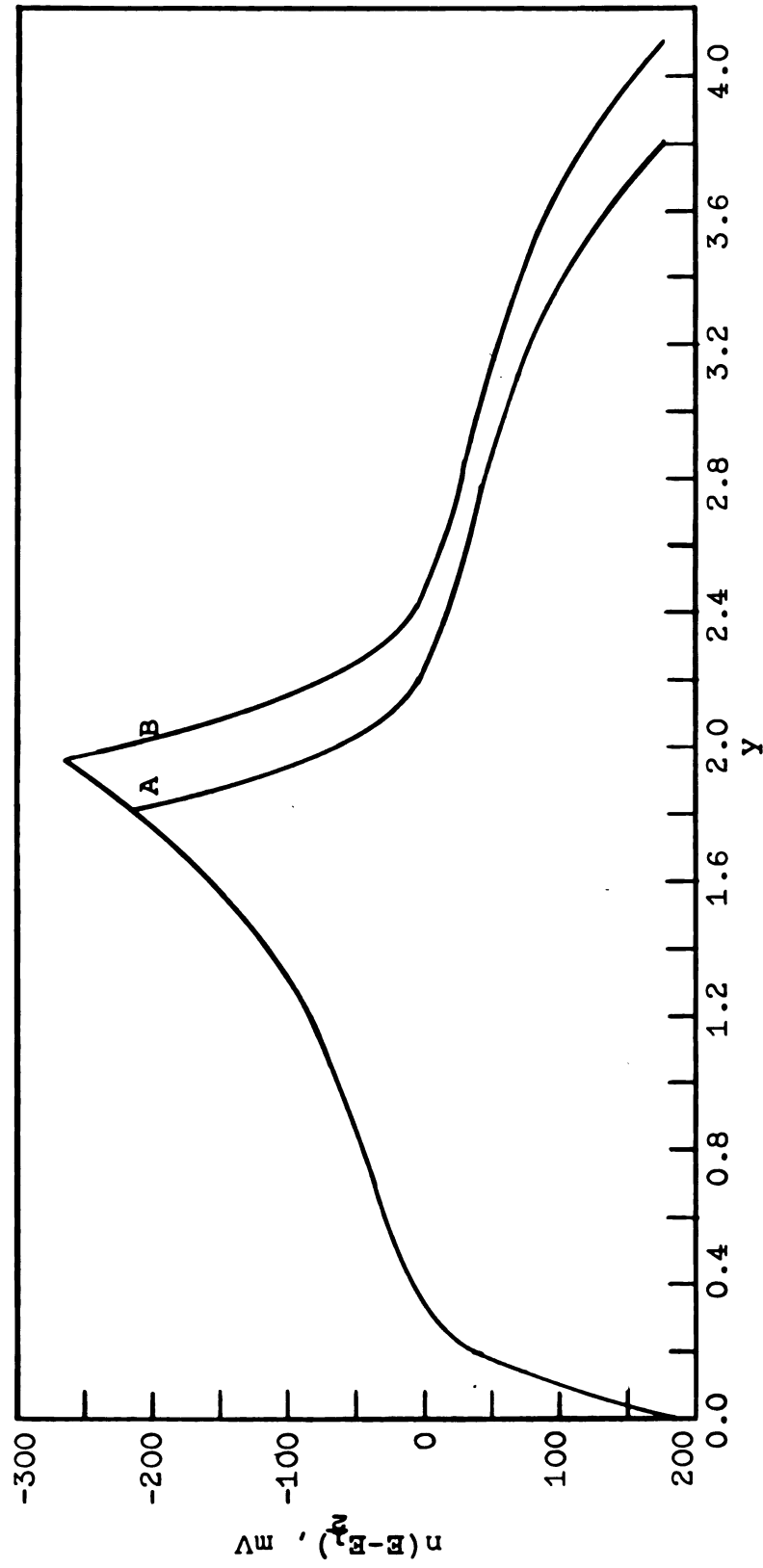


Figure 12

chronopotentiogram on the time axis. It was found by calculation that the shape of the reverse part of the curve becomes independent of current reversal potential, except for small differences near the anodic transition time, provided switching potential is greater than $-210 \text{ mV vs. } \underline{E}_2$.

Effect of Ψ and ρ . The effect of Ψ and ρ was considered briefly above, and will be analyzed now in greater detail. In particular, several limiting cases exist which can be evaluated and quantitatively defined. The case for ρ equal zero and finite Ψ already has been discussed in the literature by several groups (21,50,53). Similarly, the case of zero Ψ and finite ρ was discussed in detail in the first part of this thesis. The calculations developed above permit conditions for which these limiting cases hold to be defined quantitatively.

First, as Ψ and ρ both approach zero (small $\underline{C}_1$ and/or $\underline{i}_{T_F}$, or large $\underline{C}_0^*$, and large $\underline{k}_s$ and/or $\underline{i}_{T_F}$, or large $\underline{C}_0^*$, respectively) no kinetic or double-layer charging effects are expected. This condition corresponds to uncomplicated reversible electron transfer, and was discussed earlier in connection with Equations 33 and 34. It was found from the theoretical $\underline{E}$ - $\underline{y}$ curves that Equations 33 and 34 are obeyed within 2-3 mV whenever $\Psi \leq 0.0005$ and $\rho \leq 0.01$.

A second limiting case arises when Ψ approaches zero, and ρ is finite. This situation corresponds to the case where double-layer charging is negligible, and therefore is the case

discussed earlier in this thesis in connection with Equations 27 and 31. It was determined from $\underline{E}$ - $\underline{\gamma}$ curves that Equations 27 and 31 are obeyed within 2-3 mV whenever $\Psi \leq 0.0005$, regardless of the value of ρ .

A third limiting case occurs when ρ approaches zero, and Ψ is finite. This situation corresponds to reversible electron transfer where double-layer charging is prevalent, which is the case already discussed in the literature (21,50,53). Theoretical $\underline{E}$ - $\underline{\gamma}$ curves were found to agree with these literature data within 2-3 mV whenever $\rho \leq 0.01$, regardless of the value of Ψ .

The final limiting case arises when ρ is sufficiently large (small $\underline{k}_s$ and/or large $\underline{i}_{T_F}$, or small $\underline{C}_O^*$) that the processes of oxidation and reduction can be treated separately as the totally irreversible case (large overpotentials) (15). For zero Ψ this situation is described exactly by Equations 35 and 36. It was found that these equations are applicable in the present case within 2-3 mV whenever $\rho \geq 2.5$ and $\Psi \leq 0.0005$. The case of $\rho \geq 2.5$ and $\Psi \geq 0.0005$ has been discussed in detail by Dracka (23), and Rodgers and Meites (53), and therefore was not investigated further.

Overpotential, ΔE , as a Measure of $\underline{k}_s$. In the first part of this thesis a simple relationship between ΔE and $\underline{k}_s$ in the absence of double-layer charging was developed. It would be desirable to develop a similar relationship for finite Ψ , but in view of the strong interaction discovered

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between Ψ and ρ this possibility is not very promising. Nevertheless, it is known that the Berzins-Delahay method accurately locates $\underline{E}_2$, and therefore the possibility of using this approach was investigated. To do this a number of $\underline{E}$ - γ curves were calculated for many values of Ψ and ρ , and values of $\underline{E}_F$ and $\underline{E}_R$ were determined by the method of Berzins and Delahay (to eliminate human prejudice the graphical constructions were performed by the computer). From these values of $\underline{E}_F$ and $\underline{E}_R$, $\Delta \underline{E}$ was calculated and the results are summarized in Figure 13. The fact that a family of curves is obtained proves conclusively that the method of Berzins and Delahay does not satisfactorily compensate for double-layer charging when electron transfer is kinetically controlled. The reasons for this fact are apparent from the data of Figure 14, which illustrate the effect on $\Delta \underline{E}$ of the strong interaction between Ψ and ρ . Figure 14 shows how the ratio $\underline{i}_f/\underline{i}_T$ (faradaic current efficiency) varies for three values of Ψ and a fixed value of ρ . Thus, as Ψ increases, the fraction of the total current which is consumed by the faradaic process decreases, as the charging current component increases (see Equation 64). Since overpotential is determined only by the faradaic current density, the value of $\Delta \underline{E}$ decreases as Ψ increases. Therefore, a new value of $\Delta \underline{E}$ results for each value of Ψ , which in turn leads to a family of working curves.

Figure 13. Working curves showing variation of ΔE with ρ for several values of γ , when $R_i = -0.5$ and $\alpha = 0.5$.

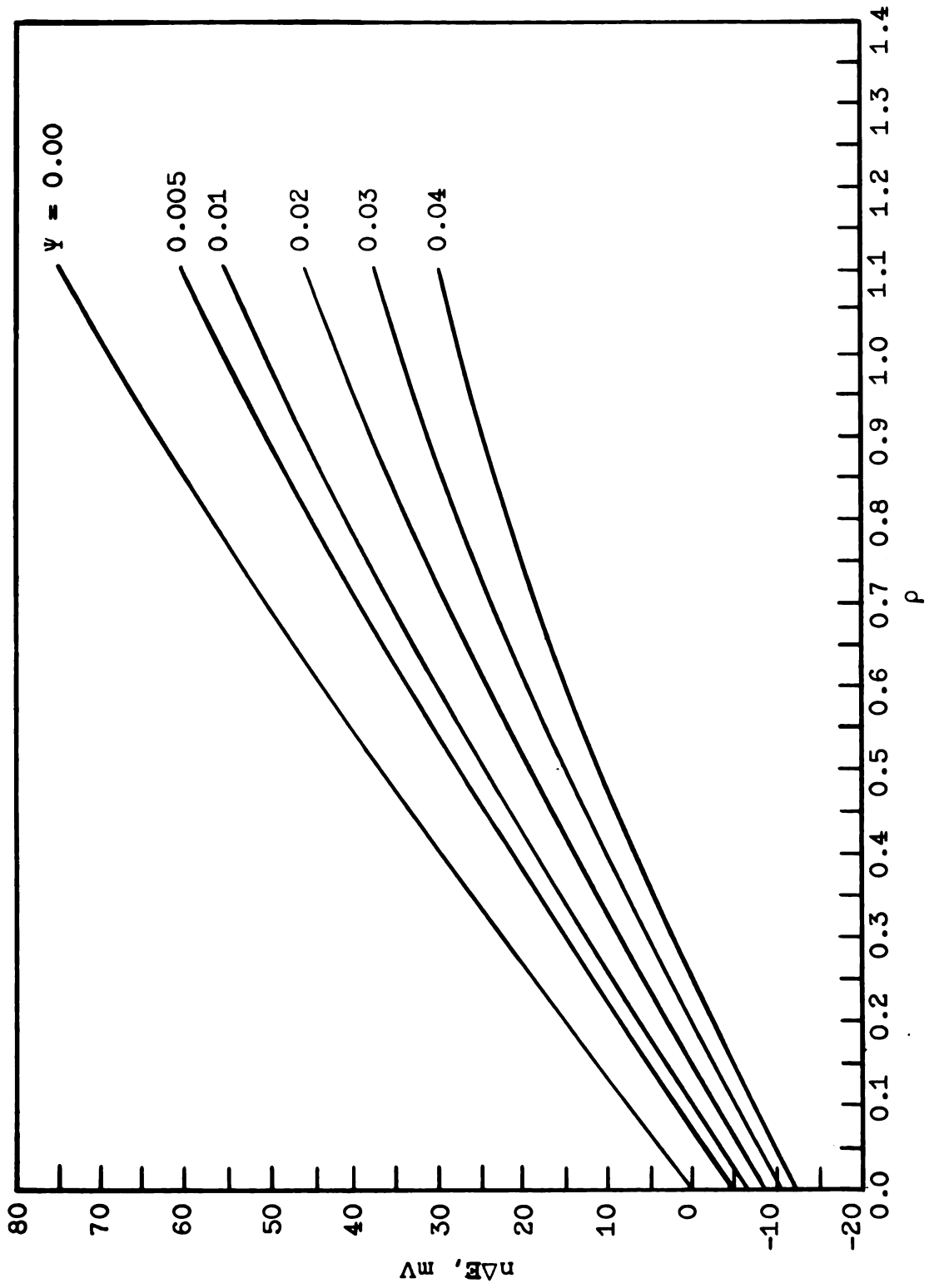


Figure 13

Figure 14. Variation of faradaic current efficiency with γ for
 $\rho = 0.5$, $\alpha = 0.5$, and $R_i = -0.5$.

