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Voltammetry at Constant Current and Its Application to Electrochemical Kinetics.

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VOLTMETRY AT CONSTANT CURRENT AND ITS APPLICATION

TO ELECTROCHEMICAL KINETICS

A Dissertation

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

in

The Department of Chemistry

by

Calvin G. Mattax

B. Chem., University of Tulsa, 1950
M. S., Louisiana State University, 1952
June, 1954
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TABLE OF CONTENTS

Acknowledgment ........................................... ii
List of Tables ............................................. v
List of Figures ............................................. vi
Abstract .................................................. ix

CHAPTER

I. INTRODUCTION AND REVIEW OF LITERATURE ........ 1
   Principle of the constant current method .......... 1
   Survey of the literature ................................ 2
   Scope of the dissertation ................................ 9

II. EXPERIMENTAL METHODS ................................ 10
   Apparatus for studies with stationary electrodes .... 12
   Electrolytic cells ........................................ 12
   Recorder and related equipment ......................... 15
   Apparatus for studies with the dropping mercury electrode ........................................ 18

III. EXPERIMENTAL STUDY OF REVERSIBLE AND IRREVERSIBLE PROCESSES ........ 21
   Reversible processes ..................................... 21
   Irreversible processes ................................... 26
   Verification of the theoretical treatment of irreversible polarographic waves ........ 30

IV. ANODIC OXIDATION OF METALS WITH THE FORMATION OF A PRECIPITATE OR A COMPLEX ION ........ 32
   Anodic oxidation with the formation of a complex ion ........................................ 33
   Anodic oxidation with the formation of a precipitate ........................................ 39
   Experimental verification for the anodic oxidation of silver in presence of cyanide or halides ........................................ 40

V. ELECTRODE PROCESSES WITH PREFERENTIAL ADSORPTION OF THE ELECTROLYSIS PRODUCT ........ 47
   Simplified derivation of the transition time for the adsorption step ......................... 48
   Experimental study ........................................ 51
VI. CATALYTIC PROCESSES

The boundary value problem. ................................. 55
Differential equations for the concentrations $C_0(x,t)$ and $C_R(x,t)$. ................................. 55
Variations of concentrations $C_0(x,t)$ and $C_R(x,t)$. .................................................. 57
Transition time. .................................................. 58
Transition time and determination of $k_f$. .................. 58
Properties of the transition time. ................................ 60
Validity of the assumption embodied in the relationship $C_0(0,t) = C_0^0$. ......................... 63
Application to the catalytic reduction of titanium(IV) in the presence of hydroxylamine .......... 64
VII. INFLUENCE OF IONIC INTERACTION AND TEMPERATURE ON THE KINETICS OF ELECTRODE PROCESSES

Ionic interaction in the electrolytic reduction of iodate. .................................................. 67
Introduction. .................................................. 67
Description and discussion of results. ........................................ 70
Influence of temperature on the kinetics of electrode processes. ........................................ 77
Introductory remarks. ........................................ 77
Description and discussion of results. ........................................ 80
VIII. CONCLUSION

APPENDIX

I. VALUES OF THE FUNCTION ........................................ 87
II. ANALYSIS OF IRREVERSIBLE POLAROGRAPHIC WAVES. ................ 88

General Considerations. ........................................ 88
Derivation of Delahay. ........................................ 89
Correction for the movement of the electrode through the solution. ........................................ 91
Derivation of Koutecky. ........................................ 92
Comparison of the treatments. ........................................ 93

Selected Bibliography. ........................................ 96
Vita ........................................ 99
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Half-wave potentials for the reduction of cadmium(II) and thallium(I) on mercury and for the reduction of ferriyanide ion on platinum</td>
<td>26</td>
</tr>
<tr>
<td>II</td>
<td>Values of ( \frac{i \nu^{3/2}}{2} ) for the anodic oxidation of silver in 5 mM potassium bromide</td>
<td>42</td>
</tr>
<tr>
<td>III</td>
<td>Potential corresponding to the electrocapillary maximum of mercury in solutions of various electrolytes</td>
<td>74</td>
</tr>
<tr>
<td>IV</td>
<td>Values of ( \frac{i}{i_d} ) according to Koutecky</td>
<td>94</td>
</tr>
</tbody>
</table>
**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Schematic diagram of potential-time curves obtained in voltammetry at constant current density</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>Basic lay-out for electrolysis at constant current</td>
<td>11</td>
</tr>
<tr>
<td>3</td>
<td>Cells for electrolysis at constant current</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>Schematic circuit of apparatus for recording of potential-time curves</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>Schematic circuit of synchronisation device for electrolysis with the dropping mercury electrode</td>
<td>19</td>
</tr>
<tr>
<td>6</td>
<td>Potential-time curve for the reduction of 4 mM cadmium(II) and the subsequent anodic oxidation of cadmium amalgam. Supporting electrolyte: 1 M potassium nitrate</td>
<td>22</td>
</tr>
<tr>
<td>7</td>
<td>Plot of log[($c^{-1/2} - e^{1/2}$)/$c^{1/2}$] against potential for reversible electrode processes: 4 mM potassium ferricyanide in 0.1 M sulfuric acid; 4 mM thallium(I) in 1 M potassium nitrate; 4 mM cadmium(II) in 1 M potassium nitrate</td>
<td>24</td>
</tr>
<tr>
<td>8</td>
<td>Potential-time curve for the irreversible reduction of nickel in 1 M potassium chloride</td>
<td>28</td>
</tr>
<tr>
<td>9</td>
<td>Plots of log[($c^{-1/2} - e^{1/2}$)/$c^{1/2}$] versus potential for totally irreversible electrode processes: Curve 1, oxygen in acetate buffer (pH = 4.6); Curve 2, oxygen in 1 M sodium hydroxide; Curve 3, cobalt(II) in 1 M potassium chloride; Curve 4, nickel(II) in 1 M potassium chloride</td>
<td>29</td>
</tr>
<tr>
<td>10</td>
<td>Potential-time curve for the anodic oxidation of silver in the presence of cyanide ion. Solution composition: 5 mM potassium cyanide, 0.1 M potassium nitrate</td>
<td>43</td>
</tr>
<tr>
<td>11</td>
<td>Plot of log[($c^{-1/2} - e^{1/2}$)/$c^{1/2}$] for the anodic oxidation of silver in the presence of cyanide</td>
<td>44</td>
</tr>
<tr>
<td>12</td>
<td>Potential-time curves for the anodic oxidation of silver in the presence of (1) 1 mM lithium chloride; current density equals 0.198 milliamperes per square centimeter; (2) 5 mM lithium chloride; current density equals 0.584 milliamperes per square centimeter. Supporting electrolyte: 0.1 M potassium nitrate</td>
<td>45</td>
</tr>
</tbody>
</table>
13. Plots of $\log \left[1 - \left(t/t_d\right)^n\right]$ for the anodic oxidation of silver in the presence of (1) 5 mM sodium bromide, (2) 5 mM lithium chloride.


15. Plot of $1/n$ versus current density for the adsorption step in the reduction of methylene blue.

16. Plot of $\sqrt[1/2]{t_{1/2}}$ versus current density for the adsorption step in the reduction of 4 mM methylene blue (line 1), 2.4 mM methylene blue (line 2), 1 mM thionine (line 3).

17. Variations of the function $2\gamma/\gamma'$ against constant current.

18. Plots of the ratio $\left(t_c/t_d\right)^{1/2}$ against current density for catalytic reduction at constant current.

19. Plots of the ratio $\left(t_c/t_d\right)^{1/2}$ against current density for the catalytic reduction of titanium(IV) in the presence of hydroxylamine.

20. Plots of $\log k_{ch}$ versus potential for the reduction of iodate in 0.05 M sodium hydroxide in the presence of varying amounts of "indifferent" electrolytes.

21. Plots of $\log k_{ch}$ against the logarithm of the ionic strength for the reduction of iodate in 0.05 M sodium hydroxide.

22. Plots of $\log k_{ch}$ against the logarithm of the cation concentration for the reduction of iodate in 0.05 M sodium hydroxide in the presence of various amounts of indifferent electrolytes. Values of $k_{ch}$ were calculated at the potential corresponding to the electrocapillary maximum.

23. Plots of $\log \left[1 - \left(t/t_d\right)^{1/2}\right]$ versus potential for the irreversible reduction of chromium(III) in 1 M potassium nitrate at various temperatures.

24. Plots of $\log \left[1 - \left(t/t_d\right)^{1/2}\right]$ versus potential for the irreversible reduction of oxygen in acetate buffer at various temperatures.

25. Plots of $\alpha_n$ versus temperature for various irreversible processes: Curve 1, iodate in 1 M sodium hydroxide; Curve 2, nickel(II) in 1 M potassium chloride; Curve 3, chromium(III) in 1 M potassium nitrate; Curve 4, oxygen in acetate buffer.
26. Plots of $\log k_{f,h}^0$ versus reciprocal temperature for various irreversible processes; Curve 1, iodate in 1 M sodium hydroxide; Curve 2, nickel(II) in 1 M potassium chloride; Curve 3, chromium(III) in 1 M potassium nitrate; Curve 4, oxygen in acetate buffer.

27. Plots of $\log k_{r,h}$ versus potential according to Delahay (line 1) and Koutecky (line 2) for the reduction of iodate in 1 M sodium hydroxide.
ABSTRACT

Quantitative treatments for several types of electrode processes in voltammetry at constant current are discussed, and experimental methods for the study of these processes are described. Application is made to the study of the effect of ionic interaction and temperature in electrochemical kinetics.

The following processes were treated in this dissertation:
(1) anodic oxidation of a metal with formation of a sparingly soluble substance or a complex ion; (2) processes with preferential adsorption of the main product of electrolysis; (3) catalytic processes in which the electrolyzed substance is regenerated by a first order chemical reaction. The validity of the theoretical conclusions for the above three cases was confirmed experimentally. Additional experimental confirmation was obtained for the treatments of reversible and irreversible processes previously developed in this laboratory.

Application to the study of ionic interaction in electrochemical kinetics has led to the fundamental observation that indifferent ions are involved in electron transfer processes. Furthermore, the rate constant for the electron transfer process is a linear function of the concentration of indifferent electrolyte.

The influence of temperature on the rate of an electrode process is far more complex than the effect one would expect on the basis of a variation of the free energy of activation with temperature. Possible complications are discussed and experimental results are presented.
CHAPTER I

INTRODUCTION AND REVIEW OF LITERATURE

Voltammetry at constant current, although one of the oldest electrochemical methods, has seldom been applied. The method was originally applied to the verification of Fick's diffusion laws but the potentialities of electrolysis at constant current in electrochemical kinetics and analytical chemistry were only recently recognized. We must be indebted to Gierst and Juliard (16) (17) for having revived the method.

The essential features of voltammetry at constant current may be summarized as follows:

(1) The current passing through the cell is constant, regardless of the state of polarization of the electrodes.

(2) The apparatus is such that mass transfer occurs only by diffusion - in general, semi-infinite linear diffusion.

(3) The potential of one of the electrodes (the working electrode) is measured against a reference electrode.

The concentrations of the electrolyzed substance and of its main electrolysis product vary during electrolysis, and consequently the potential of the working electrode varies. The resulting potential-time curve obtained under the above conditions is shown in Figure 1. Four characteristic segments of the curve can be distinguished.
Figure 1. Schematic diagram of potential-time curves obtained in voltammetry at constant current density.
(1) At the beginning of electrolysis, the potential varies rapidly until the working electrode reaches a potential at which the electrochemical reaction occurs. The slope in the initial segment (AB) is related to the quantity of electricity used in charging or discharging the electrical double layer at the electrode surface. At sufficiently low current densities the effect of the capacity of the double layer may be neglected, and segment AB is virtually parallel to the ordinate axis.

(2) In segment BC the electrochemical reaction occurs at a rate prescribed by the current density, and consequently the concentration of the electrolyzed substance at the electrode surface decreases.

(3) When the concentration of electrolyzed substance becomes virtually equal to zero, the potential varies rapidly toward more cathodic (or anodic) values. The segment CD is practically parallel to the ordinate axis when the effect of the charging of the double layer can be neglected, i.e., when the current density is relatively low.

(4) A new electrochemical process such as the reduction of the supporting electrolyte occurs along segment DE, and the electrode potential is more or less stabilised until the concentration of the new substance being electrolyzed becomes equal to zero.

The time required to completely deplete the electrolyzed substance is termed the "transition time." If segments AB and CD are almost vertical, the transition time can be readily measured in Figure 1.

The earliest theoretical treatment related to concentration changes in electrolysis at constant current was reported by Weber (30) in 1879. Weber obtained an expression for concentration as a function of time and distance from the electrode surface. The treatment of Weber is somewhat cumbersome to apply because the concentration of electrolyzed substance is expressed under the form of an infinite series. A more elegant approach was followed by Sand who derived the value of the transition time. His reasoning is as follows. Sand assumed that mass transfer
is diffusion controlled, and applied Fick's second law of diffusion

\[
\frac{dC_0(x,t)}{dt} = D_0 \frac{d^2C_0(x,t)}{dx^2}
\]  

(1-1)

as written on the assumption that the diffusion coefficient \(D\) is independent of the concentration of electrolyzed substance. In equation (1-1) \(x\) and \(t\) represent the distance from the electrode and the time elapsed since the beginning of electrolysis.