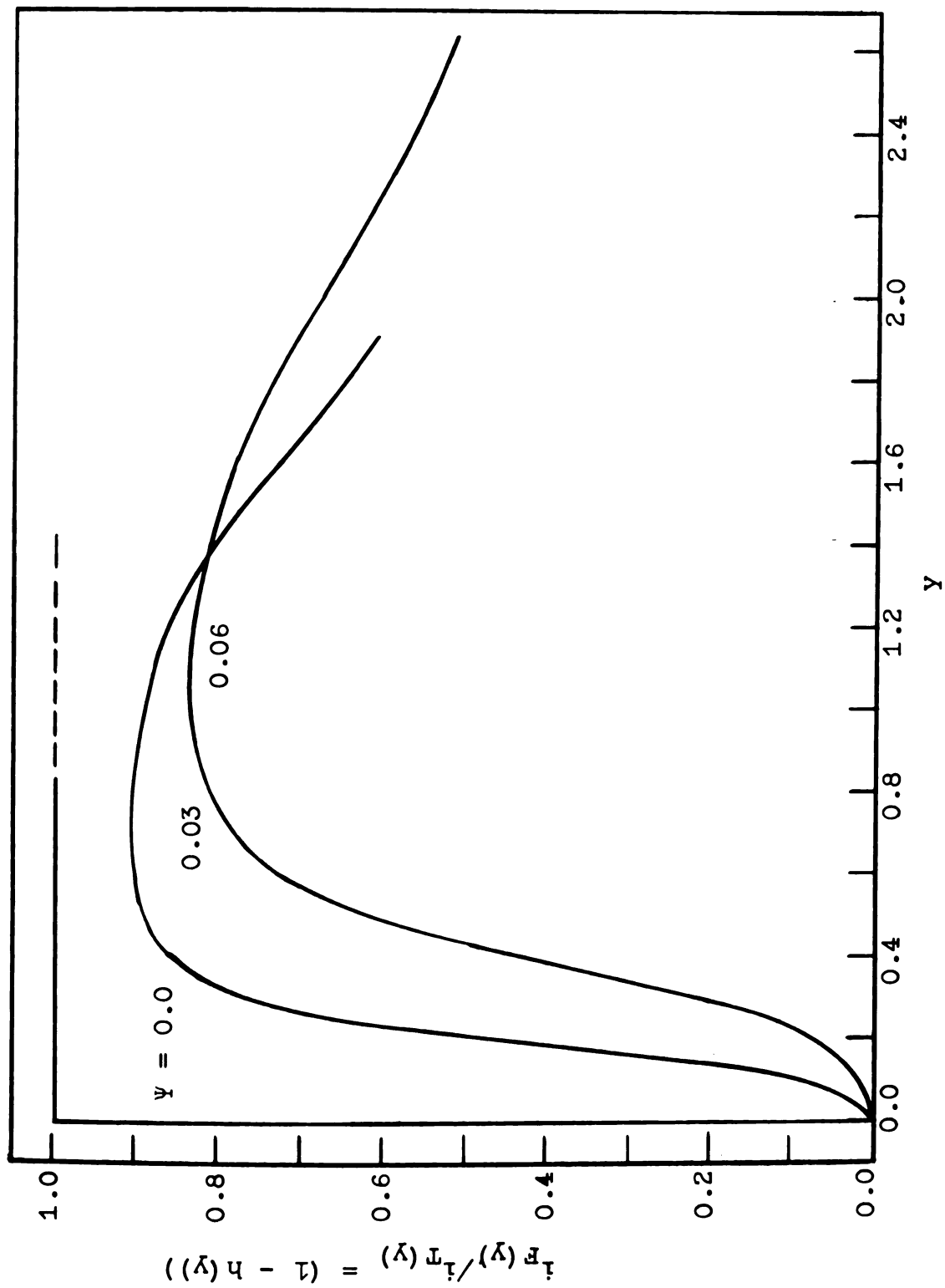


Figure 14

Although not as simple as hoped for, the working curves of Figure 13 do provide a basis for estimating $\underline{k}_s$. Thus, if Ψ can be determined independently, then the proper working curve can be identified and measured values of ΔE correlated with ρ (and hence $\underline{k}_s$). Fortunately, Ψ can be determined experimentally, and therefore this approach is feasible. One method of estimating Ψ is as follows. The initial potential rise for a chronopotentiogram is almost entirely due to the charging current required to bring the working electrode to the potential at which discharge of the electroactive species occurs, as shown by the curves of Figure 14. Thus, during this part of the experiment $\underline{i}_c(t)$ is nearly equal to $\underline{i}_{T_F}$. Combining this fact with the definition of $\underline{i}_c(t)$ (Equation 65) gives

$$\underline{i}_{T_F} = -C_1 S \quad (112)$$

where $\underline{S}$ is $dE(t)/dt$, i.e., the slope of the initial linear portion of the potential-time curve. Equation 112 combined with the definition for Ψ (Equation 77) and the Sand equation yields the following expression

$$\Psi = -(RT/nF) (i_{T_F}^2 / S \tau_s i_{T_s}^2) \quad (113)$$

To use Equation 113 to estimate Ψ it is necessary to perform two separate experiments on the same solution. One experiment is performed at a current density $\underline{i}_{T_s}$ where no

double-layer charging or kinetic effects are detectable, and the transition time corresponding to this current density is τ_s . The second experiment is performed at a current density i_{TF} , where both double-layer charging and kinetic effects are significant, and $\underline{s}$ is taken as the initial slope of the resulting potential-time curve.

Conditions of Applicability of Working Curves. The working curves of Figure 13 in general depend on the same parameters as $\underline{E}$ - $\underline{y}$ curves. Thus, the working curves of Figure 13 were calculated for $\underline{R}_1 = -0.5$, $\alpha = 0.5$, and current reversal potential of -240 mV vs. $\underline{E}_2$, and they are rigorously applicable only when these conditions are met experimentally. Additional calculations have shown, however, that for current reversal potentials more negative than -210 mV, the effect on $\Delta \underline{E}$ is only of the order of 2-3 mV. Thus, provided current reversal potential is more negative than -210 mV, the curves of Figure 13 can be regarded as independent of current reversal potential.

The working curves also depend on α , but for reasonable values of α and ρ , the dependence is not very great, as shown by the data of Table I. These data also show that as ρ decreases the dependence of $\Delta \underline{E}$ on α also decreases. Comparison of values of ρ obtained from Figure 13 with values of ρ calculated rigorously for α in the range $0.3 \leq \alpha \leq 0.7$, show that values of $\underline{k}_s$ accurate within about 10% can be

Table I. Variation of ΔE with Charge Transfer Coefficient for Several Values of Ψ and ρ^a

Ψ	ρ	$n\Delta E, \text{mV}$	α
0.005	0.00	-4.4	0.3
		-4.4	0.5
		-4.4	0.7
0.005	0.50	29.5	0.3
		28.1	0.5
		22.6	0.7
0.005	1.00	65.4	0.3
		56.1	0.5
		40.8	0.7
0.03	0.00	-10.2	0.3
		-10.2	0.5
		-10.2	0.7
0.03	0.50	14.3	0.3
		15.2	0.5
		11.0	0.7
0.03	1.00	33.4	0.3
		35.0	0.5
		20.7	0.7

$$^a E_i = -0.5$$

obtained from the working curves for any α in this range, provided $\Psi \leq 0.03$ and $\rho \leq 1.0$.

Limits of Applicability of Working Curves of Figure 13.

It is useful to determine how much the range of rate constants which can be measured can be extended by using the working curves of Figure 13. An estimate can be obtained by combining Equations 77 and 78 and solving for $\underline{k}_s$

$$\underline{k}_s = n^2 F^2 \pi C_0^* D_0 \Psi / 4 \gamma^\alpha R T \rho C_1 \quad (114)$$

Evaluating the above result at 25°C for $\underline{n} = 2$ and $\gamma (= \sqrt{D_0/D_R}) = 1.0$ gives

$$\underline{k}_s = 1.2 \times 10^7 C_0^* D_0 \Psi / C_1 \rho \quad (115)$$

By substituting the following typical values in Equation 115: $C_0^* = 1 \times 10^{-6}$ mole/cm³, $D_0 = 1 \times 10^{-5}$ cm²/sec, and $C_1 = 3 \times 10^{-5}$ farads/cm², the following expression is obtained

$$\underline{k}_s = 3.9 \Psi / \rho \quad (116)$$

The largest value of $\underline{k}_s$ that can be measured is set by the restriction $\Psi \leq 0.03$ and $\rho \geq 0.1$ to observe kinetic effects. Equation 116 predicts that values of $\underline{k}_s \leq 1.2$ cm/sec can be determined. This limit corresponds to extremely rapid electron transfer, and thus a significant extension of the method has resulted, but at the cost of increased complexity of data analysis.

OTHER POSSIBLE APPLICATIONS OF THE THEORETICAL DATA

The main objective of the theoretical calculations just presented was to determine the influence of double-layer charging on correlations between overpotential (ΔE) and electron transfer kinetics. There are, however, several other areas in which the calculations could be useful. For example, the results could be used to evaluate the several different literature methods for measuring transition times in a manner similar to that employed by Olmstead and Nicholson (50). Also, the results could be used to evaluate derivative chronopotentiometry, to determine whether recent claims by Burden and Peters (10) for advantages of derivative chronopotentiometry are real. Finally, the results could be used to define quantitatively the effects of linearization of the rate law. Of these possibilities the second was examined briefly (but will not be discussed here), and the third in some detail. Since results for this latter case are interesting, they will be discussed briefly.