Since the electrolysis current is constant, the flux of electrolyzed substance at the electrode surface is constant. Hence

\[
D_0 \int_{-\infty}^{x=0} \frac{dC_0(x,t)}{dx} \, dx = \frac{i_o}{nF}
\]  

(1-2)

where \(i_o\) is the current density, \(n\) the number of electrons involved in the electrochemical reaction, and \(F\) the faraday. Equation (1-2) is the boundary condition for the present problem. Furthermore, one has \(C(x,0) = C^0\) and \(C(x,t) \to C^0\) for \(x \to \infty\), where \(C^0\) is the initial concentration of electrolyzed substance. The solution - as written for \(x \geq 0\) - is

\[
C_0(x,t) = C^0 - \frac{2i_o t}{\pi F D_0} \frac{1}{x^{1/2}}
\]  

(1-3)

At the transition time \(\tau\) the concentration \(C(x,t)\) is equal to zero and one derives from (1-3)

\[
\tau^{1/2} = \frac{\pi F D_0^{1/2} C^0}{2 i_o}
\]  

(1-4)
It is seen from equation (6-4) that the square root of the transition time is proportional to the bulk concentration of electrolyzed substance and inversely proportional to the current density \( i_0 \). The transition time is directly proportional to the diffusion coefficient of the electrolyzed substance. This last relationship was used by Sand, Cottrell (9), and von Stackelberg and coworkers (29) in the determination of diffusion coefficients of various inorganic ions.

The value of the electrode potential during electrolysis was derived by Karaoglanoff (21) for the case of reversible processes, i.e., for processes for which the Nernst equation can be applied. The potential is calculated by introducing the concentration \( C_0(0,t) \) given by equation (1-5) and the concentration of the product of electrolysis in the Nernst equation. The latter concentration is derived by solving Fick's equation for proper boundary and initial conditions. If \( R \) symbolizes the product of electrolysis, one has the boundary condition

\[
D_R \left[ \frac{dC_R(0,t)}{dx} \right]_{x=0} = -\frac{C_0}{nF}
\]

which expresses that the sum of the fluxes of substances \( O \) and \( R \) is equal to zero (see equation (1-2)). Furthermore, one has \( C_R(x,0) = 0 \) if substance \( R \) is not present in solution before electrolysis. Finally, the function \( C_R(x,t) \) is bounded for large values of \( x \), i.e., \( C_R(x,t) \to 0 \) for \( x \to \infty \). The value of \( C_R(x,t) \) at the electrode surface is

\[
C_R(0,t) = \left( \frac{D_0}{D_R} \right)^{1/2} \left[ C_0 - C_0(0,t) \right]
\]
By introducing $C_0(0,t)$ and $C_R(0,t)$ in the Nernst equation, Karaoglanoff obtained

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{C_{0i}}{C_{0i}^*}$$

(1-7)

where

$$E_{1/2} = E^o + \frac{RT}{nF} \ln \frac{D_0^*}{D_0}$$

(1-8)

If substance 0 is electrolyzed on a mercury electrode, the potential $E_{1/2}$ is equal to the polarographic half-wave potential (2).

By relating the flux of the substance undergoing electrochemical reaction to the kinetics of the electrode process Delahay and Berzins treated the case in which the electrochemical reaction is irreversible. Thus

$$\frac{C_0}{nF} = \frac{b}{b'} C_0(0,t) - \frac{b}{b'} C_R(0,t)$$

(1-9)

where the C's are the concentrations at the electrode surface ($x = 0$), and the k's are the formal rate constants for the forward and backward electrochemical reactions, respectively. The k's are rate constants for an heterogeneous process and are expressed in units cm. sec. \(^{-1}\).
The concentrations \( C_Q(0,t) \) and \( C_R(0,t) \) derived by Kar&oglonoff (21) may be directly introduced into equation (1-9) above since Kar&oglonoff made no assumption as to the kinetics of the electrode process. For the case in which \( k_{b_{h}} \) may be neglected, i.e., when the overvoltage is greater than 0.1 volt (15), the following relationship is obtained

\[
\frac{i_0}{nF} = \frac{2i_0}{\pi} \left( C_0 - P \theta^{1/2} \right)
\]  

(1-10)

where \( P \) is defined as follows:

\[
P = \frac{2i_0}{\pi} \frac{D_0}{nF \theta^{1/2}}
\]  

(1-11)

As in the case of the reversible electrode process the transition time obeys the relationship \( C_0 = P \theta^{1/2} \). Upon introducing the transition time in (1-10) one obtains:

\[
\frac{2i_0}{\pi} \theta^{1/2} = \frac{D_0}{2(\theta^{1/2} - \theta^{1/2})}
\]  

(1-12)

The rate constant \( k_{f_{h}} \) is an exponential function of the electrode potential of the form

\[
k_{f_{h}} = k_{0} f_{h} e^{\frac{-\Delta E_{f_{h}}}{nF}}
\]  

(1-13)

where \( k_{0} f_{h} \) is the value of \( k_{f_{h}} \) for \( E = 0 \) in the normal hydrogen electrode scale, \( \alpha \) is the transfer coefficient, and \( n_{a} \) the number of electrons
involved in the activation step. The combination of equations (1-12) and (1-15) yields

\[
E = \frac{RT}{\alpha F} \ln \left( \frac{k_0^d T^{1/2}}{T^{1/2} D_0} + \frac{RT}{\alpha F} \ln \left[ 1 - \frac{t}{t/2} \right] \right)
\]

which shows that a plot of the decimal logarithm of \((1 - (t/2)^{1/2})\) against potential should yield a straight line whose reciprocal slope is \(RT/\alpha n_a F\). Hence the value of \(\alpha n_a\) may be determined from analysis of the potential-time curves. The rate constant \(k_0^d T_{sh}\) is calculated by extrapolation to zero potential and by application of equation (1-13).

Theoretical treatments for the following types of electrochemical reactions were also developed by Delahay and Bersins:

1. Electrode processes preceded by a first order chemical reaction.
2. Electrode processes followed by reversal of current.
3. Electrolysis of two component systems.

For Case 1 it was shown by Delahay and Bersins (12) that the transition time depends on the kinetics of the chemical reaction preceding the electrochemical process. Application was made to the study of the mechanism of the electrolysis of complex ions. It was revealed that certain complex ions are directly reduced at the electrode, while other complexes undergo a chemical reaction before the electron transfer takes place.

For processes involving reversal of the current (Case 2) Bersins and Delahay showed that the transition time for the process is one-third of the preceding transition time. By analysis of potential-time curves.
it is possible to study the kinetics of the electrode process in both directions when overvoltages are larger than 0.1 volt.

The transition time for the second step in the electrolysis of a two component system depends not only on the bulk concentration of this substance but also on the concentration of the component more easily reduced or oxidized. This problem was treated quantitatively by Berzins and Delahay. The stepwise reduction of a single substance also lends itself to quantitative treatment.

**Scope of this dissertation**

The primary purpose of this dissertation is to develop quantitative treatments of various types of electrode processes which were not considered by previous investigators. In addition, application has been made to the study of various factors such as temperature and ionic interaction which influence the kinetics of electrode processes.

The various phases of this investigation are as follows:

1. Development of experimental methods.
2. Experimental study of reversible and irreversible electrode processes.
3. Case of the anodic oxidation of a metal which is followed by a chemical reaction involving the metallic ion with the formation of (a) a sparingly soluble precipitate and (b) a stable complex ion.
4. Case in which there is preferential adsorption of the main product of the electrochemical reaction.
5. Electrode processes in which the electrochemical reaction is coupled with a chemical reaction involving regeneration of the substance undergoing electrochemical reaction.
6. Applications of voltammetry at constant current and polarography to electrochemical kinetics: (a) study of the effect of temperature and ionic interaction; (b) study of the influence of temperature in electrochemical kinetics.
CHAPTER II

EXPERIMENTAL METHODS

Potential-time curves were obtained either with stationary electrodes or the dropping mercury electrode. A pen-and-ink recorder was generally used in the case of stationary electrodes, although a few recordings were made with a cathode-ray oscillograph. With the dropping mercury electrode recordings must be made in a fraction of the drop life, if the electrode is to behave as a stationary electrode; hence a cathode-ray oscillograph must be utilized. Recordings with the latter instrument are less precise than with a pen-and-ink recorder, and the cathode-ray oscillograph was utilized only at high current densities or when it was essential to use the dropping mercury electrode; this was the case when the electrode surface had to be continuously renewed as in the adsorption studies (Chapter V).

The apparatus for both the dropping mercury electrode and stationary electrodes is schematically represented in Figure 2. The voltage regulator P supplies a constant voltage of 200 to 300 volts to the electrolysis vessel C connected in series with the large resistance $R_1$. Resistance $R_1$ is made so large that most of the voltage drop (99% or more) in the circuit occurs across $R_1$. Thus, the current passing through the cell is essentially determined by $R_1$ and is virtually independent of the process occurring in the cell C. The current
Figure 2. Basic lay-out for electrolysis at constant current.
through the cell is determined by measuring the potential drop across the calibrated resistance $R_2$. The potential of the working electrode is recorded by means of instrument $V$, which will be discussed in detail below.

The modifications necessary to adapt the apparatus to recordings with stationary electrodes and with the dropping mercury electrode are considered separately in the following sections.

APPARATUS FOR STUDIES WITH STATIONARY ELECTRODES

Electrolysis cells

Electrolytic cells were designed to reproduce as well as possible the conditions of semi-infinite linear diffusion at the polarizable electrode. Solid electrodes (platinum) and mercury pool electrodes were used. The cells designed for the latter type of electrode will be first described. The mercury pool electrode was used by Delahay and Berzins but various modifications of their design were introduced. The two types of cell represented in Figure 3 were finally adopted.

The cells were composed of three electrodes: the mercury pool, the auxiliary platinum electrode and the reference electrode. The first two electrodes were connected to the constant current power supply, and the voltage between the mercury pool and the reference electrode was recorded. The mercury pool was renewed before each recording. In the case of cell A, one arm of the three-way stopcock was connected to a mercury reservoir of 200 ml. A constant level was thus obtained. The stopcock was closed to avoid contamination of the mercury in the reservoir. A mercury pool of reproducible area was obtained in cell B by
introducing a known volume of mercury in the cell. The diameter of the mercury in cell A was 1.4 cm, but even larger diameters are advisable in order to minimize the effect of the mercury meniscus. The area of the mercury pool varies with potential, because the interfacial tension mercury-solution - and consequently the curvature of the meniscus - depend on the potential of the mercury pool. The movement of the surface of the pool causes a slight stirring of the solution, and a departure from conditions of mass transfer under the sole influence of diffusion. In cell B the diameter of the mercury pool was approximately 2.5 cm.

A commercial saturated calomel electrode (Beckman industrial model) was used. To avoid errors resulting from the ohmic drop in the solution the reference electrode was immersed in a sleeve whose tip (outside diameter 1 mm.) was very close (0.5 mm. or less) to the surface of the mercury pool. Since the value of the potential of the auxiliary platinum electrode was unimportant, both compartments of the cell were filled with the solution being electrolysed. Diffusion from one compartment to the other was practically prevented by a disk of fritted glass as in H cells used in polarography. No plug of agar-agar, as customarily used in polarography, was needed.

Cell A is somewhat more convenient to use than cell B because of the ease of renewing the mercury pool and the simplicity of design. This cell can thus be recommended for exploratory work or for analytical determinations. It has, however, the disadvantage of not providing for a uniform distribution of current density (asymmetric position of the auxiliary electrode with respect to the mercury pool). This disadvantage is eliminated in cell B of Figure 3. The results reported below
Figure 3. Cells for electrolysis at constant current.
were obtained with cell A, but it was verified that the operation of
cell B is entirely satisfactory.

The platinum electrode was constructed by scaling a platinum disk
(approximately 0.3 cm\(^2\)) in a glass sleeve in the form of a U tube. The
platinum disk was horizontal, and the lid of the sleeve extended approx-
imately 0.5 cm. above the disk.

**Recorder and related equipment**

The electrolytic cell in series with resistance \(R_1\) (Figure 4) was
connected to a commercial power supply with electronic regulation of
the output voltage (200-300 volts). The current intensity was determined
from the ohmic drop in a calibrated resistance \(R_2\), the cell being short-
circuited by means of switch \(S_4\) (to avoid progressive polarisation and
a drift in reading). The current intensity measured in this manner was
slightly too high since there was no counter e.m.f. of the cell. The
corresponding relative error is of the order of 0.3 per cent (total
applied voltage 300 volts, counter e.m.f. of 1 volt). A manually
operated quadruple pole double throw relay was inserted in the cell to
reverse the current through the cell at some stage of the electrolysis
(the time elapsed during the reversal of current is smaller for a relay
than for a toggle switch). At the time of the current reversal, resis-
tance \(R_5\) was automatically introduced in the circuit by relay RL 1, and
the current could thus be decreased during electrolysis with reversed
current. This is advantageous because the transition time for the
reversed process is only one third of the transition time for the direct
process when the current density is the same in both processes (2).
Figure 4. Schematic circuit of apparatus for recording of potential-time curves.
When the current density during the reversed process is decreased, the transition time increases and more precise results are obtained.