Because of the functional dependence of heterogeneous rate constants on potential, the rate law is nonlinear, which prevents analytical solutions for any boundary value

problems which use this rate law as a boundary condition. To avoid these mathematical intractabilities it has been common practice in the electrochemical literature to employ a linearized form of the rate law (5,8,44,51). This approach usually permits closed form solutions to be obtained, but necessarily limits the corresponding techniques to small departures from the equilibrium potential. Thus, it is usually estimated from the way in which the rate law is linearized, that results are applicable only if overpotentials are less than about 2-3 mV (5). The use of such small overpotentials has obvious experimental disadvantages. Moreover, the way in which the limit of 2-3 mV is estimated does not take into account the fact that there may be compensating effects, and therefore the equations may actually be valid for larger overpotentials. This possibility has only been investigated rigorously in one case. Nicholson (46) found that for the coulostatic relaxation method, linearized equations were actually valid for overpotentials of about 25 mV, as compared to the 2-3 mV that had been previously claimed. This conclusion is very important, especially if it proves to be generally true for all electrochemical relaxation techniques.

One of the popular relaxation techniques is called the galvanostatic method (5,6,7,9,34,35,36,37,43). With this method an electrode is initially at some equilibrium potential, usually near the half-wave potential (*i.e.*, both O and R are initially present at approximately equal concentrations).

The electrode is then perturbed by a constant current pulse, and overpotential is recorded as a function of time as the electrode potential is driven from its equilibrium value. Theory for this method was first derived by Berzins and Delahay (5), who used the linearized form of the rate law. Thus, according to these authors only the first 2-3 mV of overpotential on overpotential-time curves are interpretable in terms of their equations.

On reflection it will become apparent to the reader that from an experimental point of view the galvanostatic method is merely a special case of chronopotentiometry in which different initial potentials are used, and only the very first part of the chronopotentiogram is recorded. When it is recalled that the theory of the preceding section was derived for any arbitrary initial equilibrium potential (any C_0^* and C_R^* , see parameter b , Equation 76) it is apparent that the computer program of Appendix C can be used to calculate theoretical galvanostatic curves, which do not encompass the assumption of a linearized rate law. Thus, it is possible to determine unambiguously the overpotential range for which the theory of Berzins and Delahay is valid, and thereby determine if the conclusions of Nicholson for the coulstatic method extend to the galvanostatic method.

To make this comparison the final equation given by Berzins and Delahay [Equation 18 of Reference (5)] could be used to calculate overpotential curves for the linearized

case. Unfortunately, this is difficult because for certain combinations of experimental variables, it requires evaluation of error functions which have imaginary arguments. Although it is possible to evaluate these functions, the computer calculations would be complex and therefore a simpler approach was sought.

In this alternate approach the linear boundary value problem originally solved by Berzins and Delahay was transformed directly to the following linear integral equation, which is equivalent to the linearized form of Equation 80:

$$\rho \exp(\alpha b) [1 - h(y)] = - [1 + \exp(b)] y^{\frac{1}{2} + \frac{1}{2}} [1 + \exp(b)] \int_0^y \frac{h(x) dx}{\sqrt{y - x}} + 1/\Psi \int_0^y h(x) dx \quad (117)$$

This integral equation was solved by the step-functional method, and results were in agreement with those calculated from the Berzins and Delahay equation.

Galvanostatic curves were calculated from Equations 80 and 117 for identical values of Ψ , ρ , and $\underline{b}$, and the results compared to determine the overpotential at which the rigorous nonlinearized theory begins to deviate significantly from the linearized theory. Typical results are shown in Figure 15, where the solid curve is obtained from the linearized equation, and the dashed curve from the nonlinearized equation. At least for the values of Ψ , ρ and $\underline{b}$ used in Figure 15, it is apparent that linearized theory is valid for considerably larger overpotentials than the 2-3 mV usually assumed.

Figure 15. Calculated galvanostatic curves when $\rho = 0.5$, $\psi = 0.01$,
and $\alpha = 0.5$.

Solid curve, linearized.
Dashed curve, nonlinearized.

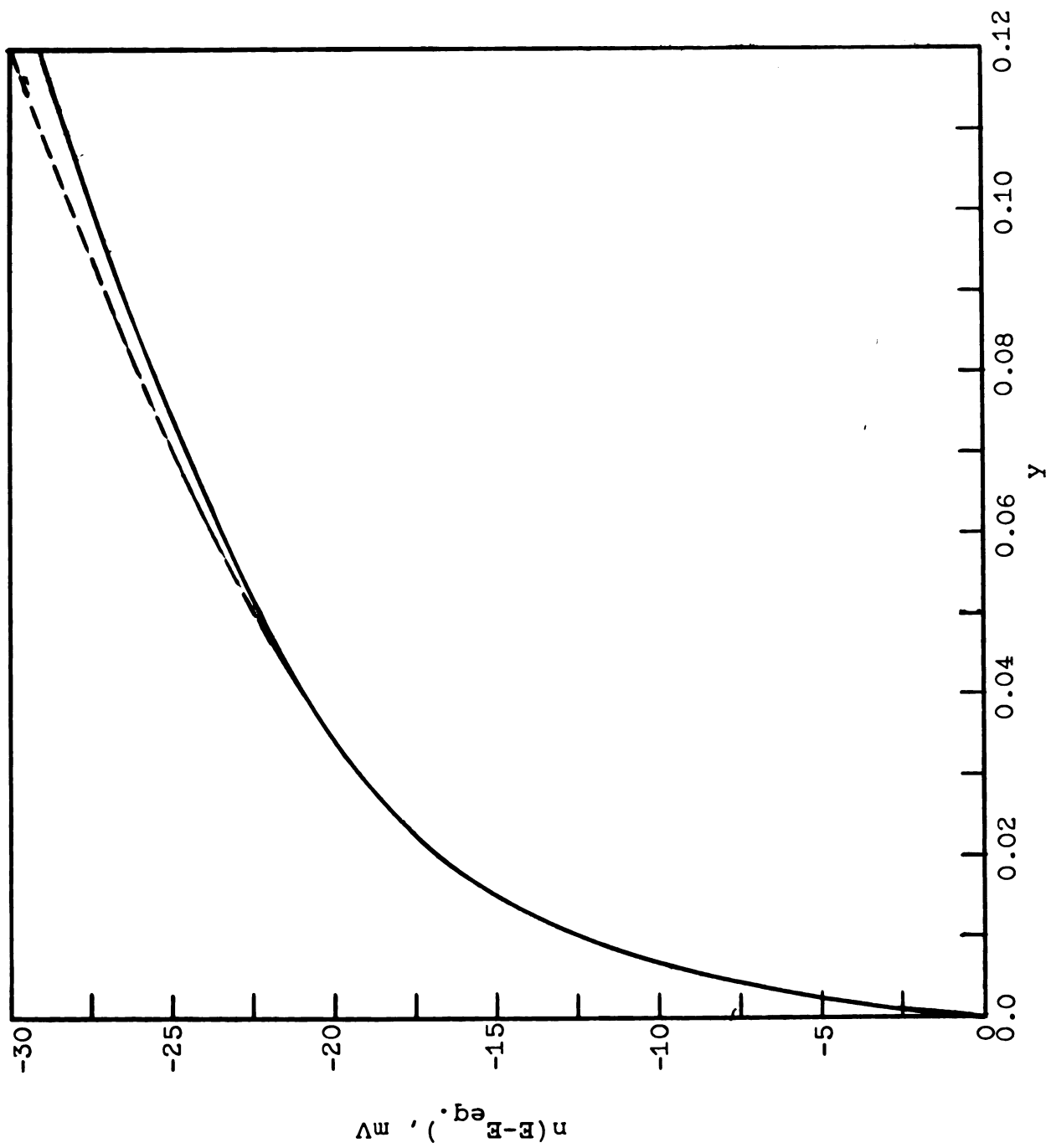


Figure 15

The range of overpotential for which the two equations agree is, of course, strongly dependent on the values of Ψ , ρ and $\underline{b}$. This fact is illustrated by the data of Table II, where the numerical quantities listed under various values of $\underline{b}$ are the overpotentials at which linearized and non-linearized results begin to differ by more than 1 mV.

The data of Table II show that in general linearized theory can be used for overpotentials of about 30 mV, which is nearly an order of magnitude larger than assumed in the literature. This fact is significant in terms of the galvanostatic method, because it means that it can be used over an experimentally more convenient range of potentials, while still analyzing the results with the simple closed form theory of Berzins and Delahay. Moreover, together with the results of Nicholson for the coulostatic method, it is likely that linearized theories for all electrochemical techniques are valid for much larger overpotentials than previously assumed in the literature.

Table II. Variation of Overpotential^a with Ψ and ρ for Several Values of b for the Galvanostatic Method^b

Ψ	ρ	b				
		0.0	1.0	2.0	3.0	7.0
0.005	0.0	20.5 ^a	11.9	10.3	12.4	>30.0
	0.5	29.8	23.7	25.7	27.9	>30.0
	1.0	>30.0 ^c	>30.0	>30.0	>30.0	>30.0
	5.0	>30.0	>30.0	>30.0	>30.0	>30.0
0.01	0.0	20.8	12.2	11.3	14.0	>30.0
	0.5	30.0	24.5	25.8	29.8	>30.0
	1.0	>30.0	>30.0	>30.0	>30.0	>30.0
	5.0	>30.0	>30.0	>30.0	>30.0	>30.0
0.03	0.0	21.8	13.9	13.6	17.8	>30.0
	0.5	>30.0	25.5	26.1	29.5	>30.0
	1.0	>30.0	>30.0	>30.0	>30.0	>30.0
	5.0	>30.0	>30.0	>30.0	>30.0	>30.0
0.05	0.0	22.6	15.3	15.0	19.5	>30.0
	0.5	>30.0	25.5	26.3	30.0	>30.0
	1.0	>30.0	>30.0	>30.0	>30.0	>30.0
	5.0	>30.0	>30.0	>30.0	>30.0	>30.0
0.05	0.0	22.6	15.3	15.0	19.5	>30.0
	0.5	>30.0	25.5	26.3	30.0	>30.0
	1.0	>30.0	>30.0	>30.0	>30.0	>30.0
	5.0	>30.0	>30.0	>30.0	>30.0	>30.0
0.07	0.0	23.3	15.8	16.1	20.7	>30.0
	0.5	>30.0	25.6	26.3	>30.0	>30.0
	1.0	>30.0	>30.0	>30.0	>30.0	>30.0
	5.0	>30.0	>30.0	>30.0	>30.0	>30.0

^aNumerical values for overpotential arbitrarily defined as the potential at which linearized and nonlinearized results begin to differ by more than 1 mV.

^b $\alpha = 0.5$ and $\delta = 0.001$.

^cThe maximum departure from the equilibrium potential investigated was 30 mV, which explains why some values give agreement for greater than 30 mV.

EXPERIMENTAL

The experimental work which constitutes the last major section of this thesis was designed to evaluate the scope and limitations of the theoretical calculations already described. To do this two different systems were studied for which the electron transfer rate constants had been measured by accepted methods. The first system studied was azobenzene in water-ethanol solvent. This system was selected because the apparent electron transfer rate is a function of pH, and therefore the measurable rate constant could easily be varied by changing pH. Thus, the new technique could be evaluated for a fairly large range of rate constants without changing the depolarizer. The second system studied was the reduction of cadmium in aqueous solvent. This system was used primarily to evaluate the effect of double-layer charging, since the standard rate constant is sufficiently large to require experimental conditions for which double-layer charging is a significant factor.

To perform the experiments a simple instrument was assembled from commercially available components. Although this equipment performed satisfactorily, it was found that with current reversal adjustment of the switching time by

trial and error was tedious, and also inaccurate at short times. Thus, a more sophisticated instrument with automatic current reversal also was constructed. Since both of these instruments were used to collect data, and both have individual merits, a description of both instruments will be presented.

Instrumentation

The first instrument was simply a constant current source which could be programmed to provide bipolar currents of independently variable magnitude and duration. A block diagram of the circuit is shown in Figure 16a.

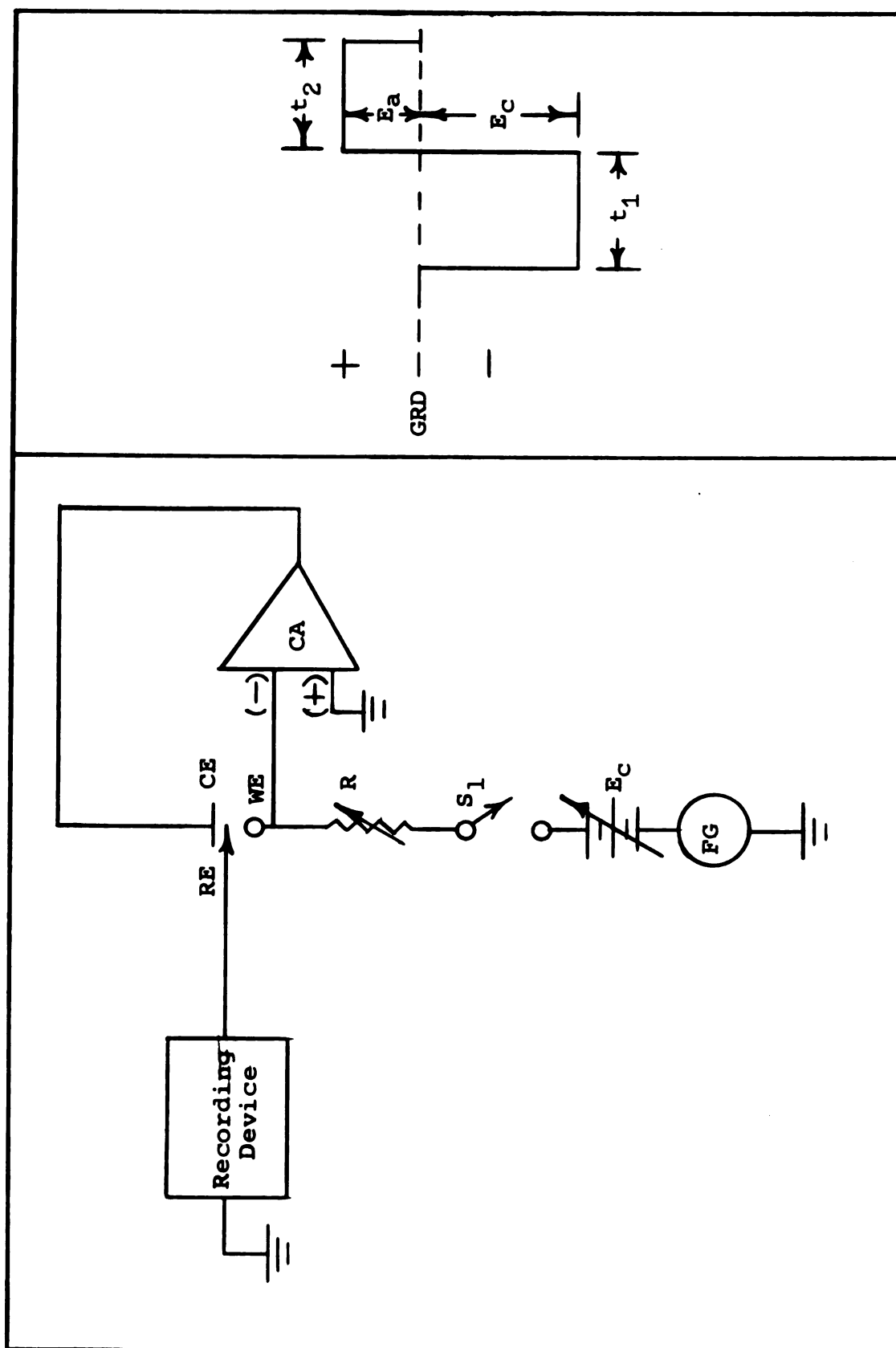
The control amplifier, CA, is a high gain differential amplifier (Wenking Potentiostat, Model 61RS, Brinkman Instruments) provided with negative feedback to maintain zero potential difference between the inverting (-) and noninverting (+) inputs. Since in the circuit of Figure 16a the noninverting input is grounded, the inverting input is maintained at virtual ground. Thus, if a voltage gate of amplitude $\underline{E}$ is applied to the resistor, $\underline{R}$, from the function generator (FG), a constant current given by $\underline{E}/\underline{R}$ flows from the output of amplifier CA. Since the electrolysis cell is in series with the output of CA, the constant current $\underline{E}/\underline{R}$ also passes between the counter electrode, $\underline{CE}$, and the working electrode, $\underline{WE}$. The chronopotentiogram is obtained by recording the potential of the reference electrode, $\underline{RE}$, vs. ground

Figure 16. (a) Circuit diagram of constant current instrument.

CA: Control amplifier
 (-): Inverting input
 (+): Noninverting input
 RE: Reference electrode
 CE: Counter electrode
 WE: Working electrode
 FG: Function generator
 Ec: Adjustable bias voltage
 R: Decade resistance box
 S1: Applies biasing voltage to voltage gate and
 applies trigger to ramp generator

(b) Programmed waveform applied through R for current switching.

GRD: Ground potential
 Ec: Cathodic voltage gate amplitude
 Ea: Anodic voltage gate amplitude
 t₁: Time duration of cathodic voltage gate
 t₂: Time duration of anodic voltage gate



b

a

Figure 16

(potential of WE) as a function of time on a suitable recording device.

The voltage gate for programming the constant current generator was obtained from a commercial function generator (Exact Electronics, Inc., Model 255). This instrument is equipped with both a main function generator, which generates triangular, sine, and square waveforms, and a ramp generator. Timing for the two function generator sections is independently adjustable, and a variety of different triggering modes can be selected from a single front-panel program switch.

For the present application an external trigger was used to start the ramp generator, which in turn was programmed to trigger the main generator at the end of the ramp cycle. In this mode a time delayed square wave could be obtained from the function generator (FG), the time delay being inversely proportional to the ramp frequency. When switch S_1 (Figure 16a) is closed a biasing voltage, $\underline{E}_C$, is applied to the current generator (causing a current $\underline{E}_C/\underline{R}$ to flow through the cell), and simultaneously a trigger pulse is applied to the ramp generator. The frequency of the ramp generator is adjusted to give the time delay, $\underline{t}_1$, shown in Figure 16b. The time interval, $\underline{t}_1$, is adjusted by trial and error to equal the forward transition time on the chronopotentiogram. After the interval, $\underline{t}_1$, the ramp generator internally triggers the main generator, which provides a square wave of amplitude $\underline{E}_C + \underline{E}_a$, and causes a current equal to $\underline{E}_a/\underline{R}$ to flow through

the electrolysis cell. Since $\underline{E}_c$ and $\underline{E}_a$ are of opposite polarity, current reversal occurs at this point, and electrolysis proceeds at the constant current $\underline{E}_a/\underline{R}$. By adjusting the amplitude of the main square wave, any value of $\underline{R}_i$ ($\underline{i}_R/\underline{i}_F$, see Equation 14) can be conveniently selected. The time interval, $\underline{t}_2$, is determined by the frequency of the main generator, and is simply adjusted to be large enough that the reverse transition time on the chronopotentiogram is observed.

Although this instrument functioned satisfactorily, adjustment of $\underline{t}_1$ by trial and error was very time consuming and difficult at short times. Thus, a second instrument was designed to overcome these problems by automatic current reversal at the forward transition time. This was accomplished with an electronic voltage comparator which provided automatic current switching when the potential of the working electrode reached a preselected potential corresponding to the potential at the transition time. A description of this instrument is contained in the following paragraphs.

The circuit for the instrument is shown in Figure 17. The amplifiers are solid state operational amplifiers which are identified in the legend of Figure 17. Power for the operational amplifiers was provided by a commercial power supply (Deltron Model OS 15-.3D, ± 15 V, ± 300 ma).

The circuit can be divided conceptually into three main parts. The current generating section involves amplifier CA,

Figure 17. Circuit diagram of constant current instrument with automatic current switching.

F: Voltage follower amplifier, Philbrick P25AU
 I: Inverter amplifier, Philbrick P25AU
 DA: Comparator amplifier, Philbrick P65AU
 B₁: Booster amplifier, Philbrick P66A
 DG: Differential gain amplifier, Analog 147A
 B₂: Booster amplifier, Analog B100
 CA: Control amplifier, Philbrick P25AU
 D₁, D₂: Zener diodes
 D₃: Solid state diode
 E_c: Adjustable comparison voltage
 E_B: Adjustable bias voltage
 P₁: Ten turn potentiometer
 R: Decade resistance box
 RE: Reference electrode
 CE: Counter electrode
 WE: Working electrode

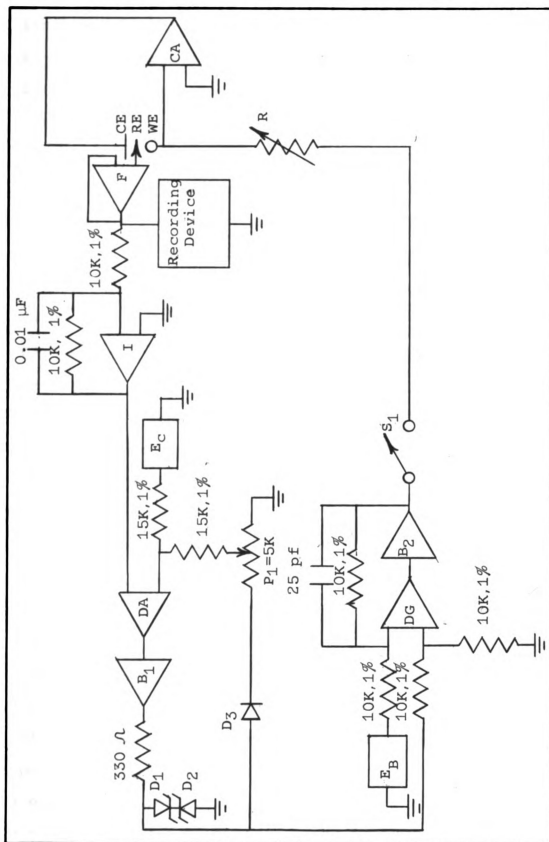


Figure 17

and its operation is identical with the instrument described above--i.e., a voltage E applied through R causes a constant current E/R to flow through the electrolysis cell. Amplifier DA is the comparator, which compares the voltage of the working electrode with a preselected transition time switching potential. Amplifiers I and DA provide signal conditioning described below for the comparator. The comparator is simply an operational amplifier operated in an open loop configuration. For example, whenever the noninverting input is at a potential more negative than the inverting input, the output of the amplifier is at its negative limit. Conversely, when the potential of the inverting input becomes more negative than the noninverting input, the output of the amplifier swings to its positive limit. The zener diodes on the output of the voltage comparator clip the voltage swings of the amplifier to provide symmetrical outputs. The booster (B_1) is used to provide sufficient current to ensure proper operation of the zeners. Amplifier DG biases the output of the voltage comparator, and supplies the appropriate square waves to R for generation of the cell current.