The voltage between the mercury pool (grounded) and the reference electrode was applied to a Brown recorder having a pen speed of 1 second for full scale deflection, a chart speed of 480 inches per hour, and a sensitivity corresponding to full scale deflection for a 2.5 millivolt input voltage. A compensating voltage was applied to the input of the recorder for the following reason. In the initial step of a potential-time curve there was generally a rapid and large (several tenths of a volt) variation of the potential of the mercury pool electrode. Only low sensitivities could thus be used and potentials were inaccurate. This was avoided by almost completely compensating the change of voltage corresponding to the initial segment of the potential-time curve. The compensating voltage, supplied by a student potentiometer (switch S2 in position 1), was applied between points A and B. The input of the recorder was disconnected from point B (relay RL 2) before the electrolysis was started. In this manner the pen of the recorder was not swung violently against the zero point of its course before recording. The electrolysis was started by closing relay RL 2, the motor driving the chart of the recorder being always started a few seconds before the closing of relay RL 2 to avoid missing the initial segment of the potential-time curve.

The recorder scale was calibrated by turning switch S2 in position 2, and applying a known voltage (potentiometer to AB) to the recorder. The sensitivity of the recorder was adjusted by means of resistance R3. The resistance of the circuit connected to the cell e1 e2 was approximately 1 megohm (R4 = 1 megohm) and the current drawn from the cell
$e_1 - e_3$ was approximately $0.2 - 1$ microampere. This current was negligible in comparison with the current through $e_1 - e_2$ ($100$ microamperes or more). No preamplifier was used in these studies since the potential readings depend on the gain of such an instrument. In analytical applications of the method one is primarily interested in measuring the transition time, and the use of a preamplifier (direct-reading pH meter for example) is recommended.

Potential-time curves could also be observed on the screen of a DuMont 304 H cathode-ray oscillograph (switch $S_3$ in position 2). The signal actuating the driven sweep of the oscillograph was taken from the positive terminal of the coil of relay $RL_2$, the negative terminal of the coil being grounded (not shown in Figure 4).

APPARATUS FOR STUDIES WITH THE DROPPING MERCURY ELECTRODE

Potential-time curves must be recorded in a fraction of a second when a dropping mercury electrode is utilized; the electrode area virtually does not vary under such conditions, and the electrode behaves as a stationary electrode. To obtain reproducible current densities it is essential to make the recordings always at the same stage of the drop life. This can be done by the following method which was originally developed by Gierst and Juliard (16)(17).

The mercury drop was dislodged by a magnetic hammer whose operation was controlled (Figure 5) by closing relay $RL_1$ with the manually operated switch $S$. At the moment the drop was dislodged, the time relay $RL_2$ was activated, and, after a given time, the electrolysis was started. The
Figure 5. Schematic circuit of synchronization device for electrolysis with the dropping mercury electrode.
time between the fall of the drop and the recording of the potential-
time curve was adjusted by varying resistance $R_1$; this time could be
varied between 5 and 11 seconds. The current passing through the cell
was adjusted so that the time of electrolysis was less than about 1
second. It has been shown (14) that conditions of linear diffusion
virtually hold if the duration of electrolysis is less than one second.

The area of the mercury drop (the drop was assumed to be a sphere)
was calculated from the following relationship

$$A = \frac{4\pi}{4\pi d} \left( \frac{3mt}{4\pi d} \right) \frac{2}{3}$$

where $d$ is the density of mercury, $m$ the rate of flow of mercury, and
$t$ the time elapsed between the fall of the drop and the beginning of
the recording of the potential-time curve.

Other parts of the apparatus illustrated in Figure 5 have functions
similar to those described for use with stationary electrodes.
CHAPTER III

EXPERIMENTAL STUDY OF REVERSIBLE AND IRREVERSIBLE PROCESSES

Experimental studies of potential-time curves have been very scanty (21), and this part of the thesis deals with such studies for reversible and irreversible processes. The data obtained for a few irreversible processes are also used in a verification of the theory of irreversible polarographic waves.

Reversible processes

The following processes were studied: reduction of cadmium and thallium on a mercury electrode, and reduction of ferricyanide on a platinum electrode. The temperature of the electrolyzed solutions was 30 ± 2°C; no closer control of temperature was required as will be apparent from the following discussion.

The tracing of a potential-time curve for the reduction of cadmium and thallium on mercury and for the corresponding re-oxidation process is shown in Figure 6. As was pointed out in Chapter I, reversible cathodic potential-time curves such as the one of Figure 6 obey the following equation when the main reaction product is soluble, either in the electrode (mercury) or the solution

\[ E = E'_{\text{a}} + \frac{RT}{nF} \ln \frac{C^{\frac{n}{2}}}{C_{\text{a}}^{\frac{n}{2}}} \]

(3-1)
Figure 6. Potential-time curve for the reduction of 4 mM cadmium(II) and the subsequent anodic oxidation of cadmium amalgam. Supporting electrolyte: 1 M potassium nitrate.
The notations in equation (3-1) are as follows: \( E \) is the potential of the electrode, \( \tau \) the transition time, \( t \) the time elapsed since the beginning of electrolysis, and \( E_0 \) is defined by

\[
E_{1/2} = E_0 + \frac{RT}{nF} \ln \frac{f_0 D_{E}^{1/2}}{f D_{0}^{1/2}}
\]  

(3-2)

where \( E^0 \) is the standard potential for the electrode process, the \( f \)'s are activity coefficients, and \( D \)'s diffusion coefficients. According to equation (3-1) a plot of \( \log \left[ \tau (\frac{1}{2} - \frac{t}{2})/\tau \right] \) against \( E \) should yield a straight line of reciprocal slope \( 2.3 \, \text{RT}/nF \). Such plots for a few electrode reactions are shown in Figure 7. The experimental reciprocal slopes of \( 0.061 \) for thallium and \( 0.032 \) for cadmium are in good agreement with the theoretical values of \( 0.060 \) and \( 0.030 \) respectively. The slope \( 0.068 \) for ferricyanide is somewhat higher than the expected value \( 0.060 \), possibly because of secondary effects (impurities, adsorbed oxygen, etc.) resulting from the use of a platinum electrode. Experimental reciprocal slopes even for results obtained with the mercury pool are slightly higher than the theoretical values at least for three reasons: 1. Distortion of potential-time curves by the recorder; 2. Interference of convection with diffusion at the electrode; 3. Uncertainty in the determination of the transition time from the potential-time curve.

As was shown by Berzens and Delahay (2), the equation of the potential-time curve for the re-oxidation process is

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

(3-3)
Figure 7. Plot of $\log \left[ \frac{[\text{Fe}^{2+}][\text{Fe}^{3+}]}{[\text{Fe}^{3+}][\text{Fe}^{2+}]} \right]$ against potential for reversible electrode processes: 4 mM potassium ferricyanide in 0.1 M sulfuric acid; 4 mM thallium(I) in 1 M potassium nitrate; 4 mM cadmium(II) in 1 M potassium nitrate.
where the notations are the same as in equations (3-1) and (3-2) and
where \( t' \) is the time elapsed since the transition time \( t \). According
to (3-3) the logarithmic term varies linearly with potential, and the
reciprocal slope of the resulting line is \( 2.3 \frac{RT}{
F n} \) (decimal logarithm).
This slope is the same as for the logarithmic plot for the cathodic
process. The validity of this conclusion is apparent from the diagram
of Figure 7.

According to equations (3-1) and (3-3) the potential \( E_\frac{1}{2} \) is the same
for the cathodic and anodic curves. This potential corresponds to
\( t \geq \frac{1}{\mathcal{E}} t \) for the cathodic curve and to \( t' \geq 0.222 \left( \mathcal{E}/3 \right) \)
for the anodic curve. Finally \( E_\frac{1}{2} \) from (3-2) is the same as the corresponding polaro-
graphic half-wave potential. Experimentally it was found that there is
a difference of the order of 10 millivolts between the cathodic and
anodic values of \( E_\frac{1}{2} \). This could be caused by a slight degree of irrev-
sibility of the electrode processes, but it is more likely that differ-
ences between the cathodic and anodic values of \( E_\frac{1}{2} \) result from the ohmic
drop in solution between the tip of the sleeve of the reference elec-

trode (Figure 3) and the polarized electrode. With current intensities of the
order of 100 microamperes the ohmic drop between two points at a distance
of 1 mm or so in a 1 molar electrolyte (potassium nitrate or chloride)
is a few millivolts, the cross section area of the cell being of the
order of 1-2 cm\(^2\). Since the current was reversed during re-oxidation,
the difference between cathodic and anodic values of \( E_\frac{1}{2} \) is the double
of the ohmic drop. The average of the two values of \( E_\frac{1}{2} \) would be the
correct experimental value of \( E_\frac{1}{2} \) if it were not for the ohmic drop in
the circuit $e_1 e_3$ as resulting from the current consumption by the input element of the recorder. The corresponding correction and corrected values of $E_{\frac{1}{2}}$ are listed in Table I together with polarographic half-wave potentials. The agreement is good if one takes into account: 1. The usual error of approximately 0.005 volt for polarographic half-wave potentials; 2. Possible minor errors in the values of $E_{\frac{1}{2}}$ as determined by the constant current method; 3. The difference between the temperatures at which our $E_{\frac{1}{2}}$ values ($30 \pm 2^\circ$) and the polarographic half-wave potentials were determined ($25^\circ$).

### TABLE I

<table>
<thead>
<tr>
<th>Potential $E_{\frac{1}{2}}$ (in volts vs. S.C.E.)</th>
<th>cathodic</th>
<th>anodic</th>
<th>correction</th>
<th>corrected</th>
<th>polarographic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>-0.578</td>
<td>-0.569</td>
<td>-0.006</td>
<td>-0.580</td>
<td>-0.586</td>
</tr>
<tr>
<td>Tl</td>
<td>-0.463</td>
<td>-0.455</td>
<td>-0.004</td>
<td>-0.463</td>
<td>-0.475</td>
</tr>
<tr>
<td>Fe(CN)$_{6}^{3-}$</td>
<td>0.240</td>
<td>0.232</td>
<td>0.007</td>
<td>0.253</td>
<td>0.240*</td>
</tr>
</tbody>
</table>

*Approximate value of the standard potential.

**Irreversible processes**

The following processes were studied: reduction of oxygen, nickel (II), and cobalt(II) in various media. A mercury pool electrode was
used in this study. The tracing of a potential-time curve for the
reduction of nickel(II) is shown in Figure 8. As was shown by Delahay
and Berszins (see Chapter I) the potential should vary abruptly at time
t = 0 (neglecting the charging of the double layer) for a totally
irreversible electrode process which involves only one rate determining
step. This is virtually the case in Figure 8 and for the other elec-
trode processes studied here. A perfectly sharp angle was nevertheless
not observed even when potential-time curves were recorded by means of
a cathode-ray oscillograph. This discrepancy probably results from
some kinetic complications which are not taken into account. The
effect appears minor in the cases studied here.

It follows from equation (1-14) that a plot of \( \log \left[ 1 - (t/T)^{1/2} \right] \)
against \( E \) should yield a straight line whose reciprocal slope is
\( (2.3 RT)/(\alpha n_a F) \), \( \alpha \) being the transfer coefficient for the cathodic
process and \( n_a \) the number of electrons involved in the rate determining
step. Such diagrams are shown in Figure 9 for various irreversible
processes. Values of \( n_a \) deduced from Figure 9 were: 0.49 for oxygen
in acetate buffer, 0.59 for oxygen in sodium hydroxide, 0.70 for nickel
in potassium chloride and 0.82 for cobalt. Values of \( E \) for \( t = 0 \)
were determined from Figure 9 and corrections were made as for the
potentials \( E_e \) above, taking 0.005 volt as the ohmic drop between mer-
curry and the tip of the sleeve of the reference electrode. The formal
rate constant \( k_{f, h} \) at \( E = 0 \) was calculated by applying the equation
(see Chapter I)

\[
E_{t=0} = \frac{RT}{\alpha n_a F} \ln \left( \frac{n_b E_k b_0}{b_0} \right)
\]  
(3-4)
Figure 8. Potential-time curve for the irreversible reduction of nickel in 1 M potassium chloride.
Figure 9. Plots of $\log \left[1 - \left(\frac{E}{E^\circ}\right)^2\right]$ versus potential for totally irreversible electrode processes: Curve 1, oxygen in acetate buffer; Curve 2, oxygen in 1 M sodium hydroxide; Curve 3, cobalt(II) in 1 M potassium chloride; Curve 4, nickel(II) in 1 M potassium chloride.
where $C^0$ is the bulk concentration of reducible substance in moles.cm$^{-3}$, and $i^0$ is the current density. The rate constant $k_{f,h}^0$ at the potential $E = 0$ in the normal hydrogen electrode scale was finally computed from

$$k_{f,h}^0 = \frac{i^0}{e^{aFE/RT}}$$

(3-5)

Values of log $k_{f,h}^0$ as deduced from the data of Figure 9 were as follows: -12.53 for nickel in potassium chloride, and -15.69 for cobalt. The value of $k_{f,h}^0$ for the reduction of oxygen was not calculated because the concentration $C^0$ of this substance was not determined. These data are used below.

Summarizing, one can determine by the present method the parameters $n_a$ and $k_{f,h}^0$ which characterize the kinetics of a totally irreversible electrode process involving one rate determining step.

VERIFICATION OF THE THEORETICAL TREATMENT OF IRREVERSIBLE POLAROGRAPHIC WAVES

The experimentally determined values of $\alpha n_a$ and $k_{f,h}^0$ reported above can be used in a test of the theoretical treatment of irreversible polarographic waves. It can be shown (13) that the half-wave potential for an irreversible wave, the characteristics of which are determined by a single rate determining step, is

$$E_{1/2} = \frac{RT}{\alpha n^a F} \ln \frac{k_{f,h}^0}{\beta D_0^{1/2}}$$

(3-6)
where $E_1$ is referred to the normal hydrogen electrode, $\phi$ is a quantity which varies with drop time, $D_0$ is the diffusion coefficient of the substance being reduced, and the other notations are those of equation (3-6). For usual drop times from 2 to 4 seconds, $\phi$ is such that log $\phi$ is comprised between -0.33 and -0.47. Values of $E_1$ obtained from equation (3-6) and for a drop time of 4 seconds were as follows (vs. S.C.E.):

-1.14 volts for nickel(II) in 1 M potassium chloride, and
-1.09 volts for cobalt(II) in 1 M potassium chloride. The corresponding experimental values as reported in the literature are: -1.1, and -1.2 volts, respectively. The agreement is good since there are two causes of discrepancy. 1. Polargraphic half-wave potentials were measured in presence of some maximum suppressor such as gelatin, whereas the calculated $E_1$ values were determined from data obtained without maximum suppressor. This is important because the product $n_a$ varies when traces of substances such as gelatin are added to the solution. 2. Equation (3-6) is approximate because it was derived by adapting the solution of the corresponding boundary value problem for semi-infinite linear diffusion to the case of the dropping mercury electrode.

It should be added that data obtained from the constant current method were interpreted by assuming that the electrode process involves only one rate determining step without kinetic complications. The same hypothesis was made in the derivation of equation (3-6). Hence the agreement between calculated and experimental half-wave potentials does not imply that this hypothesis is correct. However, a relatively conclusive proof of the validity of this hypothesis is to be found in the fact that the curves of Figure 9 are linear as predicted by theory.
We consider in this chapter the anodic oxidation of a metal \( M \) in a solution in which a precipitate \( M\Lambda \) or a complex ion \( MB_2^- \) is formed. This case is more involved than the process in which the metal undergoes anodic dissolution with the formation of a soluble species. It is therefore fruitful to consider this latter case first. This will be done on the assumption that linear diffusion is the sole mode of mass transfer of the oxidized species.

Since the electrolysis current is constant, the flux of the metal cations is constant at the electrode surface. The concentration of cations can thus be calculated by using Fick's equation as was done by Sand for the reduction of a soluble species on an inert electrode. The result obtained in this fashion is obtained on the implicit assumption that the electrode area does not vary during oxidation. The concentration of cation \( M^{++} \) at the electrode surface is (see equation (1-3)):

\[
C_{M^+}(0,t) = \frac{2ie}{\pi F(\nu D)} t^{1/2} \tag{4-1}
\]

The electrode potential during oxidation can be calculated by introducing the concentration of \( M^{++} \) from (4-1) in the suitable equation
for the potential, it being assumed that the activity of the metal undergoing oxidation is equal to unity. If the electrode is reversible, one deduces from the Nernst equation

$$E = E^0 + \frac{RT}{nF} \ln \left[ \frac{[M]}{[M]^n} \right]$$

(4-2)

Quite naturally no transition time can be observed as long as the solution is not saturated with the product of electrolysis. This case is of little practical value.

ANODIC OXIDATION WITH THE FORMATION
OF A COMPLEX ION

Consider the oxidation of metal M with the formation of a complex $MA_2^-$. Because of the consumption of $A^-$ there is progressive depletion of this ion at the electrode surface. This causes a variation of the electrode potential which can be accounted for in the following manner.

Fick's equation for linear diffusion must be modified to take into account the formation of the complex ion in solution. Thus

$$\frac{\partial C_{M+}(x,t)}{\partial t} = D_{M+} \frac{\partial^2 C_{M+}(x,t)}{\partial x^2} - \Phi_{M+}$$

(4-3)

where $\Phi_{M+}$ represents the rate of concentration change resulting from the formation of the complex ion $MA_2^-$. An exact knowledge of $\Phi_{M+}$ is not necessary as will be shown later. Likewise, one has

$$\frac{\partial C_A^{-}(x,t)}{\partial t} = D_A^{-} \frac{\partial^2 C_A^{-}(x,t)}{\partial x^2} - \Phi_{A^-}$$

(4-4)
and

\[ \frac{\partial C_{\text{MA}_2^-}}{\partial t} = D \frac{\partial^2 C_{\text{MA}_2^-}}{\partial x^2} + \frac{\partial}{\partial t} C_{\text{MA}_2^-} \]  

(4-5)

Since the chemical reaction involves two anions (A\(^-\)) for each metal ion, one has

\[ q_A^- = 2 q_{n+} \]  

(4-6)

and

\[ q_{\text{MA}_2^-} = q_{\text{M}^+} \]  

(4-7)

The above system of differential equations will be solved for the particular case in which the following assumptions are valid:

(1) Equilibrium for the formation of the complex ion is reached, and consequently one may write

\[ k = \frac{C_{n^+} C_{\text{A}^2^-}}{C_{\text{MA}_2^-}} \]

for any values of x and t;

(2) The diffusion coefficients in equations (4-5), (4-4) and (4-5) are equal;

(3) The area of the electrode remains constant during electrolysis.

If these assumptions are not made, the mathematical treatment becomes very difficult because it involves the solution of non-linear partial differential equations.

The initial conditions are:

\[ \frac{\partial C_{m^+}(x,0)}{\partial t} = C^0_{m^+} \]  

(4-8)
The boundary conditions are:

\[ D \frac{\partial C_{m^+}(x,t)}{\partial x} \bigg|_{x=0} = -\frac{I_0}{nF} \]  \hspace{1cm} (4-11)

\[ \left[ \frac{\partial C_{m^+}(x,t)}{\partial x} \right]_{x=0} = \left[ \frac{\partial C_{mA^-}(x,t)}{\partial x} \right]_{x=0} = 0 \]  \hspace{1cm} (4-12)

Furthermore, one has

\[ C \xrightarrow{\text{m}^+} C^\circ, \quad C \xrightarrow{\text{A}^-} C^\circ, \quad C \xrightarrow{\text{mA}^-} C^\circ \quad \text{for} \quad x \to \infty. \]

Condition (4-11) states that the current density is constant, i.e., that the flux of metal ions at the electrode surface is constant.

Condition (4-12) expresses that the ions A^- and mA^- do not undergo any electro-chemical reaction; hence the flux of these substances at the electrode surface is equal to zero.

By making the following substitutions

\[ \gamma = 2C_{m^+} - C_A^- \]  \hspace{1cm} (4-13)

\[ \phi = C_{m^+} + C_{mA^-} \]  \hspace{1cm} (4-14)
one transforms equations (4-8), (4-9) and (4-10) into the following
differential equations

\[
\frac{\partial \psi(x,t)}{\partial t} = \rho \frac{\partial^2 \psi(x,t)}{\partial x^2} \tag{4-15}
\]

\[
\frac{\partial \phi(x,t)}{\partial t} = \rho \frac{\partial^2 \phi(x,t)}{\partial x^2} \tag{4-16}
\]

The initial and boundary conditions are now:

\[
\psi(x,0) = 2C_0 \cos \frac{\pi x}{\ell} - \frac{C_0}{A^2} \tag{4-17}
\]

\[
\phi(x,0) = C_0 \cos \frac{\pi x}{\ell} + \frac{C_0 \cos \frac{k \pi x}{\ell}}{\kappa} \tag{4-18}
\]

\[
D \left[ \frac{\partial \psi(x,t)}{\partial x} \right] \bigg|_{x=0} = -\frac{2 \psi_0}{\ell F} \tag{4-19}
\]

\[
D \left[ \frac{\partial \phi(x,t)}{\partial x} \right] \bigg|_{x=0} = -\frac{\phi_0}{\ell F} \tag{4-20}
\]

Furthermore, \( \psi \rightarrow 2C_0 \cos \frac{\pi x}{\ell} \quad \text{and} \quad \phi \rightarrow C_0 \cos \frac{\pi x}{\ell} + \frac{C_0 \cos \frac{k \pi x}{\ell}}{\kappa} \) as \( x \rightarrow \infty \).

The above boundary value problem will be solved by applying the
Laplace transformation. The transforms for the solution of (4-15)
and (4-16) are:

\[
\bar{\psi}(x,s) = \frac{\psi_0}{s} + m e^{-\left(\frac{s}{\ell}\right)\kappa x} \tag{4-21}
\]

\[
\bar{\phi}(x,s) = \frac{\phi_0}{s} + n e^{-\left(\frac{s}{\ell}\right)\kappa x} \tag{4-22}
\]
where \( M \) and \( N \) are integration constants. The values of \( M \) and \( N \) are obtained by satisfying the transforms of the initial and boundary conditions. Thus

\[
M = \frac{2ic_0}{S^{3/2} \eta FD^{1/2}} \quad N = \frac{ic_0}{S^{3/2} \eta FD^{1/2}} \quad (4-25)
\]

Hence the transforms at \( x = 0 \) are

\[
\left[ \frac{\mathcal{Y}(x, \xi)}{\xi} \right]_{x=0} = \frac{\mathcal{Y}^0}{\xi} + \frac{2ic_0}{S^{3/2} \eta FD^{1/2}} \quad (4-24)
\]

\[
\left[ \frac{\phi(x, \xi)}{\xi} \right]_{x=0} = \frac{\phi^0}{\xi} + \frac{ic_0}{S^{3/2} \eta FD^{1/2}} \quad (4-25)
\]

By inverse transformation (7) one obtains:

\[
\mathcal{Y}(0, \xi) = 2 \rho \xi^{1/2} + \mathcal{Y}^0 \quad (4-26)
\]

\[
\phi(0, \xi) = \rho \xi^{1/2} + \phi^0 \quad (4-27)
\]

where

\[
\rho = \frac{2ic_0}{TT^{3/2} \eta FD^{1/2}} \quad (4-27a)
\]

In view of equations (4-15) and (4-14) one has

\[
2\frac{c_{m+}}{\eta} - \frac{c_m}{\eta^2} = 2 \rho \xi^{1/2} + 2c^0_{m+} - c^0_m \quad (4-28)
\]

\[
c_{m+} + \frac{c_m}{\eta^2} = \rho \xi^{1/2} + c^0_m + \frac{c^0_{m+} \cdot c^0_{m-}}{\eta} \quad (4-29)
\]
The concentration of the metallic ion at \( x = 0 \) is obtained by introducing \( C_{M^-} \) and \( C_{M^2^-} \) in the expression for the instability constant.

The resulting cubic equation in \( C_{M^+} \) is rather cumbersome to handle and it is fruitful to consider the case in which the initial concentration of the anion \( A^- \) is much larger than the initial concentrations of ions \( M \) and \( M^2^- \). The cubic equation in \( C_{M^+} \) is then:

\[
C_{m^+}^3 + C_{m^+}^2 \left( C_{M^+}^0 - 2 p \varepsilon \right) + C_{m^+} \left[ \left( C_{M^+}^0 - 2 p \varepsilon \right)^2 + \frac{e}{4} \right] = \frac{K_p \varepsilon \varepsilon^2}{\varepsilon^2} \quad (4-30)
\]

We shall define the transition time \( \tau \) by the relationship \( C_{A^-}^0 = 2p \varepsilon \). Upon introducing the transition time in (4-30) one has

\[
C_{m^+}^3 + C_{m^+}^2 \left( 2p \varepsilon \tau - \varepsilon \right) + C_{m^+} \left[ \frac{p}{\tau} \left( \varepsilon - \varepsilon \right)^2 + \frac{e}{4} \right] = \frac{K_p \varepsilon \varepsilon^2}{\varepsilon^2} \quad (4-31)
\]

For small values of \( \varepsilon \) equation (4-31) yields the following solution

for \( C_{M^+} \):

\[
C_{m^+} = \frac{K}{p \varepsilon \varepsilon^2} \left[ \frac{1}{1 - \left( \varepsilon / \varepsilon \right)^{1/2}} \right] \left[ \frac{1}{(\varepsilon / \varepsilon)^{1/2} - 1} \right] \quad (4-32)
\]

or in terms of \( C_{A^-}^0 \):

\[
C_{m^+} = \frac{2K}{C_{A^-}^0} \left[ \frac{1}{1 - \left( \varepsilon / \varepsilon \right)^{1/2}} \right] \left[ \frac{1}{(\varepsilon / \varepsilon)^{1/2} - 1} \right] \quad (4-33)
\]

Substitution into the Nernst equation yields the following equation

for the potential-time curve:

\[
E = E^0 + \frac{RT}{nF} \ln \frac{2K}{C_{A^-}^0} - \frac{RT}{nF} \ln \left[ 1 - \left( \varepsilon / \varepsilon \right)^{1/2} \right] \left[ (\varepsilon / \varepsilon)^{1/2} - 1 \right] \quad (4-34)
\]
The validity of equation (4-34) is determined below.

**ANODIC OXIDATION WITH FORMATION OF A PRECIPITATE**

Consider the oxidation of metal $M$ with the formation of a precipitate $MA$. By a reasoning analogous to that presented in the previous section one may modify Fick's law to account for the formation of the precipitate. A similar result may be obtained from the following considerations.