Detailed operation of the circuit can be understood by considering the following example. Suppose that initially a reduction is to be performed requiring a cathodic current. The potential of the working electrode will initially be at some equilibrium value, and then become progressively negative as electrolysis proceeds, until it reaches some negative

potential, $\underline{E}_C$, corresponding to the forward transition time. When the electrode reaches this potential, current reversal should take place. Thus, the potential $\underline{E}_C$ is selected and applied to the noninverting input of the voltage comparator. Since the potential of the reference electrode will become increasingly positive as electrolysis proceeds, this potential must be inverted before applying it to the other input of the voltage comparator. This inversion is accomplished with Amplifier I, which has a gain of -1. Amplifier F is a voltage follower, which is used to provide impedance matching. Since initially $\underline{E}_C$ is more negative than the inverting input of the voltage comparator (effectively the potential of the working electrode), the output of the voltage comparator is at its negative limit, and the circuit remains in this state as long as S_1 is open. When S_1 is closed, amplifier DG adds the output of the comparator to an adjustable bias voltage, $\underline{E}_B$, and the sum, $\underline{E}$, is applied through $\underline{R}$ generating the constant current $\underline{E}/\underline{R}$. As electrolysis continues the potential at the inverting input of the comparator becomes increasingly negative until it passes the preselected transition time potential, $\underline{E}_C$. When this happens, the output of the comparator (amplifier DA) swings to its positive limit, and if $\underline{E}_B$ is properly adjusted, the polarity of $\underline{E}$ changes causing current reversal. To ensure that the circuit remains in this state until the reverse transition time is observed, when the output of the comparator swings positive, diode D_3 becomes

forward biased, applying a positive reference to the comparator through potentiometer P_1 . By simply adjusting E_B , any ratio of current densities, R_1 , can be obtained.

Thus, a current reversal chronopotentiogram is recorded by setting E_C to the desired transition time potential, closing S_1 , and recording the potential at the output of the follower (Amplifier F) vs. time.

Cell and Electrodes. The electrolysis cell was a 200 ml Pyrex weighing bottle with a 60/12 standard taper joint. It was equipped with a tight-fitting Teflon lid, in which holes were provided for the various electrodes, nitrogen inlet, and a scoop used to transfer mercury drops. The working electrode was a hanging mercury drop, which was constructed according to the directions of Underkofler and Shain (59). Normally, two drops of mercury from a DME capillary were collected and transferred to the working electrode. The counter electrode was a platinum wire in the form of a spiral embedded in soft glass tubing, which was immersed directly in the solution under study.

The reference electrode was a saturated calomel contained in a separate compartment, and connected to the cell through a double junction salt bridge ending in a Luggin capillary. The section of the salt bridge adjacent to the SCE compartment contained 1 M sodium nitrate, while the Luggin capillary section was filled with the solution under study.

Chemicals. Zone refined azobenzene (Litton Chemicals, Inc.) was used without further treatment. Other chemicals were reagent grade with solids being dried at 110°C for several hours.

RESULTS AND DISCUSSION OF EXPERIMENTS

Kinetics of Reduction of Azobenzene

The reduction of azobenzene in protic solvents has been studied extensively (11,12,25,26,30,31,32,33,42,49,60). The most detailed research is that of Lundquist (41), who investigated the reduction in both aqueous and nonaqueous solvents. In aqueous solvents he showed that the overall reaction involves two electrons and two protons per molecule of azobenzene. He found that the apparent reversibility of the reduction is a function of pH, with reversibility increasing as pH decreases. He used cyclic voltammetry to measure the apparent heterogeneous rate constant for electron transfer as a function of pH under conditions where the rate of the reaction is pseudo first order. Thus, the heterogeneous rate constants he obtained are apparent k_s values with the pH dependence predicted by several possible mechanisms for the electrode reaction, he was able to arrive at a reasonable mechanism for reduction of azobenzene. He obtained further support for this mechanism from experiments in an aprotic solvent to which varying concentrations of acid were added.

Azobenzene appeared to provide an ideal system for evaluating the simple overpotential equation for chronopotentiometry (Equation 48), since based on Lundquist's results

a range of rate constants could be measured without changing the depolarizer (simply changing pH). Lundquist tabulated the rate constants as a function of pH, and therefore direct comparisons could be made with his data. Hence, measurements were made on azobenzene for experimental conditions identical to those employed by Lundquist (see footnotes to Table III).

The results of these measurements at several hydrogen ion concentrations are summarized in Table III, together with the values reported by Lundquist. A comparison of these two sets of data shows that at higher values of pH, where $\underline{k_s}$ is small, agreement is good, but at lower pH the values of $\underline{k_s}$ determined by chronopotentiometry are always larger than those obtained by Lundquist. It is interesting to note that these facts are consistent with the very approximate estimates made earlier for the upper limit of $\underline{k_s}$ that could be determined with Equation 48. Thus, it was estimated that double-layer effects should prevent accurate measurement for $\underline{k_s}$ greater than about 0.02 cm/sec. This prediction is in good agreement with the data of Table III. Moreover, the direction of the deviation for larger values of $\underline{k_s}$ is consistent with the effects predicted for double-layer charging. Thus, at low values of pH, where $\underline{k_s}$ is larger, it is necessary to employ higher current densities so that experimentally measurable values of ΔE are obtained. At these higher current densities charging current increases and the resulting current available for the faradaic process decreases. Since the faradaic

Table III. Variation of $(k_s)_{app}$ with Hydrogen Ion Concentration for Reduction of Azobenzene in 50% by Weight Ethanol-Water

$[H]^c$	$i_F \times 10^3, A/cm^2$	$\Delta E^b, mV$	ρ^e	$(k_s)_{app}^{e,f,h} \times 10^2, cm/sec$	$(k_s)_{app}^{e,g} \times 10^2, cm/sec$
0.01	0.656	39 $\pm$ 5	1.00-1.40	0.24-0.34	0.29
	0.659	33 $\pm$ 5	0.98-1.13	0.30-0.35	
	0.790	41 $\pm$ 5	1.05-1.43	0.29-0.39	
	0.815	45 $\pm$ 5	1.23-1.64	0.26-0.34	
0.05	2.63	14 $\pm$ 5	0.24-0.52	2.6-6.7	1.2
	3.98	25 $\pm$ 5	0.70-0.90	2.3-2.9	
	5.30	31 $\pm$ 5	0.72-1.05	2.6-3.8	
	7.86	41 $\pm$ 5	1.05-1.43	2.8-3.9	
	7.97	45 $\pm$ 5	1.20-1.59	2.6-3.4	
0.10	5.30	20 $\pm$ 5	0.40-0.70	3.9-6.9	1.9
	7.97	26 $\pm$ 5	0.58-0.88	4.7-7.1	
	9.96	33 $\pm$ 5	0.78-1.12	4.6-6.6	
	11.4	41 $\pm$ 5	1.05-1.43	4.1-5.6	
0.50	15.9	18 $\pm$ 5	0.35-0.63	13-24	6.1
	39.8	27 $\pm$ 5	0.61-0.92	22-34	
	40.8	20 $\pm$ 5	0.40-0.70	30-53	
	52.6	25 $\pm$ 5	0.55-0.85	32-50	

^a $1.0 \times 10^{-3} M$ azobenzene with sufficient lithium perchlorate added to maintain ionic strength at 0.75 M .

^b $A \pm 5$ mV reading error assumed for ΔE .

^c Adjusted by adding perchloric acid.

^d $R_i = -0.447$ and for the remaining results $R_i = -0.474$.

^e Range determined by assuming a constant error of ± 5 mV in measurement of ΔE .

^f Chronopotentiometric values.

^g Values tabulated by Lundquist.

^h Each value of $(k_s)_{app}$ listed is the average of 2 experiments.

current density determines overpotential, the magnitude of ΔE should decrease as the faradaic current density decreases. Thus, if ΔE decreases because of the influence of double-layer charging, the value of ρ obtained from Equation 48 will be smaller than if double-layer charging effects were negligible. Since ρ is inversely proportional to k_s , the value of k_s calculated would be too large, which is precisely the trend observed in Table III.

In summary, the experiments on azobenzene confirm the theory of the new method for measuring electron transfer rate constants. In addition, application of the technique proved to be as simple as anticipated, and therefore the method meets most of the requirements set forth in the Introduction. The experimental results further show that double-layer charging sets the upper limit for measurement of k_s , and that this upper limit is about 0.02 cm/sec. It was an attempt to extend this limit that prompted the calculations for the influence of double-layer charging, and the experiments for this case, which are discussed next.

Kinetics of Reduction of Cadmium

As mentioned earlier reduction of cadmium was used to evaluate the effects of double-layer charging. These experiments were necessarily performed at higher current densities, and therefore the instrument with automatic current reversal was employed (see discussion of Figure 17). To ensure that

this instrument functioned properly, experiments initially were performed on reduction of cadmium under conditions devoid of both double-layer and kinetic effects. These chronopotentiograms were displayed on an oscilloscope (Tektronix, Type 564), and photographed with a Polaroid camera attachment (Model C-12, and projected graticule, Model 100). The working electrode was a hanging mercury drop of radius 0.064 cm, and the current density was 9.99×10^{-4} A/cm². The half-wave potential measured by the method of Berzins and Delahay was -0.582 V vs. SCE. A diffusion coefficient of 2.8×10^{-5} cm²/sec was calculated from the Sand equation, after τ was determined by the procedure of Laity and McIntyre (39). These results compare with the values of -0.585 V vs. SCE and 6.5×10^{-6} cm²/sec obtained from the literature (27).

Next, reduction of cadmium was investigated under conditions where electron transfer is kinetically controlled, and where double-layer effects are necessarily prevalent. To evaluate the precision and scope of the theory, experiments were performed at several different current densities, and the observed values of ΔE recorded. In addition, values of the double-layer parameter were determined experimentally by the procedure described earlier (see discussion of Equation 113). These values of Ψ were used to identify the proper working curve in Figure 13, from which values of ρ corresponding to the observed ΔE were obtained. From these values of ρ ,

the corresponding values of $\underline{k}_s$ were calculated. Results of these experiments are summarized in Table IV, from which an average value of $\underline{k}_s$ equal 0.16 ± 0.04 cm/sec is obtained. The literature value of $\underline{k}_s$ determined by ac polarography is 0.60 cm/sec, which is outside the estimated experimental error for the value reported here. There are several equally reasonable explanations for this discrepancy, and therefore no attempt will be made to justify the difference between the value reported above and the literature value.