If one assumes that the precipitate $MA$ is formed at the electrode surface, Fick's equation can be applied. The concentration of the anion at the electrode surface is, then (see equation (1-3)).

$$C_A(x, t) = C_A^o - P \sqrt{t}$$

(4-35)

where $P$ is defined by equation (4-27a). One may determine $C_M^+$ at $x = 0$, by substitution into the expression for the solubility product constant $S$. Thus,

$$C_{M^+}(x, t) = \frac{S}{C_A^o - P \sqrt{t}}$$

(4-36)

If one defines the transition time by the relationship $C_A(x, t) = 0$,

one deduces from (4-36) the equation

$$C_{M^+}(x, t) = \frac{S}{P \sqrt{t} + C_A^o - P \sqrt{t}}$$

(4-37)

which may also be written under the form

$$C_{M^+}(x, t) = \frac{S}{C_A^o} \left[ \frac{P \sqrt{t}}{C_A^o - P \sqrt{t}} \right]$$

(4-38)
By substitution into the Nernst equation the following expression for the potential-time curve is obtained:

\[ E = E^0 + \frac{RT}{nF} \ln \frac{\alpha}{C_0} - \frac{RT}{nF} \ln \left[1 - (\frac{t}{T})^{1/2}\right] \]  

\[(4-39)\]

**EXPERIMENTAL VERIFICATION FOR THE ANODIC OXIDATION OF SILVER IN PRESENCE OF CYANIDE OR HALIDES**

The preceding treatment was verified in the case of the anodic oxidation of silver in the presence of cyanide ion and various halides. Potential-time curves were recorded with a pen-and-ink recorder as indicated in Chapter II. The area of the silver electrode was approximately 1 cm.$^2$ in each case.

A tracing of a potential-time curve for the anodic oxidation of silver in the presence of cyanide ion is shown in Figure 10. The potential-time curve exhibits two steps, the first due to the formation of the stable complex ion Ag(CN)$_2^-$, the second step due to the precipitation of Ag(CN). The foregoing analysis is applicable to the first of these two steps.

One deduces from equation (4-34) that a plot of \[ \log \left[ \frac{1 - (t/T)^{1/2}}{(E/E^0)^{1/2}} \right] \] against potential should yield a straight line whose reciprocal slope is 2.3 RT/nF. Such a diagram is shown in Figure 11 for the oxidation of silver in the presence of cyanide. The reciprocal slope of 0.064 is in reasonably good agreement with the theoretical value of 0.060.

Figure 12 is a tracing of potential-time curves obtained for the anodic oxidation of silver in 1 mM and 5 mM lithium chloride. The solid curves are those calculated from equation (4-39), while the
points represent experimental data. The theoretical plots were extended
past the transition time by equation (4-2). The value of the solubility
product of silver chloride was selected to fit the curve in one point,
and the value $S_{AgCl} = 4 \times 10^{-10}$ was adopted. This value is appreciably
larger than the value $S = 1.1 \times 10^{-10}$ for $30^\circ C$. This difference is to
be expected since the particles of silver chloride, which are formed at
the surface of the silver electrode are much smaller (the thickness of
the silver chloride layer is only a few angstroms in our experimental
conditions) than those for which the reported value $S$ has been deduced.

It is well known that the solubility of a precipitate decreases.

One deduces from equation (4-39) that a plot of $\log \left[ 1 - \left( \frac{t}{t_r} \right)^{1/2} \right]$ should yield a straight line whose reciprocal slope is $2.3 RT/\mu F$. The
validity of this analysis is confirmed by the experimental data of
Figure 13. The reciprocal slope of the $\log \left[ 1 - \left( \frac{t}{t_r} \right)^{1/2} \right]$ versus $E$ line
is 0.067 for chloride and 0.061 for bromide while the theoretical
slope is 0.060.

It should be added that the derivation of equation (4-39) is based
on the implicit assumption that the layer of silver halide at the elec-
trode surface is so thin that the rate of diffusion of silver ions
through this layer is so high that it need not be taken into account.
The quantity $i_0^{-1/2}$ should be independent of current density if this
assumption is correct, while otherwise one might expect that $i_0^{-1/2}$
increases with current density (the thickness of the layer decreases
as the current density increases since the quantity of electricity
$i_0^{-1/2}$ decreases for increasing values of $i_0$). Actually, $i_0^{-1/2}$ is inde-
pendent of current density as is apparent from Table II, and the
derivation of (4-39) rests on a sound basis.
TABLE II

Values of $i_o \sqrt{t}$ for the anodic oxidation of silver in 5 mM KBr

<table>
<thead>
<tr>
<th>$i_o \times 10^{-3}$ (amp. cm.$^{-2}$)</th>
<th>$t$ (sec.)</th>
<th>$i_o \sqrt{t}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.198</td>
<td>166.0</td>
<td>2.50</td>
</tr>
<tr>
<td>0.328</td>
<td>53.6</td>
<td>2.40</td>
</tr>
<tr>
<td>0.365</td>
<td>41.5</td>
<td>2.35</td>
</tr>
<tr>
<td>0.418</td>
<td>32.5</td>
<td>2.38</td>
</tr>
<tr>
<td>0.486</td>
<td>20.7</td>
<td>2.22</td>
</tr>
<tr>
<td>0.401</td>
<td>35.8</td>
<td>2.40</td>
</tr>
<tr>
<td>0.584</td>
<td>17.7</td>
<td>2.48</td>
</tr>
</tbody>
</table>
Figure 10. Potential-time curve for the anodic oxidation of silver in the presence of cyanide ion. Solution composition: 5 mM potassium cyanide, 0.1 M potassium nitrate.
Figure 11. Plot of \( \log \left( \frac{1}{i} \right)^{1/2} \left[ \frac{1}{i} \right] - 1 \) for the anodic oxidation of silver in the presence of cyanide.
Figure 12. Potential-time curves for the anodic oxidation of silver in the presence of
(1) 1 mM lithium chloride; current density equals 0.198 milliamperes per square centimeter;
(2) 5 mM lithium chloride; current density equals 0.584 milliamperes per square centimeter.
Supporting electrolyte: 0.1 M potassium nitrate.
Figure 13. Plots of $\log \left( 1 - \frac{(e/\tau)^{1/2}}{n} \right)$ for the anodic oxidation of silver in the presence of (1) 5 mM sodium bromide, (2) 5 mM lithium chloride.
It has been observed by Brdička (6) that the polarographic reduction of certain dyes and other organic substances, riboflavin for example, yields two waves, while only a single wave would be expected. In cathodic processes the first wave occurs at less cathodic potentials than one would expect from the equilibrium potential of the redox couple, i.e., for the dye and its reduced form. The appearance of this first wave was ascribed by Brdička to the preferential adsorption of the reduced form of the dye. Brdička developed a theoretical treatment which accounts for the essential features of these adsorption waves. His treatment is based on the assumption that equilibrium for the adsorption process is reached at the electrode, and no information on the kinetics of the adsorption process can be gathered by the polarographic method.

Voltaammetry at constant current is somewhat more powerful in this respect because the current density can be varied over a wide range while this not possible in polarography. The kinetics of the adsorption process - or rather the desorption process - can thus be studied in a fairly quantitative fashion.
SIMPLIFIED DERIVATION OF THE TRANSITION TIME FOR THE ADSORPTION STEP

Potential-time curves for the substances studied by Brdicka also exhibit two steps. The transition time for the first step is determined by the adsorption process of the reduced species, while the transition time for the second step is determined by diffusion of the reducible species. As the current density increases the second step becomes progressively shorter in comparison with the first step and finally disappears entirely. Tracings of actual curves are shown in Figure 14 for the reduction of methylene blue, in a universal buffer of pH 6 (acetate-phosphate-borate buffer (6)). These curves were recorded by the oscillographic method described in Chapter XI.

It is possible to relate the characteristics of the first transition time to the kinetics of the adsorption process provided the following assumptions are made:

(1) The electrode reaction proceeds in the following manner

\[ 0 + ne \rightarrow R_{(adsorbed)} \xrightleftharpoons[k_a]{k_d} R_{(desorbed)}; \]

(2) The desorption process is first order with respect to the adsorbed species;

(3) The second wave does not appear until the surface of the electrode contains the maximum possible number of adsorbed molecules. This maximum number is constant for the adsorbed form of any particular substance.
Figure 14. Potential-time curves for the reduction of methylene blue in a universal buffer, pH = 6. Time scale is in milliseconds.
Under these conditions the rate of production of the species adsorbed at the electrode may be written in the following form

\[
\frac{dC_a}{dt} = \frac{C_0}{nF} - k_d C_a + v_a
\]  

(5-1)

where \( k_d \) is the rate constant for the desorption process, \( C_a \) the surface concentration of the adsorbed species and \( v_a \) the rate of adsorption. It will be assumed in the following treatment that \( v_a \) can be neglected. This simplifying modification is introduced for two reasons: 1. The bulk concentration of reduced species is virtually equal to zero before electrolysis, and the major fraction of reduced species produced during electrolysis is retained on the surface of the electrode; 2. The complete treatment in which the adsorption term is taken into account leads to differential equations whose solution appears very difficult. Because the adsorption term in equation (5-1) is neglected, one should remember that the following treatment is only approximate.

The solution of equation (5-1) is

\[
C_a(0, t) = \frac{C_0}{k_d n F} \left( 1 - e^{-k_d t} \right)
\]  

(5-2)

where the integration constant has been calculated from the initial condition: \( C_a = 0 \) for \( t = 0 \). At the transition time the electrode is covered by the maximum number of adsorbed molecules. Hence one has

\[
(C_a)_\text{max.} = \frac{C_0}{k_d n F} \left( 1 - e^{-k_d T} \right)
\]  

(5-3)
EXPERIMENTAL STUDY

In a process purely controlled by diffusion the product $i_0C^{1/2}$ is independent of current density as can be ascertained from equation (1-4). This is not the case when there is preferential adsorption as is shown in Figure 16. The points represent experimental values of $i_0C^{1/2}$ for the reduction of methylene blue. The curve represents the theoretical variation as predicted from equation (5-3) on the basis of the following data: $k_d = 0.68 \text{ sec}^{-1}$, $(C_h)_\text{max} = 5 \times 10^{-10} \text{ moles/cm}^2$. The agreement is good if one takes into the account the approximate nature of the theoretical analysis.

Equation (5-3) predicts that a plot of the reciprocal of $(1 - \exp (-kC))$ against current density should yield a straight line. Such a diagram is shown in Figure 16 for the reduction of methylene blue in universal buffer of pH 6 and for the reduction of thionine in a universal buffer of pH 4.6. The temperature was controlled at $30 \pm 0.2^\circ C$. This diagram yields the following values of the rate constant $k_d$: 0.01 sec.$^{-1}$ (thionine) and 0.68 sec.$^{-1}$ (methylene blue).

In conclusion, voltammetry at constant current may supply some information on the kinetics of desorption processes. Admittedly, this treatment is approximate, but any method for kinetic studies of adsorption processes should be useful because of the experimental difficulties involved in the investigation of these relatively rapid reactions.
Figure 15. Plot of $i_0 \tau^{1/2}$ versus current density for the adsorption step in the reduction of methylene blue.
Figure 16. Plot of $\frac{1}{1 - \exp(-k\tau)}$ for the adsorption step in the reduction step of 4 mM methylene blue (line 1), 2.4 mM methylene blue (line 2), 1 mM thionine (line 3).
CHAPTER VI

CATALYTIC PROCESSES

Consider the electrode process in which the electrochemical reaction is coupled with a chemical reaction according to the following symbolic equations:

\[ \text{O + me} \rightarrow \text{R} \]  \hspace{1cm} (6-1)

\[ \text{R + Z} \rightarrow \text{O + Y} \]  \hspace{1cm} (6-2)

A substance O is reduced to R, and the latter is oxidised by a third substance Z. All substances involved are soluble. Because of reaction (6-2), substance O is partially regenerated and the rate of reduction of substance O depends on the kinetics of reaction (6-2). Such processes are termed "catalytic" electrode processes.

Various catalytic processes of this type have been reported and several have been extensively studied polarographically. For example, hydrogen peroxide causes a large increase in the polarographic limiting currents of ferric iron and of peroxy-compounds of molybdenum, tungsten, and vanadium (22). Proteins containing sulphydryl groups yield catalytic waves which have been explained by a mechanism involving similar reactions.
It is observed in voltammetry at constant current that the transition time for the reduction of substance O becomes longer under conditions of electrolysis in which there is regeneration of substance O. The transition time for catalytic processes will be derived below for the case in which semi-infinite linear diffusion is the sole mode of mass transfer.

THE BOUNDARY VALUE PROBLEM

Differential equations for the concentrations $C_O(x,t)$ and $C_R(x,t)$

Because reaction (6-2) occurs in solution, kinetic terms must be introduced in Fick's second law of diffusion, and the concentrations $C_O(x,t)$ and $C_R(x,t)$ of substances O and R obey the following equations:

$$\frac{\partial C_O(x,t)}{\partial t} = D_O \frac{\partial^2 C_O(x,t)}{\partial x^2} + \frac{k_1}{f} C_R(x,t) C_O(x,t) - \frac{k_2}{f} C_O(x,t) C_R(x,t)$$  \hspace{1cm} (6-3)

$$\frac{\partial C_R(x,t)}{\partial t} = D_R \frac{\partial^2 C_R(x,t)}{\partial x^2} - \frac{k_1}{f} C_R(x,t) C_O(x,t) + \frac{k_2}{f} C_O(x,t) C_R(x,t)$$  \hspace{1cm} (6-4)

in which the $C$'s are concentrations and the $k$'s the formal rate constants for reaction (6-2).