Because of the discrepancy with literature values for $\underline{k}_s$, it seemed appropriate to investigate the extent to which the theoretical model on which the calculations were based agreed with experiment for the entire chronopotentiometric curve. To do this one of the experimental chronopotentiograms used above in connection with Table IV was compared with a computer generated chronopotentiogram. The experimental chronopotentiogram was recorded with $\underline{R}_i = -0.5$ and $\underline{i}_{T_F} = 2.6 \times 10^{-2}$ A/cm², and is represented by the points in Figure 18. For this curve $\underline{n}\Delta E$ equals 40 mV and $\Psi = 0.015$ (calculated from Equation 113 for $\underline{i}_{T_s} = 1.0 \times 10^{-3}$ A/cm², $\tau_s = 0.83$ sec, $\underline{S} = -6.7 \times 10^5$ mV/sec). Using these data and the working curves of Figure 13, ρ equal 0.85 was obtained, which corresponds to $\underline{k}_s$ equal 0.16 cm/sec. Next, the computer program of Appendix C was used to calculate a theoretical chronopotentiogram for the same parameters as the experimental curve--i.e., $\Psi = 0.015$, $\rho = 0.85$, $\underline{R}_i = -0.5$, $\alpha = 0.5$, and

Table IV. k_s for Reduction of Cadmium^a

$i_{T_F} \times 10^2, A/cm^2$	$n\Delta E, {}^b mV$	ρ^c	ψ	$k_s^{c,e}, cm/sec$
2.3	31±5	0.57-0.76	0.014	0.16-0.21
2.6	42±5	0.78-1.00	0.015	0.13-0.17
2.6 ^d	40±5	0.74-0.95	0.015	0.14-0.18
3.6	48±5	1.01-1.30	0.019	0.14-0.18

^a1.0 x 10⁻³ M cadmium and 1.0 M potassium nitrate.

^bA ± 5 mV reading error assumed for $n\Delta E$.

^cRange determined by assuming a constant error of ± 5 mV in measurement of $n\Delta E$.

^dNew solution

^eEach value of k_s listed is the average of 2 experiments.

$\underline{n} = 2$. This theoretical chronopotentiogram is represented by the solid line in Figure 18. Actually, to place the theoretical chronopotentiogram on the potential axis of Figure 18, the theoretical curve was shifted to give the best fit between experiment and theory. This best fit corresponds to a half-wave potential of -0.590 V vs. SCE , which is in excellent agreement with the literature value for cadmium. The normalized transition time for the theoretical curve corresponds to a diffusion coefficient of $2.7 \times 10^{-5} \text{ cm}^2/\text{sec}$, which also agrees well with the value reported earlier.

The excellent agreement between theory and experiment illustrated by Figure 18 demonstrates conclusively that the model assumed for the theoretical calculations is a reasonable one. Thus, it at least seems unlikely that the discrepancy between the $\underline{k}_s$ reported here and the literature value can be attributed to inadequacies of the theory.

Figure 18. Chronopotentiogram for reduction of cadmium.
Line, theoretical.
Points, experimental.

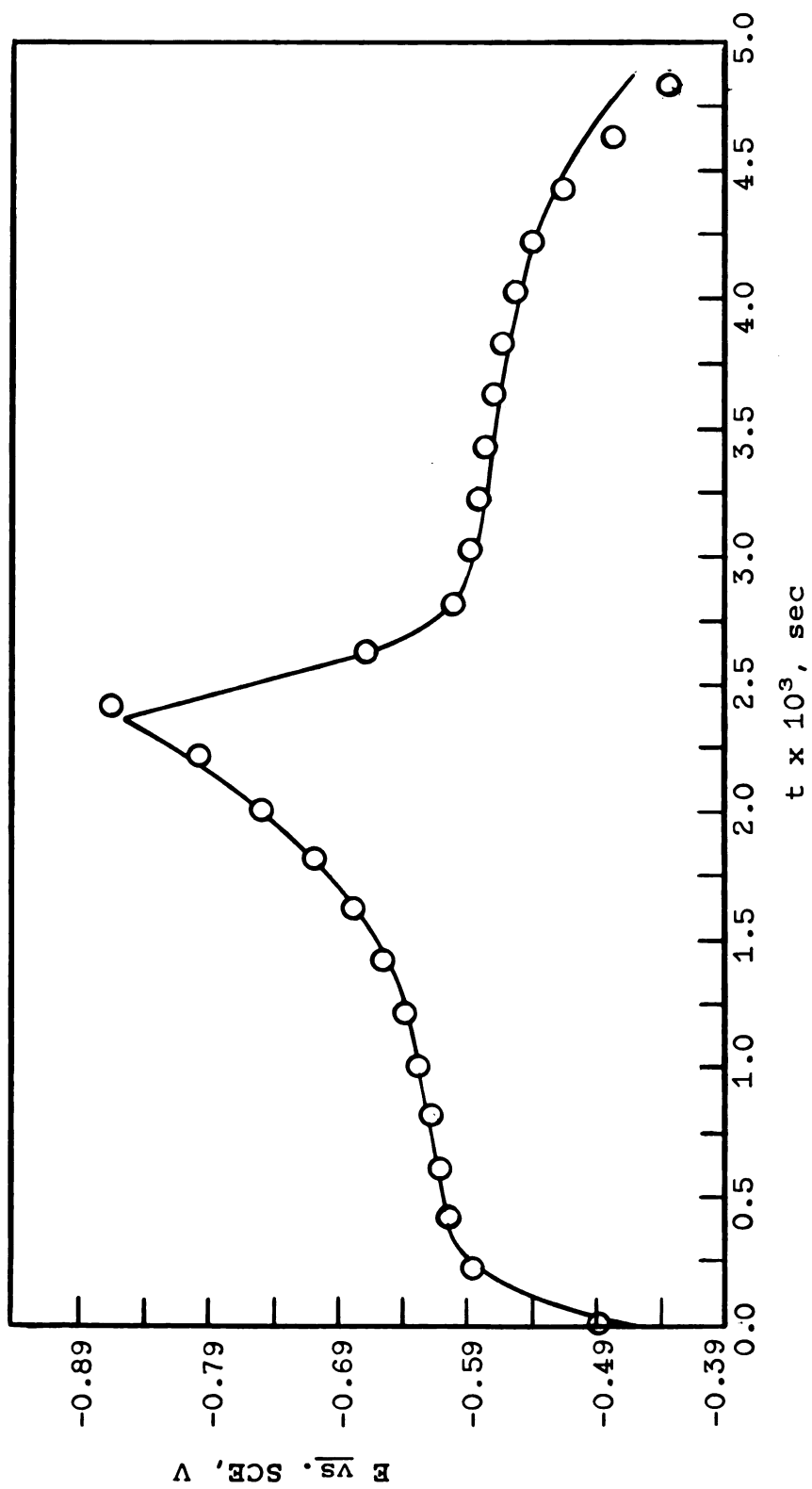


Figure 18

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LITERATURE CITED

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APPENDICES

APPENDIX A

Reduction of Boundary Value Problem to Integral Form

Equations 59 and 60 of the text can be integrated easily with the aid of the Laplace transformation, for which the following definition and notation will be adopted

$$\{C_0(x,t)\} = C_0(x,s) = \bar{C}_0 = \int_0^\infty [\exp(-st)] [C_0(x,t)] dt \quad (A1)$$

Thus, the Laplace transformation of Equation 59 with incorporation of Equation 61 is

$$D_0 \frac{d^2 \bar{C}_0}{dx^2} = s \bar{C}_0 - C_0^* \quad (A2)$$

The general solution for Equation A2 is

$$\bar{C}_0 = A \exp(-x \sqrt{s/D_0}) + B \exp(x \sqrt{s/D_0}) + C_0^*/s \quad (A3)$$

where A and B are integration constants. To satisfy Equation 62, B must be zero, which reduces Equation A3 to

$$\bar{C}_0 = A \exp(-x \sqrt{s/D_0}) + C_0^*/s \quad (A4)$$

the value of A can be determined by evaluating Equation A4 at $x = 0$

$$A = \bar{C}_0|_{x=0} - C_0^*/s \quad (A5)$$

Equations A4 and A5 can be combined to give

$$\bar{C}_0 = (\bar{C}_0|_{x=0} - C_0^*/s) \exp(-x \sqrt{s/D_0}) + C_0^*/s \quad (A6)$$

Since the remaining boundary conditions are in terms of flux it is necessary to derive an expression for the flux. This can be accomplished by differentiating Equation A6 with respect to x and evaluating the resulting expression at $x = 0$. The final result is

$$\left(\frac{\partial \bar{C}_0}{\partial x} \right)_{x=0} = (-\sqrt{s/D_0}) (\bar{C}_0|_{x=0} - C_0^*/s) \quad (A7)$$

Equation A7 can be rewritten in terms of concentration and flux of substance 0 as follows

$$\bar{C}_0|_{x=0} = C_0^*/s - D_0 f_0(s) / \sqrt{s} \quad (A8)$$

where the function $f_0(\underline{t})$ is used to represent the surface flux of 0 (see Equation 9 of the text)

$$f_0(t) = D_0 \left(\frac{\partial C_0(x,t)}{\partial x} \right)_{x=0} \quad (A9)$$

The inversion of Equation A8 can be accomplished with tables of Laplace transform pairs and the convolution theorem (13)

$$C_0|_{x=0} = C_0^* - 1/\sqrt{\pi D_0} \int_0^t \frac{f_0(\tau) d\tau}{\sqrt{t-\tau}} \quad (A10)$$

At this point the final boundary condition for surface flux (Equation 68 of the text) can be substituted in Equation A10, which gives

$$C_{O \ x=0} = C_O^* - 1/nF \sqrt{\pi D_O} \int_0^t \frac{i_f(\tau) d\tau}{\sqrt{t - \tau}} \quad (A11)$$

Treatment of the equation in $C_R(x,t)$ (Equation 60 of the text) is identical to that for $C_O(x,t)$, and the final result is

$$C_{R \ x=0} = C_R^* + 1/nF \sqrt{\pi D_R} \int_0^t \frac{i_f(\tau) d\tau}{\sqrt{t - \tau}} \quad (A12)$$

Equations A11 and A12 are general expressions valid for all times during electrolysis. In the case of current reversal, however, the function $i_f(t)$ is discontinuous (see Equations 68 and 69 of the text). Therefore, in applying Equations A11 and A12 to times greater than τ_F it is convenient to rewrite the integrals so that integration occurs over the intervals for which $i_f(t)$ is defined explicitly. Thus, for $\tau_F \leq t \leq \tau_R$ Equations A11 and A12 can be written as

$$C_{O \ x=0} = C_O^* - 1/nF \sqrt{\pi D_O} \int_0^{\tau_F} \frac{i_f(\tau) d\tau}{\sqrt{t - \tau}} - 1/nF \sqrt{\pi D_O} \int_{\tau_F}^t \frac{i_f(\tau) d\tau}{\sqrt{t - \tau}} \quad (A13)$$

and

$$C_{R \ x=0} = C_R^* + 1/nF \sqrt{\pi D_R} \int_0^{\tau_F} \frac{i_f(\tau) d\tau}{\sqrt{t - \tau}} + 1/nF \sqrt{\pi D_R} \int_{\tau_F}^t \frac{i_f(\tau) d\tau}{\sqrt{t - \tau}} \quad (A14)$$