The derivation of the functions $C_O(x,t)$ and $C_R(x,t)$ is greatly facilitated if one makes the following simplifications:
(1) The concentration \( C_2(x,t) \) will be assumed constant and equal to the bulk concentration \( C^0_2 \) of this substance. This hypothesis is entirely justified if \( C^0_2 \) is much larger than the bulk concentration of substance \( O_j \); a more quantitative statement of this condition is expressed below.

(2) It will be assumed that the effect of the backward reaction can be neglected.

(3) Finally, it will be assumed that the diffusion coefficients \( D_0 \) and \( D_R \) are equal. The common value of \( D_0 \) and \( D_R \) will be represented by \( D \).

Equations (6-3) and (6-4) can now be written in the following form:

\[
\frac{\partial C_0(x,t)}{\partial t} = D \frac{\partial^2 C_0(x,t)}{\partial x^2} \quad \text{and} \quad \frac{\partial C_R(x,t)}{\partial t} = D \frac{\partial^2 C_R(x,t)}{\partial x^2} \tag{6-5, 6-6}
\]

The initial and boundary conditions are as follows:

\[
C_0(x,0) = C^0 \quad \text{and} \quad C_R(x,0) = 0 \tag{6-7}
\]

\[
\left[ \frac{\partial C_0(x,t)}{\partial x} \right]_{x=0} = - \left[ \frac{\partial C_R(x,t)}{\partial x} \right]_{x=0} \tag{6-8}
\]

\[
\left[ \frac{\partial C_0(x,t)}{\partial x} \right]_{x=0} = \frac{c_0}{\eta F D} \quad \text{and} \quad \lambda \tag{6-9}
\]

where \( C^0 \) is the bulk concentration of substance \( O \), and \( \lambda \) is defined by equation (6-9). Condition (6-8) expresses that the sum of the fluxes of substances \( O \) and \( R \) are equal (note that the \( D \)'s cancel), and condition (6-9) states that the current density is constant.

Finally, \( C_0(x,t) \) and \( C_R(x,t) \) are bounded for large values of \( x \). Thus, \( C_0(x,t) \to C^0 \) and \( C_R(x,t) \to 0 \) for \( x \to \infty \).
Variations of concentrations $C_0(x,t)$ and $C_R(x,t)$

The boundary value problem stated by equations (6-5) to (6-9) will be solved by applying the Laplace transformation. In order to apply this method it is useful to introduce the following function:

$$u(x,t) = C_0 - C_0(x,t)$$

Equation (6-6) is reduced to the following ordinary differential equation

$$\frac{d^2 \bar{C}_R(x,s)}{dx^2} - \frac{S + \frac{k}{D} + C_0}{D} \bar{C}_R(x,s) = 0$$

the solution of which is

$$\bar{C}_R(x,s) = N \exp \left[ -\left( \frac{S + \frac{k}{D} + C_0}{D} \right)^{1/2} x \right]$$

where $s$ is the parameter introduced by the Laplace transformation, and $N$ is an integration constant which is determined below.

Similarly the transform of (6-5) is

$$\frac{d^2 \bar{C}_R(x,s)}{dx^2} - \frac{S}{D} \bar{C}_R(x,s) - \frac{\frac{k}{D} + C_0}{D} \bar{C}_R(x,s) = 0$$

which has the solution

$$\bar{C}_R(x,s) = N \exp \left[ -\left( \frac{S}{D} \right)^{1/2} x \right] + M \exp \left[ -\left( \frac{S + \frac{k}{D} + C_0}{D} \right)^{1/2} x \right]$$

in which $N$ is an integration constant.
The values of \( M \) and \( N \) are obtained by satisfying the transforms of the boundary conditions expressed in equations (6-8) and (6-9). In this manner it is found that \( N \) equals zero and that the value of \( M \) is

\[
M = \frac{\lambda D^{1/2}}{S(S + Ef C_0^{1/2})^{1/2}} \quad (6-15)
\]

By introducing the above values of \( M \) and \( N \) into equations (6-12) and (6-14) one obtains the transforms \( u(x,t) \) and \( C_R(x,t) \). After returning to the function \( C_0(x,t) \) and introducing the condition \( x = 0 \), one obtains the concentrations of substances 0 and \( R \) at the electrode surface. Thus:

\[
C_0(0,t) = C^0 - \frac{C_0}{mFD^{1/2}(k/2)^{1/2}} \exp\left[\frac{k}{2}C_0^{1/2}\right] \quad (6-16)
\]

\[
C_R(0,t) = C^0 - C_0(0,t) \quad (6-17)
\]

The notation "erf" in equation (6-16) represents the error function having the quantity between brackets as argument.

**TRANSITION TIME**

**Transition time and determination of \( k_f \)**

The transition time \( \tau \) will be defined by the condition \( C_0(0, \tau_e) \geq 0 \), or in view of equation (6-16) by the following relationship:

\[
\frac{C^0}{mFD^{1/2}} = \frac{1}{(k/2)^{1/2}} \exp\left[\frac{k}{2}C_0^{1/2}\right] \quad (6-18)
\]
Equation (6-18) may be modified by considering the case in which there is no catalytic process. Thus, when $k_f C_2^0$ is equal to zero, the transition time is $T_d$ and equation (6-18) takes the form

$$ T_d \beta = \frac{\pi C_2^0 NFD_1}{2C_0} \quad (6-19) $$

as can be readily ascertained by expansion of the error function for small arguments and by introducing the value $k_f C_2^0 = 0$ into the resulting formula. This is precisely the value of $T_d$ which was derived by Sand (27) for a purely diffusion controlled process. The combination of equations (6-18) and (6-19) yields, after a simple transformation, the following relationship

$$ \left( \frac{T_c}{T_d} \right)^{1/2} = 2\gamma / \pi^{1/2} \text{erf} (\gamma) \quad (6-20) $$

with

$$ \gamma = \left( k_f C_2^0 T_c \right)^{1/2} \quad (6-21) $$

Equation (6-20) can be applied to the determination of the rate constant $k_f$, once the transition times $T_c$ and $T_d$ have been measured. Thus, if $\left( T_c / T_d \right)^{1/2}$ is known, the value of $\gamma$ can be read from a table giving values of the function $2\gamma / \pi^{1/2} \text{erf} (\gamma)$, and the corresponding rate constant $k_f$ is immediately calculated from equation (6-21). Values of the function $2\gamma / \pi^{1/2} \text{erf} (\gamma)$ are listed in Appendix I for values of the argument between zero and 2.3. The values of the error function needed in preparation of the table were taken from Pierce (26).
(five decimals), and the results were calculated to one more decimal than indicated in the table in order to ascertain the last figure.

When \( \gamma \) approaches zero, the value of this function approaches unity as can be shown by expanding the error function for small arguments. The variation of this function with \( \gamma \) are also shown in Figure 17.

**Properties of the transition time \( T_c \)**

Since the smallest value of the function \( 2\gamma / \pi \text{erf}(\gamma) \) is unity, it results from equation (6-20) that the transition time \( T_c \) is always larger than the value \( T_d \) which would be obtained if there were no catalytic effect. The ratio \( (T_c / T_d)^{1/2} \) is not independent of the current density; indeed, the argument \( \gamma \) of the error function in (6-18) must decrease when the current density is increased, and consequently the function \( 2\gamma / \pi \text{erf}(\gamma) \) and the ratio \( (T_c / T_d)^{1/2} \) decrease. Hence the transition time \( T_c \) approaches \( T_d \) when the current density is made sufficiently large. Conversely, the ratio \( (T_c / T_d)^{1/2} \) increases as the current density decreases. The limit of the ratio \( (T_c / T_d)^{1/2} \) tends toward infinity as the current density approaches zero.

The foregoing considerations can be conveniently summarized by plotting the value of the product \( (T_c / T_d)^{1/2} \) against the current density \( j_0 \). Such a diagram is shown in Figure 18. The almost vertical segments of the curves correspond to transition times for which the function \( \text{erf}(\gamma) \) is virtually equal to unity; under which condition the transition time varies rapidly for small changes in current density.
Figure 17. Variations of the function \( \frac{2 \gamma}{\pi^{1/2}} \text{erf}(\gamma) \) with \( \gamma \).
Figure 18. Plots of the ratio \( (\tau_c/\tau_d)^{1/2} \) against current density for catalytic reduction at constant current. Values of the product \( (k_\phi C_0^0) \) are indicated on the curves. \( \tau_d \) is taken as unity in each case.
Validity of the Assumption Embodied in the Relationship \( C_2(x,t) = C_2^0 \)

It was assumed in the foregoing derivation that the concentration of substance Z in the vicinity of the electrode is constant and equal to the concentration of this substance in the bulk of the solution. The conditions under which this assumption is valid can now be stated quantitatively.

If substance Z were reducible at the electrode, the corresponding transition time at current density \( i_0 \) would be (see equation (6-19)):

\[
\left( \frac{Z_d}{2} \right)^{1/2} = \frac{\pi^{1/2} C_2^0 \eta F D^{1/2}}{2 i_0} \quad (6-22)
\]

Since substance Z is consumed in the vicinity of the electrode in the catalytic process, concentration polarization for this substance is avoided if the fictitious transition time \( \frac{Z_d}{2} \) is much larger than the transition time \( Z_0 \). Therefore, the following condition should be fulfilled (see equations (6-20) and (6-22)):

\[
\frac{Z_d^{1/2}}{2 \eta \mu g(y)} \ll \frac{\pi^{1/2} C_2^0 \eta F D^{1/2}}{2 i_0} \quad (6-23)
\]

or in view of equation (6-19):

\[
C_2^0 \gg \frac{C_2^0 \eta F D^{1/2}}{\eta^{1/2} \mu g(y)} \quad (6-24)
\]

The condition (6-24) can be regarded as fulfilled when the left member is, for example, 100 times larger than the right member. As
small a multiple as 10 should cause no serious error. It is important to realize that the function \( \sqrt{2 \pi / \eta' \nu f(\xi)} \) is much larger than unity for sufficiently large arguments, and consequently condition (6-24) might very well not be satisfied even when \( C_2^0 \) is say 100 times \( C^0 \). It is therefore useful to verify this condition in each experimental determination of \( k_p \). This condition can be conveniently written by combining equations (6-20) and (6-24). Thus:

\[
C_2^0 \gg C^0 \left( \frac{Ze}{Z_d} \right)^{\frac{1}{2}}
\]

(6-25)

**APPLICATION TO THE CATALYTIC REDUCTION OF TITANIUM(IV) IN THE PRESENCE OF HYDROXYLAMINE**

The preceding treatment was applied to the catalytic reduction of Ti(IV) in the presence of hydroxylamine. Titanium(III) produced by electrolysis is oxidized to the 4 state by hydroxylamine. The mechanism of this reaction has been extensively studied by Davis, Evans and Higginson (10) who showed that the reaction is of the first order with respect to titanium. The rate determining step is

\[
\text{Ti}^{(III)} + \text{NH}_3\text{CH} \rightarrow \text{Ti}^{(IV)} + \text{NH}_2 + \text{H}_2\text{O}
\]

NH radicals can be removed from solution by the addition of oxalic acid. The kinetics of this reaction was also studied polarographically by Blasek and Koryta (3) who applied the treatment of catalytic limiting currents recently developed by Koutecky (24).
Potential-time curves were recorded with a cathode-ray oscillograph as indicated in Chapter II. Transition times were determined for various concentrations of Ti(IV) in 0.2 M oxalic acid, and for the same concentrations of titanium and oxalic acid in the presence of varying amounts of hydroxylamine (0.49 and 1.46 M). The concentration of hydroxylamine in each case was determined by titration with potassium permanganate after the addition of an excess of ferric iron (28). It was not necessary to determine the exact concentration of titanium(IV) since the transition time \( \tau_0 \) and \( \tau_d \) were determined for solutions having the same concentration in titanium.

The experimental results are summarized in this plot of the ratio \( \left( \frac{\tau_0}{\tau_d} \right)^{\frac{1}{2}} \) against current density (Figure 19). The solid curves are those calculated for \( k_F = 30 \text{ sec}^{-1} \text{(moles/1)}^{-1} \), and for the concentrations of hydroxylamine indicated. The points were experimentally determined. The agreement between theory and experiment is fair; the main source of error in this case is the relatively poor definition of the transition time, because of the distortion of the potential time-curves. The value of \( 30 \text{ sec}^{-1} \text{(moles/1)}^{-1} \) is somewhat lower than the value of \( 42 \text{ sec}^{-1} \text{(moles/1)}^{-1} \) obtained polarographically by Blasek and Koryta (3) for 25°. However, this experimental study shows that the foregoing theoretical analysis is essentially correct.

Applications of this method to the study of the kinetics of certain reactions which are too rapid to be studied by conventional method should be of interest.
Figure 19. Plots of the ratio $\left( \frac{c}{d} \right)^{1/2}$ against current density for the catalytic reduction of titanium(IV) in the presence of hydroxylamine: Curve 1, no hydroxylamine, Curve 2, 1.46 M hydroxylamine, Curve 3, 0.49 M hydroxylamine.
CHAPTER VII

INFLUENCE OF IONIC INTERACTION AND TEMPERATURE ON THE KINETICS OF ELECTRODE PROCESSES

The present chapter deals with the influence of ionic strength and temperature in electrochemical kinetics. These are rather different topics, and consequently the discussion and presentation of results will be divided in two parts.

IONIC INTERACTION IN THE ELECTROLYTIC REDUCTION OF IODATE

Introduction

Very little is known about the influence of ionic interaction on the kinetics of electrode processes. Certain effects can be predicted from present knowledge. For example the mean activity of ions varies with the ionic strength, and this might result in variation of the rate of electron transfer if the Debye-Hückel treatment is still valid for processes occurring at the interface electrode-solution. Another effect is the formation of complex ions which changes the equilibrium potential and causes a concomitant variation in the rate of the electrode process. The study of these effects, which have been investigated (11), adds very little to the knowledge of electrochemical kinetics. More puzzling is the observation that anions markedly influence the rate of electrode
processes. This effect of anions has been studied in great detail by Piontelli and coworkers (26) for the anodic oxidation of various metals. However, several difficulties are encountered in such studies: (1) Results on kinetic processes occurring at solid electrodes are never highly reproducible because of variations in the nature of the surface of the metal (film, change in structure, etc.); (2) The interpretation is clouded by the formation of complex ions. Because of these uncertainties no definite conclusion could be reached by Piontelli and coworkers. The effect of ionic interaction was also studied by Elving and coworkers (15) by polarography. These authors summarized their results in a diagram showing the variations of half-wave potential with ionic strength for the reduction of \(-\)bromo-n-butyric acid.

This study does not go beyond the simple observation that the half-wave potential depends on the ionic strength of the electrolyte.

Great care should be taken in the selection of a suitable electrode process to avoid the simultaneous variations of several parameters. The following conditions must be fulfilled.

(1) The involved substance should not form stable complex ions with the anion present in solution.

(2) The kinetic characteristics of the electrode process should not be affected by a change in hydrogen activity, since a variation in ionic strength obviously causes a change in the activity of hydrogen ion.

(3) The use of a solid electrode should be avoided because of the relatively poor reproducibility of kinetic data.

(4) The electrode process should preferably be totally irreversible at the current densities being utilized; the influence of the backward reaction can then be neglected, and the interpretation of experimental data is somewhat simplified. Furthermore, the kinetics of the reaction should be essentially determined by a single rate determining step.
The electrode process should preferably occur in the range of potential in which the nature of the anion in the electrolyte virtually does not influence the structure of the double layer. The advantages gained by the fulfillment of this condition appeared in the course of this study, as will be pointed out below.

The previous requirements are fulfilled in the case of the reduction of iodate in alkaline solution (pH 12 to 14) on a mercury cathode. The kinetics of this electrode process can be studied by voltammetry at constant current or by polarography. The method of interpretation in voltammetry at constant current is discussed in Chapter I. The kinetic parameters can also be determined by polarography on the basis of a treatment developed by Delahay (13) and recently improved by Koutecky (25). It is in order to test the treatment of the latter author that the polarographic method was applied in this investigation. A comparison between the treatments of Delahay and Koutecky will be found in Appendix II.

The kinetics of the iodate reduction will be characterized by the two quantities $k_{f,h}^0$ and $\alpha n_a$ which are related to the rate constant $k_{f,h}$ of the electrode process by the equation

$$k_{f,h} = k_{f,h}^0 \frac{\exp \left( \frac{-\alpha n_a F E}{RT} \right)}{\alpha n_a}$$

where the potential $E$ is referred to the potential of the normal hydrogen electrode. The quantities $k_{f,h}^0$ and $k_{f,h}$ are formal rate constants which include the mean activity coefficient of iodate ion. The quantity $\alpha$ in equation (7-1) is the transfer coefficient for the electrode process, and $n_a$ is the number of electrons involved in the
activation step; the value of \( n \) is presumably one. The method for the
determination of \( k_{f_h}^0 \) and \( \triangle n_a \) from polarographic data is outlined in
Appendix II.

**Description and discussion of results**

The composition of the electrolyzed solution was as follows: 0.5
mM potassium iodate, 0.05 M sodium hydroxide, 0.002% gelatin and varying
amounts of electrolyte. The temperature was kept at 30 ± 0.1°C.
Potentials were measured against a saturated calomel electrode.

An example of the log \( k_{f_h} \) versus potential diagram obtained for
varying concentration of sodium sulfate is given in Figure 20. Note
that the addition of sodium sulfate causes a marked increase in the rate
constant \( k_{f_h} \) at a given potential. Furthermore, the slope of the log
\( k_{f_h} \) versus \( E \) line remains unchanged, i.e., the quantity \( \triangle n_a \) of
equation (7-1) remains unchanged. The same observation was made for
all the electrolytes studied here; the average value of \( \triangle n_a \) is 0.77
with a maximum deviation of ± 0.02. Data obtained with various
electrolytes are summarized in the diagram of Figure 21 which shows the
variation of the rate constant \( k_{f_h}^0 \) with the ionic strength of the
medium. The choice of ionic strength as variable is somewhat arbi-
trary, and the concentration of cation or anion could as well be
adopted as variable. It is apparent from Figure 21 that the addition
of electrolyte causes a marked increase - by one or two order of
magnitude - in the rate constant \( k_{f_h}^0 \). The effect is in the opposite
direction from the variation of the formal rate constant \( k_{f_h}^0 \) one
would have expected in the concentration of electrolyte studied here
on the basis of the usual ionic interaction effect treated in the
Figure 20. Plots of log $k_{f,h}$ versus potential for the reduction of iodate in 0.05 M sodium hydroxide in the presence of varying amounts of "indifferent" electrolytes: Curve 1, no sodium sulfate; Curve 2, 0.1 M sodium sulfate; Curve 3, 0.75 sodium sulfate; Curve 4, 1.5 M sodium sulfate.
Figure 21. Plots of log $k_\text{f,h}$ against the logarithm of the ionic strength for the reduction of iodate in 0.05 M sodium hydroxide.
Debye-Hückel theory. Any interpretation based on liquid-liquid junction potential must also be ruled out because the order of magnitude of the change in $k_{f,h}^0$. Thus, a tenfold increase in $k_{f,h}^0$ would correspond to a variation of 0.078 volt in the junction potential; this appears improbable.

The values of the rate constant $k_{f,h}^0$ plotted in Figure 21 are not truly representative because they are computed in the normal hydrogen electrode scale of potentials. Actually the value of $k_{f,h}^0$ should be computed for the value of $E$ at which the difference of potential at the interface is equal to zero. Any change of this potential resulting from variation in the composition of the solution would thus be cancelled. Unfortunately this value of $E$ is not rigorously known, although it can be taken as being equal to the maximum of the electrocapillary curve. The charge of the electrode is undoubtedly equal to zero at that potential, but there is a difference of potential resulting from orientation of molecules of solvent (water) (19). The shift in potential resulting from dipole orientation is not known although it is probably of the order of magnitude of a few hundredths of a volt. Because of this uncertainty it is useful to calculate $k_{f,h}^0$ on the basis of an arbitrary zero of the scale of potential, i.e., in the normal hydrogen electrode scale. However, the results must be corrected to lend themselves to further interpretation. In doing so we shall identify the potential corresponding to the maximum of the electrocapillary curve (E.C.M.) with the value of $E$ for which the difference of potential at the interface is equal to zero. Results obtained in this fashion are approximate. Potentials at the E.C.M.
listed in Table III were determined by the mercury drop method (2). The values of $k_{f, h}$ at the E.C.M. potential are plotted against the concentration of cation in Figure 22. The choice of this variable will be apparent from the following discussion.

TABLE III

POTENTIAL CORRESPONDING TO THE ELECTROCAPILLARY MAXIMUM (V. vs. S.C.E.)

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<th>Concentration (moles/liter)</th>
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</table>

The potential corresponding to the electrocapillary maximum for 0.05 M sodium hydroxide was -0.500 V. vs. S.C.E.

Values marked (x) were taken from Graham (21).
Figure 22. Plots of log $k_{f,h}$ versus the logarithm of the cation concentration for the reduction of iodate in 0.05 M sodium hydroxide in the presence of various amounts of indifferent electrolytes. Values of $k_f$ were calculated at the potential corresponding to the electrocapillary maximum. Points for potassium iodide are displaced downward by three units.
It is seen from Figure 22 that with the exception of iodide the nature of the anion is of secondary importance in determining the variations of the rate constant at the E.C.M. potential. This observation can be explained as follows. Iodate ion under the experimental conditions prevailing in this study is reduced at rather negative potentials - around 1 volt versus the normal hydrogen electrode. Anions are repelled from the electrode at such negative potentials, as is indicated by the identical shape the electrocapillary curve exhibits for these various ions (19). Hence, values of $k_f,h$ are approximately the same whether a univalent ion such as fluoride or a highly charged ion such as ferrocyanide is present. The case of iodide is an exception because this ion is strongly adsorbed on mercury even at potentials as negative as those at which iodate ion is reduced (see values of the E.C.M. potential for iodide in Table III).

Another conclusion which can be drawn from Figure 22 is that the rate constant $k_f,h$ at the E.C.M. potential is approximately proportional to the concentration of cation in the range of concentration which has been explored. This can be explained if one assumes that cations are intermediate in the transfer of electrons. Thus, the probability of electron transfer, for given conditions of electrolysis, increases with the number of cations. This argument holds if one assumes that cations are not adsorbed on the mercury electrode to any appreciable extent, because if this were not so the number of cations at the interface would not be a linear function of the bulk concentration of cation. However, there is conclusive evidence that with cations of alkali, which are virtually not adsorbed on mercury, the electrocapillary curve for a given anion is not affected when the nature of the cation is changed (19).
Cations are generally separated from the electrode surface by molecules of water, and consequently the distribution of potential is not markedly affected by the presence of cations. As a result the transfer coefficient is independent of the concentration of cation in the case of the reduction of iodate. This is precisely what is observed since the product \( \alpha n_a \) for all the data of Figure 22 was \( 0.77 \pm 0.02 \).

In conclusion, it is possible to give a rational interpretation of the effect of "foreign" salts on the kinetics of electrode processes. The present study brings to light fundamental observations: (1) Electron transfer processes in electrochemical kinetics can proceed through "indifferent" ions (cation in the case of iodate); (2) The change in the rate of electron transfer is essentially proportional to the concentration of these indifferent ions. It would be of interest to compare the effect with similar observations for electron transfer in homogeneous systems as for example in isotopic exchanges.

**INFLUENCE OF TEMPERATURE ON THE KINETICS OF ELECTRODE PROCESSES**

**Introductory remarks**

According to Bokris (4), the rate constant \( k_{f,h} \) of equation (7-1) can be written in the form

\[
k_{f,h} = \frac{kT}{h} \left[ e^{\frac{\Delta G}{RT}} \right] \left[ e^{\frac{-\Delta H}{RT}} \right]
\]

(7-2)
where \( k \) is the Boltzmann constant; \( h \) the Planck constant; \( T \) the absolute temperature; \( \rho \) the thickness of the reaction layer; \( \Delta G^\neq \) the free energy of activation of the electrode process. The potential \( E_0 \) is the potential of the electrode - referred to the normal hydrogen electrode - and for which the difference of potential at the interface is equal to zero. It was seen in the previous section that \( E_0 \) is approximately equal to the potential at the maximum of the electrocapillary curve.

Equation (7-2) can also be written as

\[
\ln k^0_{f,h} = \ln \frac{kT}{h} + \frac{\Delta S^\neq}{R} - \frac{\Delta H^\neq - \alpha M_{F}F E_0}{RT} \tag{7-3}
\]

or

\[
\ln k^0_{f,h} = A - \frac{\epsilon}{RT} \tag{7-4}
\]

where \( \epsilon \) is defined by the relationship

\[
\epsilon = \Delta H^\neq - \alpha M_{F}F E_0 \tag{7-5}
\]

It is seen from equation (7-4) that the value of the quantity \( \epsilon \) can be determined approximately from a plot of \( \ln k^0_{f,h} \) against the reciprocal of absolute temperature. It must be noted, however, that the evaluation of the fundamental thermodynamic quantities \( \Delta H^\neq \) and \( \Delta S^\neq \) is complicated by uncertainty in the values of the potential \( E_0 \) and the thickness of the reaction layer. Furthermore, as is shown below, the quantity \( \alpha \) may depend on temperature, and consequently the significance of \( \epsilon \) is somewhat questionable.
Interest in the influence of temperature in electrochemical kinetics has been focused almost entirely on studies of hydrogen and oxygen evolution and of a few miscellaneous oxidation-reduction processes (26). Experimental data for these processes have been critically examined by Bokris (4). Essentially, two quantities have been calculated: the transfer coefficient $\alpha$ and the heat of activation $\Theta$ (see equation (7-5)). Some of the principles pertaining to the determination of $\Theta$ have been reviewed by Agar (1).

The present study was undertaken to demonstrate the usefulness of voltammetric methods in the study on the effect of temperature in electrochemical kinetics. The study has been mainly concerned with the determination of the parameters $J^{0}_{f,h}$ and $\alpha n_a$ and the elucidation of the mechanism of some electrode processes.

The method of determining $J^{0}_{f,h}$ and $\alpha n_a$ is outlined in Chapter I; the experimental methods are described in Chapter II. The mercury pool electrode was utilised throughout this investigation. Four processes were studied:

1. Reduction of 1 mM iodate in 1 M sodium hydroxide
2. Reduction of 4 mM nickel(II) in 1 M potassium chloride
3. Reduction of 7 mM chromium(III) in 0.5 M potassium nitrate
4. Reduction of oxygen in acetate buffer (pH = 4.6).