At this point Equations A11 and A12, and A13 and A14, can be combined with Equation 4 of the text to give equations valid for all times during the experiment. The final results after simplification are

$$0 \leq t \leq \tau_F$$

$$\begin{aligned} \frac{i_{T_F}(D_R)^{\alpha/2}}{nFC_0^*(D_0)^{\alpha/2}k_s} - \frac{i_c(t)(D_R)^{\alpha/2}}{nFC_0^*(D_0)^{\alpha/2}k_s} &= \exp(-\alpha\sqrt{D_0}C_0^*/\sqrt{D_R}C_R^*) \\ &\exp(\alpha nF/RTC_1 \int_0^t i_c(\tau) d\tau) [1 - 2i_{T_F}\sqrt{t}/nFC_0^*\sqrt{\pi D_0} + 1/nFC_0^*\sqrt{\pi D_0} \\ &\int_0^t \frac{i_c(\tau) d\tau}{\sqrt{t-\tau}} - \exp(-nF/RTC_1 \int_0^t i_c(\tau) d\tau) - (2i_{T_F}\sqrt{t}/nFC_0^*\sqrt{\pi D_0}) \\ &\exp(\sqrt{D_0}C_0^*/\sqrt{D_R}C_R^*) \exp(-nF/RTC_1 \int_0^t i_c(\tau) d\tau) + (\exp(\sqrt{D_0}C_0^*/\sqrt{D_R}C_R^*) / \\ &nFC_0^*\sqrt{\pi D_0}) \exp(-nF/RTC_1 \int_0^t i_c(\tau) d\tau) \int_0^t \frac{i_c(\tau) d\tau}{\sqrt{t-\tau}}] \end{aligned} \quad (A15)$$

$$\tau_F \leq t \leq \tau_R$$

$$\begin{aligned} \frac{R_i i_{T_F}(D_R)^{\alpha/2}}{nFC_0^*(D_0)^{\alpha/2}k_s} - \frac{R_i i_c(t)(D_R)^{\alpha/2}}{nFC_0^*(D_0)^{\alpha/2}k_s} &= \exp(-\alpha\sqrt{D_0}C_0^*/\sqrt{D_R}C_R^*) \\ &\exp[(\alpha nF/RTC_1) (\int_0^{\tau_F} i_c(\tau) d\tau + 1/C_1 \int_{\tau_F}^t i_c(\tau) d\tau)] \left\{ 1 + (2i_{T_F}\sqrt{t} / \right. \\ &nFC_0^*\sqrt{\pi D_0} - 2i_{T_F}\sqrt{\tau_F}/nFC_0^*\sqrt{\pi D_0})^{\frac{1}{2}} (1 - R_i) - 2i_{T_F}\sqrt{t}/nFC_0^*\sqrt{\pi D_0} \end{aligned}$$

$$\begin{aligned}
& + 1/nFC_0^* \sqrt{\pi D_0} \int_0^{\tau_F} \frac{i_c(\tau) d\tau}{\sqrt{t - \tau}} + 1/nFC_0^* \sqrt{\pi D_0} \int_{\tau_F}^t \frac{i_c(\tau) d\tau}{\sqrt{t - \tau}} \\
& - (\exp[(-nF/RTC_1) (\int_0^{\tau_F} i_c(\tau) d\tau + 1/C_1 \int_{\tau_F}^t i_c(\tau) d\tau)]) [1 - \\
& (\exp(\sqrt{D_0} C_0^* / \sqrt{D_R} C_R^*) (2i_{T_F} \sqrt{t} / nFC_0^* \sqrt{\pi D_0} - 2i_{T_F} \sqrt{\tau_F} / nFC_0^* \sqrt{\pi D_0})^{\frac{1}{2}} \\
& (1 - R_i)) + \exp(\sqrt{D_0} C_0^* / \sqrt{D_R} C_R^*) (2i_{T_F} \sqrt{t} / nFC_0^* \sqrt{\pi D_0}) - \exp(\sqrt{D_0} C_0^* / \\
& \sqrt{D_R} C_R^*) / nFC_0^* \sqrt{\pi D_0} \int_0^{\tau_F} \frac{i_c(\tau) d\tau}{\sqrt{t - \tau}} - \exp(\sqrt{D_0} C_0^* / \sqrt{D_R} C_R^*) / nFC_0^* \sqrt{\pi D_0} \\
& \int_{\tau_F}^t \frac{i_c(\tau) d\tau}{\sqrt{t - \tau}}] \Bigg\}
\end{aligned}$$

[A16]

APPENDIX B

Relation of the Function $h(y)$ to Potential

The relation of the function $h(y)$ (see Equation 75 of the text) to potential can be obtained from the following expression (Equation 65)

$$i_c(t) = -C_1 \frac{dE(t)}{dt} \quad (B1)$$

This equation can be integrated ($E(0) = E_i$) and combined with Equation 75 of the text to give

$$E(t) = E_i - i_T(t)/C_1 \int_0^t h(\tau) d\tau \quad (B2)$$

The constant E_i in Equation B2 can be related to the initial bulk concentrations of O and R through the Nernst equation and the following definition of half-wave potential

$$E^0 = E_{\frac{1}{2}} + (RT/nF) \ln \sqrt{D_O/D_R} \quad (B3)$$

to give the following relationship valid prior to current reversal

$$0 \leq t \leq \tau_F$$

$$n[E(t) - E_{\frac{1}{2}}] = RT/F [b - 1/\psi \int_0^t h(x) dx] \quad (B4)$$

With the changes of variable (Equations 73 and 74 used in the

text, the final expression becomes

$$0 \leq t \leq \tau_F$$

$$n[E(y) - E_{\frac{1}{2}}] = RT/F [b - 1/\psi \int_0^y h(x) dx] \quad (B5)$$

Similarly, using the approach discussed in Appendix A, the expression for times after current reversal is

$$\tau_F \leq t \leq \tau_R$$

$$n[E(y) - E_{\frac{1}{2}}] = RT/F [b - 1/\psi \int_0^{y_f} h(x) dx - R_i/\psi \int_{y_f}^y h(x) dx] \quad (B6)$$

APPENDIX C

Computer Program

The numerical solution of Equations 80 and 81 of the text was performed on a Control Data 3600 digital computer with a program written in FORTRAN IV. Since this language is compatible with most modern computers, the FORTRAN source program is listed below. The following data are read in: NRUN, which is the total number of sets of Ψ , ρ , and α used; ERROR, which is the accuracy of the Newton-Raphson iteration; $\underline{R}$, which is $\underline{R}_1$ in the text; DELTA, which is δ in the text; THETA, which is $\underline{b}$ in the text; SWITCH, which is the potential at which the current is reversed; PSI, which is Ψ in the text; and ALPHA, which is α in the text. The output involves printing of the above data followed by the values of $N(E - E_2)$, y , $H(y)$, IF/IT (the faradaic current efficiency), ITERATIONS (the number of Newton-Raphson iterations), QC/QF (ratio of the coulombs of electricity used by the charging process to that used in the faradaic process) and $N \times \text{DERIVATIVE}$ (derivative of the potential-time curve at each point on the curve). In addition, the program constructs tangents at the initial portion of the curve, and at a point just prior to current reversal, and it also constructs the Berzins and Delahay line

which intersects the curve at $\underline{E}_F$. The equations of these lines and the point on the potential-time curve where $\underline{E}_F$ occurs are printed. A similar procedure is performed for the portion of the potential-time curve after current reversal. Finally, from these values of $\underline{E}_F$ and $\underline{E}_R$, the difference ΔE ($= \underline{E}_R - \underline{E}_F$) is calculated and printed.

```

C
PROGRAM CYCHRON
  QUASI WITH DOUBLE LAYER
  DIMENSION Y(2000),H(2000),POT(2000),ITER(2000),SQR(2000),
2SQRD(2000),A(1000),A(1000),C(1000),D(1000),G(1000),V(1000),
3W(1000),T(1000),Z(1000),QRAT(1500)
  READ 100,NTOT
  2 READ 100, NRUN
100 FORMAT(13)
  READ 900,ERROR
900 FORMAT(F10.0)
  READ 10,R
10 FORMAT(F10.0)
  READ 105,DELTA,THETA,SWITCH
105 FORMAT(3F10.0)
  1 READ 106,PSI,RHO,ALPHA
106 FORMAT(3F10.0)
  P=SORTF(DELTA)
  A(1)=0.
  B(1)=EXP(-ALPHA*THETA)
  C(1)=1.
  D(1)=EXP(THETA)
  A(2)=A(1)
  B(2)=B(1)
  C(2)=C(1)
  D(2)=D(1)
  E=DELTA/PSI
  SQR(1)=1.
  SQRD(1)=1.
  Q=1.
  ZI=0.0004
  S=0.
  DO 22 N=1,600
  M=N-1
  ITER(N)=0
  Y(N)=S*DELTA
  S=S+1.

```

continued

```

Q=Q+1.
L=N+1
SQR(L)=SQRTF(Q)
SQRD(L)=SQR(L)-SQR(N)
IF(N-2) 81,99,99
99 IF(N-3) 8,97,97
97 K=N-1
A(N)=0.0
DO 9 J=2,M
A(N)=A(N)+P*H(J)*SQRD(K)
K=K-1
9 CONTINUE
B(N)=B(M)*EXPF(ALPHA*E*H(M))
C(N)=C(M)*EXPF(-E*H(M))
D(N)=D(M)*EXPF(-E*H(M))
8 ZI=X
81 ITER(N)=ITER(N)+1
PNUM=-SQRTF(Y(N))+P*ZI+A(N)-D(N)*SQRTF(Y(N))*EXPF(-E*ZI)+D(N)*P*ZI
2*EXPF(-E*ZI)+A(N)*D(N)*EXPF(-E*ZI)-(RHO-RHO*ZI)/(B(N)*EXPF(ALPHA*
3E*ZI))+1.-C(N)*EXPF(-E*ZI)
DEN=P+E*D(N)*SQRTF(Y(N))*EXPF(-E*ZI)-D(N)*E*P*ZI*EXPF(-E*ZI)+D(N)*
2P*EXPF(-E*ZI)-A(N)*D(N)*E*EXPF(-E*ZI)+(RHO+RHO*ALPHA*E-RHO*ALPHA*
3E*ZI)/(B(N)*EXPF(ALPHA*E*ZI))+C(N)*E*EXPF(-E*ZI)
X=ZI-(PNUM/DEN)
IF(ITER(N)-200) 29,29,70
29 IF(ABSF(X-ZI)/ZI)-ERROR) 7,8,8
7 H(N)=X
IF(N-3) 17,18,18
17 POT(N)=25.68857*(THETA-E*H(N))
IF(N-3) 22,18,18
18 POT(N)=POT(M)-25.68857*E*H(N)
IF(SWITCH-POT(N)) 22,23,23
22 CONTINUE
23 LIMITF=N
N=N+1
M=N-1
K=N-1

```

continued

```

A(N)=0.0
DO 15 J=2,M
  A(N)=A(N)+P*H(J)*SQRD(K)
  K=K-1
15 CONTINUE
  B(N)=B(M)*EXPF(ALPHA*E*H(M))
  C(N)=C(M)*EXPF(-E*H(M))
  D(N)=D(M)*EXPF(-E*H(M))
  U=Q-1.
  XX=U
  PLIM=Q-2.
  G(1)=D(N)
  V(1)=(SQRTF(U*DELTA-PLIM*DELTA))*(1.-R)-SQRTF(U*DELTA)
  T(1)=B(N)
  Z(1)=C(N)
  K=1
  Q=1.
  S=S-1.
  W(K)=0.0
  PP=1.
  QRAT(1)=0.0
  FSUMH=0.0
DO 176 M=2,LIMITF
  FSUMH=FSUMF+H(M)
  QRAT(M)=FSUMH/(PP-FSUMH)
  W(K)=W(K)+P*H(M)*(SQRTF(U-PP+1.)-SQRTF(U-PP))
  PP=PP+1.
176 CONTINUE
  JJ=LIMITF+1
DO 30 I=JJ,1200
  M=I-1
  S=S+1.
  ITER(I)=0
  Y(I)=S*DELTA
80 ZI=X
  ITER(I)=ITER(I)+1

```

continued

```

PNUM=V(K)+G(K)*V(K)*EXP(-R*E*ZI)+W(K)+G(K)*W(K)*EXP(-R*E*ZI)
2+R*P*ZI+G(K)*R*P*ZI*EXP(-R*E*ZI)-(R*RHO-R*RHO*ZI)/T(K)*
3EXP(ALPHA*R*E*ZI)+1.-Z(K)*EXP(-R*E*ZI)
DEN=-G(K)*V(K)*R*E*EXP(-R*E*ZI)-R*E*G(K)*W(K)*EXP(-R*E*ZI)+R*P
2-R*P*E*G(K)*R*ZI*EXP(-R*E*ZI)+G(K)*R*P*EXP(-R*E*ZI)+(R*RHO+
3ALPHA*R*R*RHO*E-ALPHA*R*R*E*RHO*ZI)/T(K)*EXP(ALPHA*R*E*ZI)+R*E*
4Z(K)*EXP(-R*E*ZI)
X=ZI-(PNUM/DEN)
IF(ITER(I)-200)58,58,92
58 IF(ABSF((X-ZI)/ZI)-ERROR)10,80,80
10 H(I)=X
Q=Q+1.
U=U+1.
K=K+1
IF(2*LIMITF-I)41,44,44
41 SQR(K)=SQRTF(Q)
SQRD(K)=SQR(K)-SQR(K-1)
44 G(K)=G(K-1)*EXP(-R*E*H(I))
V(K)=(SQRTF(U*DELTA-PLIM*DELTA))*(1.-R)-SQRTF(U*DELTA)
W(K)=0.0
PP=1.
DO 199 J=2,LIMITF
W(K)=W(K)+P*H(J)*(SQRTF(U-PP+1.))-SQRTF(U-PP))
PP=PP+1.
199 CONTINUE
L=K
DO 33 N=JJ,I
W(K)=W(K)+R*P*H(N)*SQRD(L)
L=L-1
33 CONTINUE
T(K)=T(K-1)*EXP(ALPHA*R*E*H(I))
Z(K)=Z(K-1)*EXP(-R*E*H(I))
POT(I)=POT(M)-25.68857*R*E*H(I)
IF(POT(I)-180.)30,92,92
30 CONTINUE
92 LIMITR=I

```

continued

```

SUMFLIM=FSUMH
RSUMH=SUMFLIM
DO 882 L=JJ,LIMITR
PSUMH=RSUMH+R*H(L)
QRAT(L)=RSUMH/(PLIM+R*(XX-PLIM)-RSUMH)
XX=XX+1.
882 CONTINUE
70 PRINT 115
115 FORMAT(1H1/////////)
PRINT 120
120 FORMAT(45X,26HCYCLIC CHRONOPOTENTIOMETRY/)
PRINT 121
121 FORMAT(47X,23HQUASI WITH DOUBLE LAYER/////////)
PRINT 190,R
190 FORMAT(9HITR/ITF= F10.7/)
PRINT 129,THETA
129 FORMAT(11HLN(THETA)= F6.3/)
PRINT 130,DELTA
130 FORMAT(7HDELTA= F8.5/)
PRINT 135,LIMITF,LIMITR
135 FORMAT(8HLIMITF= 13,2X,8HLIMITR= 13/)
PRINT 145,ALPHA,RHO,PSI
145 FORMAT(7HALPHA= F6.3,2X,5HRHO= F10.6,2X,5HPSI= F10.6/)
PRINT 149,SWITCH
149 FORMAT(21HSWITCHING POTENTIAL= F9.3/)
PRINT 200,ERROR
200 FORMAT(19HCONVERGENCE ERROR= F14.9/)
PRINT 150
150 FORMAT(5X,9HN(E-E1/2),6X,9HN X DELTA, 6X,4HH(Y),8X,
212HIF/IT=1-H(Y),12X,10HITERATIONS,7X,5HQC/QF,7X,14HN X DERIVATIVE)
DO 27 I=1,LIMITR
IF(I-LIMITF)109,109,110
109 DERIV=- (25.68857*H(I))/PSI
GO TO 111
110 DERIV=- (25.68857*R*H(I))/PSI
111 DIF=1.-H(I)
PRINT 89,POT(I),Y(I),H(I),DIF,ITER(I),QRAT(I),DERIV

```

continued

```

89 FORMAT (1X,E16.7,F11.5,2E16.7,I15,6X,2E16.7)
27 CONTINUE
   XF1=0.0
   YF1=25.68857*THETA
   SLOPEF1=(POT(2)-YF1)/(Y(2)-XF1)
   FINTER1=YF1
   PRINT 310
310 FORMAT (33HEQUATION FOR FIRST LINEAR PORTION/)
   PRINT 300,SLOPEF1,FINTER1
300 FORMAT (3HY= F10.4,1X,4HX + F10.4/)
   X1=(POT(LIMITF)-FINTER1)/SLOPEF1
   SLOPEF2=(POT(LIMITF-1)-POT(LIMITF))/(Y(LIMITF-1)-Y(LIMITF))
   FINTER2=POT(LIMITF)-SLOPEF2*Y(LIMITF)
   PRINT 311
311 FORMAT (53HEQUATION FOR SECOND LINEAR PORTION IN FORWARD PORTION/)
   PRINT 301,SLOPEF2,FINTER2
301 FORMAT (3HY= F10.4,1X,4HX + F10.4/)
   X2=(YF1-FINTER2)/SLOPEF2
   SLOPER1=(POT(LIMITF+1)-POT(LIMITF))/(Y(LIMITF+1)-Y(LIMITF))
   RINTER1=POT(LIMITF)-SLOPER1*Y(LIMITF)
   PRINT 312
312 FORMAT (41HEQUATION FOR FIRST PORTION AFTER REVERSAL/)
   PRINT 302,SLOPER1,RINTER1
302 FORMAT (3HY+ F10.4,1X,2HX F10.4/)
   X3=(POT(LIMITR)-RINTER1)/SLOPER1
   SLOPER2=(POT(LIMITR-1)-POT(LIMITR))/(Y(LIMITR-1)-Y(LIMITR))
   RINTER2=POT(LIMITR)-SLOPER2*Y(LIMITR)
   PRINT 313
313 FORMAT (49HEQUATION FOR SECOND LINEAR PORTION AFTER REVERSAL/)
   PRINT 303,SLOPER2,RINTER2
303 FORMAT (3HY= F10.4,1X,2HX F10.4/)
   X4=(POT(LIMITF)-RINTER2)/SLOPER2
   DFU=Y(LIMITF)-X1
   DFUQ=DFU/4.
   DFL=X2-XF1
   DFLQ=DFL/4.
   XQFU=X1+DFUQ

```

continued

```

XQFL=XF1+DFLQ
SLOPEQF=(POT (LIMITF) -YF1)/(XQFU-XQFL)
QINTERF=POT (LIMITF) -SLOPEQF*XQFU
PRINT 314
314 FORMAT(38HEQUATION FOR DELAHAY'S LINE AT Y=.25YF/)
PRINT 304,SLOPEQF,QINTERF
304 FORMAT(EHY= F10.4,2X,4HX + F10.4/)
DRL=Y (LIMITR) -X3
DRLQ=0.1803*DRL
DRU=X4-Y (LIMITF)
DRUQ=0.1803*DRU
XQRU=Y (LIMITF) +DRUQ
XQRL=X3+DRLQ
SLOPEQR=(POT (LIMITF) -POT (LIMITR))/(XQRU-XQRL)
QINTERR=POT (LIMITF) -SLOPEQR*XQRU
PRINT 315
315 FORMAT(40HEQUATION FOR DELAHAY'S LINE AT Y=.1803YR/)
PRINT 305,SLOPEQR,QINTERR
305 FORMAT(3HY= F10.4,1X,2HX F10.4/)
IDUMF=5
970 IDUMF=IDUMF+1
SLOPDUMF=(POT (IDUMF) -POT (IDUMF-1))/(Y (IDUMF) -Y (IDUMF-1))
FINTDUM=POT (IDUMF) -SLOPDUMF*Y (IDUMF)
YINTSF=(FINTDUM-QINTERF)/(SLOPEQF-SLOPDUMF)
EINTSF=SLOPEQF*YINTSF=QINTERF
IF (IDUMF-LIMITF) 971,971,974
971 IF (EINTSF-POT (IDUMF)) 970,972,972
972 IF (POT (IDUMF-1) -EINTSF) 970,974,974
974 CONTINUE
IDUMR=LIMITF
980 IDUMR=IDUMR+1
SLOPDUMR=(POT (IDUMR) -POT (IDUMR-1))/(Y (IDUMR) -Y (IDUMR-1))
RINTDUM=POT (IDUMR) -SLOPDUMR*Y (IDUMR)
YINTSR=(RINTDUM-QINTERR)/(SLOPEQR-SLOPDUMR)
EINTSR=SLOPEQR*YINTSR+QINTERR
IF (IDUMR-LIMITR) 981,981,984

```

continued

```

981 IF (EINTSR-POT(IDUMR)) 982,982,980
982 IF (POT(IDUMR-1)-EINTSR) 984,984,980
984 CONTINUE
    DELTAE=EINTSR-EINTSF
    PRINT 985,EINTSF,YINTSF
985 FORMAT(42HDELAHAY'S LINE INTERSECTS E-Y CURVE AT E= F10.4,1X,
27HAND Y= F10.4/)
    PRINT 986,EINTSR,YINTSR
986 FORMAT(50HDELAHAY'S LINE INTERSECTS E-Y AFTER REVERSAL AT E=F10.4,
21X,3HY= F10.4/)
    PRINT 987,DELTAE
987 FORMAT(7HER-EF= F10.4/)
    IF (EINTSR+30.) 980,988,988
988 CONTINUE
    NRUN=NRUN-1
    IF (NRUN) 73,73,1
73  NTOT=NTOT-1
    IF (NTOT) 74,74,2
74  CONTINUE
    END

```

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