In the latter case, the electrolyte was saturated with oxygen at the temperature of electrolysis and the concentration of oxygen was determined by the Winkler method.
Description and discussion of results

Examples of diagrams showing the variation of the logarithm of \( \left[ 1 - \left( \frac{t}{T} \right)^{\frac{1}{2}} \right] \) with potential at different temperatures are shown in Figures 23 and 24. Note that straight lines are obtained in such plots, as is to be expected from equation (1-14). The analysis of the diagrams of Figures 23 and 24 and of similar diagrams for nickel(II) and iodate yielded the data summarized in Figures 25 and 26.

It is seen from Figure 25 that the product \( \sim n_a \) varies slowly with temperature for Curves 1, 3 and 4 while there is a rather rapid decrease in \( \sim n_a \) for Curve 2. Possible explanations for the variations of \( \sim n_a \) are as follows:

(1) All the processes studied here except the reduction of chromium(III) involve the transfer of several electrons. The processes were analyzed on the assumption that the kinetics of the over-all reaction involves only one rate determining step. Although this assumption is quite often valid, it is not necessarily correct. For example, consider the reduction of Ni(II). In this process it is probable that the electrochemical reaction actually involves two steps which can be characterized at a given potential by two rate constants \( k_1 \) and \( k_2 \). At low temperatures one may assume that \( k_1 \) is much smaller than \( k_2 \); the kinetics of the electrode process is then entirely controlled by the first step. As the temperature increases, the rate constant \( k_1 \) increases more rapidly than the rate constant \( k_2 \), and consequently the kinetics of both steps must be considered. As a result, the potential-time curve is distorted and there is apparent variation of the transfer coefficient.

(2) It is probable that in some cases the variation of the product \( \sim n_a \) is due to a variation in the transfer coefficient \( \sim \). Actually, there is no fundamental reason for assuming that the transfer coefficient is temperature independent. This is probably the case for the reduction of iodate ion and oxygen.

(3) Finally, the formation of complex ions and the subsequent variation in the composition of the solution possibly influences the value of \( \sim n_a \) for substances such as chromium(III).
It is apparent from the foregoing observation that the effect of temperature on electrode processes may be quite complex. In addition to variation of rate constant arising from variations of $\Delta G^\pm$ with temperature, there are complications due to several factors: (1) Variation of the transfer coefficient; (2) Variation of the potential at which the difference of potential at the interface is equal to zero; (3) The occurrence of stepwise processes; (4) Change in the composition of the solution. As a result, heats of activation for electrode processes are at best of only qualitative value.
Figure 23. Plots of $\log \left[ 1 - \left( \frac{t}{\tau} \right)^{1/2} \right]$ versus potential for the irreversible reduction of chromium(III) in 1 M potassium nitrate at various temperatures.
Figure 24. Plots of $\log \left( \frac{1}{\left( \frac{t}{\tau} \right)^{1/2}} \right)$ versus potential for the irreversible reduction of oxygen in acetate buffer at various temperatures.
Figure 25. Plots of $\alpha_n$ versus temperature for various irreversible processes: Curve 1, iodate in 1 M sodium hydroxide; Curve 2, nickel(II) in 1 M potassium chloride; Curve 3, chromium(III) in 1 M potassium nitrate; Curve 4, oxygen in acetate buffer.
Figure 26. Plots of log $k_{p,h}^\circ$ versus reciprocal temperature for various irreversible processes: Curve 1, iodate in 1 M sodium hydroxide; Curve 2, nickel(II) in 1 M potassium chloride; Curve 3, chromium(III) in 1 M potassium nitrate; Curve 4, oxygen in acetate buffer.
It is possible to develop satisfactory treatments for a variety of electrode processes which are encountered in voltammetry at constant current. The mathematical analysis of the processes discussed in this dissertation as well as processes considered by other authors lends itself to experimental verification. The necessary experimental methods were developed in the course of the work.

The emphasis in this investigation was placed on electrochemical kinetics, but it should be noted that voltammetry at constant current has great potentialities as an analytical tool. Practical application of the method in analytical chemistry can now be made, since the characteristic features of processes generally encountered are well understood at present.

Voltammetry at constant current may also be utilized as a tool in electrochemical kinetics, and two applications - namely the study of the influence of ionic interaction and temperature - have been made in this work.

Finally, voltammetry at constant current may serve as an auxiliary tool in chemical kinetics. This type of application is of rather limited scope, but nevertheless the constant current method may be useful in the study of reactions which are too rapid to be followed by more conventional methods.
### APPENDIX I

**VALUES OF THE FUNCTION $\varphi/r^2 \exp(r)$ FOR VALUES OF $r$**

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</table>
APPENDIX II

ANALYSIS OF IRREVERSIBLE POLAROGRAPHIC WAVES

General considerations

Several treatments of irreversible polarographic waves have been reported in recent years. It is the purpose of this appendix to consider, briefly, two of the more successful treatments - the treatment of Delahay, which was presented in 1951, and the treatment of Koutecky, which was reported in 1953. The boundary value problem will first be stated.

It is assumed that the current at any point in the wave is controlled by the rate of the electrode process and by the rate of diffusion of the substance reacting at the electrode. Furthermore, this summary will deal only with the case in which the influence of the reverse (anodic) process is negligible; this is the case when the overvoltage is greater than about 0.1 volt. The diffusion problem is solved for semi-infinite linear diffusion and subsequently modified for application to the dropping mercury electrode.

Under these conditions the number $dN$ of moles of substance reduced in time $dt$ is proportional to the concentration of reducible substance at the surface of the mercury drop. Thus, one has
per unit area

\[ dN = k \frac{dN}{dt} \]  \hspace{1cm} (9-1)

where \( k \) is the rate constant of the electrode process. One notes that \( k_{f,h} \) is a heterogeneous rate constant which is expressed in units cm. sec. \(^{-1}\).

According to Fick's first law the number of moles of reducible substance diffusing toward the electrode is proportional to the concentration gradient of that substance at the electrode surface. Thus

\[ dN = D \left( \frac{\partial C(x,t)}{\partial x} \right)_{x=0} dt \]  \hspace{1cm} (9-2)

By equating the values of \( dN \) in equations (9-1) and (9-2) one obtains the following boundary condition

\[ D \left( \frac{\partial C(x,t)}{\partial x} \right)_{x=0} = \frac{2}{k_{f,h}} C(0,t) \]  \hspace{1cm} (9-3)

The initial condition is simply obtained by expressing that the concentration \( C(x,t) \) is independent of \( x \) at time \( t = 0 \). Thus \( C(x,0) = C^0 \) where \( C^0 \) is the bulk concentration of the electrolyzed species.

Furthermore, the function \( C(x,t) \) is bounded for large values of \( x \). Thus \( C(x,t) \to C^0 \) for \( x \to \infty \).

**Derivation of Delahay (13)**

By solving Fick's equation for linear diffusion for the above condition, Delahay derived the concentration \( C(x,t) \). The current is
then readily derived from the equation

\[ i' = \pi FA D \int \frac{\partial C(x,t)}{\partial x} \bigg|_{x=0} \]

When the derivative \( \int \frac{\partial C(x,t)}{\partial x} \bigg|_{x=0} \) is deduced from this general solution \( C(x,t) \) the notations in (9-4) are as follows: \( n \) is the number of electrons involved in the process, \( F \) is the faraday and \( A \) is the area of the electrode. The equation for the current is

\[ i' = \pi FA C(x,t) \sqrt{\frac{D}{t}} \left[ 1 - ef \left( \frac{k_f \sqrt{t}}{D} \right) \right] e^{\nu} \left( \frac{k_f \sqrt{t}}{D} \right) \]

Equation (9-5) which is rigorous for linear diffusion can also be applied to the dropping mercury electrode. The results, however, are approximate. After introducing the value of the electrode area \( A \) in terms of the rate of flow of mercury \( m \) and the time \( t \) elapsed since the beginning of the formation of the drop, one obtains

\[ i' = \frac{255}{2} \frac{m}{3} \frac{1}{2} \frac{k_f}{2} \sqrt{\frac{D}{t}} \left[ 1 - ef \left( \frac{k_f \sqrt{t}}{D} \right) \right] e^{\nu} \left( \frac{k_f \sqrt{t}}{D} \right) \]

The average current during the life of the drop was obtained by Delahay by graphical integration of equation (9-6). The results can be condensed in a diagram which shows the variation of the average current along the wave to the diffusion current. The calculation of the rate constant \( k_{f,h} \) as a function of potential is then a simple matter.
Correction for the movement of the electrode through the solution

Since the dropping mercury electrode is not a stationary electrode, some correction must be made for the movement of the electrode through the solution. This correction was first introduced by Ilkovic for the case in which there is purely diffusion control. The analysis of Ilkovic will be summarized here to serve as an introduction to the more involved case in which the rate of electron transfer must be taken into account.

The concentration of substance in solution is a function of the distance x from the surface of the electrode and the time t. Consequently one may write

\[ \Delta C = \frac{\partial C(x,t)}{\partial x} \Delta x + \frac{\partial C(x,t)}{\partial t} \Delta t \] (9-7)

As the electrode moves through the solution, an element in the solution approaches the surface at a velocity v. Thus, \( \Delta x = -v \Delta t \), and

\[ \left( \frac{\partial C(x,t)}{\partial t} \right)_{\text{rel.}} = \frac{\partial C}{\partial t} - v \frac{\partial C}{\partial x} \] (9-8)

where \( \left( \frac{\partial C(x,t)}{\partial t} \right)_{\text{rel.}} \) is the variation of concentration with respect to some reference point which follows the movement of the solution. The derivative \( \left( \frac{\partial C(x,t)}{\partial x} \right)_{\text{rel.}} \) is, according to Fick's law

\[ \left( \frac{\partial C(x,t)}{\partial x} \right)_{\text{rel.}} = D \frac{\partial^2 C}{\partial x^2} \] (9-9)
In view of (9-9), equation (9-8) may be written in the form

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

(9-10)

This is the modified Fick's equation for diffusion toward a plane which moves at a velocity \( v \) in solution. This equation can be applied approximately to the dropping mercury electrode, i.e., to the case of an expanding sphere. It suffices to calculate the velocity \( v \), which in the case of the dropping mercury electrode is

\[ v = \frac{x}{3t} \]  

(9-11)

The combination of (9-10) and (9-11) yields

\[ \frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} + \frac{2x}{3t} \frac{\partial C(x,t)}{\partial x} \]  

(9-12)

The current for an irreversible process is derived by solving equation (9-12) for the boundary and initial conditions previously stated. This problem was solved by Koutecky and a brief account of his work is given in the following section.

**Derivation of Koutecky (23)**

Koutecky introduced the following dimensionless parameters

\[ S = \frac{x}{\sqrt{\frac{D}{3t}}} \quad \xi = \frac{x}{\sqrt{\frac{D}{3t}}} \sqrt{\frac{12}{\nu}} \]  

(9-13)
Equation (9-12) may be written in the form

\[ \frac{d^2 C(s, \nu)}{ds^2} + 2S \frac{dC(s, \nu)}{dS} - \frac{\nu}{\gamma} \frac{dC(s, \nu)}{d\nu} = 0 \]  

(9-14)

The boundary and initial conditions can be transformed in a similar fashion. The solution of equation (9-14) can be written in the form of an infinite series

\[ C(s, \nu) = \sum_{i=0}^{\infty} \lambda_i \psi_i \]  

(9-15)

when the quantities \( \lambda_i, \psi_i \) have to be determined. These coefficients were determined by Kouteeky who summarized his results in the form of Table V. This table gives the ratio of the instantaneous maximum current \( i \) along the wave to the instantaneous maximum diffusion current \( i_d \) for different values of \( \psi \). Since the ratio \( i/i_d \) is easily measured, the value of \( k_{\psi, h} \) can be determined provided that the diffusion coefficient \( D \) is known. The latter is computed by application of the Ilkovic equation.

**Comparison of the treatments.**

Results obtained by the two methods are compared in Figure 26 for the reduction of 0.5 mM iodate in 1 M sodium hydroxide and 0.002% gelatin. One notes that the two treatments yield quite similar results; consequently the influence of the additional term is relatively minor.
### Table IV

Values of the ratio $i/i_d$ according to Koutecky

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<th>$\sqrt{\frac{12t}{10}}$</th>
<th>$\frac{i}{i_d}$</th>
<th>$\sqrt{\frac{12t}{10}}$</th>
<th>$\frac{i}{i_d}$</th>
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</thead>
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</tbody>
</table>
Figure 27. Plots of log $k_{f, h}$ versus potential according to Delahay (line 1) and Koutecky (line 2) for the reduction of iodate in 1 M sodium hydroxide.
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VITA

Calvin C. Mattax was born in Sallisaw, Oklahoma, on February 4, 1926. He received his elementary and high school education in the public schools of Lonoke, Arkansas. Immediately after graduation from high school in 1943, he entered the United States Army where he served until 1946.

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He was married to Carolyn J. Botkin of Tulsa, Oklahoma on September 4, 1949.
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Major Field: Chemistry

Title of Thesis: Voltammetry at Constant Current and Its Application to Electrochemical Kinetics

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

January 28, 1954