DROPPING ZINC AMALGAM ELECTRODES
IN POLAROGRAPHY

by

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ABSTRACT

The general principles of polarography are mentioned briefly and the equations for the polarographic diffusion current are compared. The several derivations are traced and the points of departure leading to correction terms are noted. It is known that the assumptions upon which the derived equations for the diffusion current are based are not in accord with reality. It is also known that the departures from ideality tend to oppose so that, finally, the basic assumptions, even if imperfectly fulfilled, may be considered valid. These factors are discussed during development of the equations.

A review of amalgam polarography is essentially complete. Publications dealing with the subject are reported almost in entirety.

The preparation of dilute amalgams is discussed in the light of results obtained in preliminary work. The ideal nature of these amalgams is shown in a review of several papers dealing with E. M. F. measurements. The evidence for the ionization and polymerization of zinc metal in solution in mercury is discussed briefly along with the hypothetical reactions which explain the instability of very dilute amalgams. In addition, it is noted that a few workers have investigated the behaviour of dilute amalgams during passage of direct current. The evidence indicates that a dilute amalgam has properties analogous to a salt solution. Particularly, the phenomena of transport during passage of the electrical current has been
reported. Further investigation of the phenomena is suggested since transport of the metal in amalgam during passage of the electrical current violates the conditions required by the polarographic theory. The physical properties of zinc and zinc amalgams pertinent to the polarographic method are tabulated. It is noted that the diffusion coefficient of zinc in mercury has not been satisfactorily established.

A method for stabilizing dilute zinc amalgams by impressing a voltage across the amalgam reservoir and a platinum electrode in a water layer over the amalgam is described.

The utilization of the Sargent Polarograph Model XXII in conjunction with a Leeds and Northrup Student Type potentiometer for manually recording polarograms is described.

Polarograms of standard zinc solutions in 0.1N potassium chloride plus a trace of gelatin were recorded and measured under the same conditions intended for recording and measuring the polarograms of zinc amalgams. The data so obtained agreed to within 5% of the values previously reported for the diffusion current constant and to within 2% of the reported half-wave potential for zinc salts in 0.1N potassium chloride plus traces of maximum suppressors. It was noted that the values of the diffusion current constant increased with decreasing concentration of zinc in agreement with other published reports but contrary to the findings of Kalthoff and Lingane. The deviation is believed to be due in part to the presence of traces of oxygen. Further investigation is suggested.
The behavior of dilute zinc amalgam at the dropping electrode is shown to correspond to that of mercury except for an inflection in the drop time vs potential curve. The inflection is found in the range of potential over which the 'wave' for zinc amalgam develops. It is also shown that the amalgam stabilizing circuit has a negligible effect on the recorded polarograms. In short, accuracy of the same order obtained in ordinary polarography can apparently be attained.

Reproducible polarograms of 0.000288% zinc amalgam have been obtained. Calculations fail to reveal gross error. The diffusion current constant calculated from the original Ilkovic equation is found to be 5.16 ± 0.07. The mean value of the diffusion coefficient of zinc in mercury is calculated 2.4 X 10^-5 cm^2 sec^-1 at 25.0°C from values reported in the literature. For this value of the diffusion coefficient the numerical constant 'B' in the second term of the Strehlow-Stackelberg equation, has been calculated 23.6 ± 2.3. This value is within range of the values predicted for B, from theoretical approximations. Choice of the larger values of the diffusion coefficient would give larger values for B. Here, the result is taken as evidence that streaming at the drop surface is near minimum.

From the data obtained in polarography of standard zinc solutions it is observed that the Lingane-Loveridge equation gave the best agreement with accepted values. Accordingly, the value for the diffusion coefficient of zinc in mercury at 25.0°C has been calculated according to equation as 2.58 cm^2 sec^-1 ± 0.09. A value in agreement.
ment with the larger of the several reported values.

Consistent results with amalgams less than 0.005% solute metal have not previously been reported in the polargraphic literature. In this work an amalgam 0.000288% has provided not only consistent results, but also results from which remarkable agreement with published data has been obtained. This is taken as evidence that the method is suitable for work of the precision and accuracy obtainable in ordinary polarography.

The conditions for work of greater precision and accuracy are set forth with a brief discussion of the difficulties and sources of error involved.

The practical applications of amalgam polarography are suggested.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>1</td>
</tr>
<tr>
<td>INTRODUCTORY NOTE</td>
<td>v</td>
</tr>
<tr>
<td>PART A INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>PART B POLAROGRAPHY. THEORY AND APPLICATIONS</td>
<td></td>
</tr>
<tr>
<td>1. POLAROGRAPHIC THEORY</td>
<td>2</td>
</tr>
<tr>
<td>2. DROPPING AMALGAM ELECTRODES</td>
<td>27</td>
</tr>
<tr>
<td>PART C ZINC AMALGAMS</td>
<td></td>
</tr>
<tr>
<td>1. METHODS OF PREPARING ZINC AMALGAM</td>
<td>31</td>
</tr>
<tr>
<td>2. CHEMICAL and PHYSICAL PROPERTIES of ZINC AMALGAMS</td>
<td>32</td>
</tr>
<tr>
<td>PART D EXPERIMENT</td>
<td></td>
</tr>
<tr>
<td>1. MATERIALS AND SOLUTIONS</td>
<td>41</td>
</tr>
<tr>
<td>2. APPARATUS</td>
<td>45</td>
</tr>
<tr>
<td>3. METHODS</td>
<td>49</td>
</tr>
<tr>
<td>PART E RESULTS AND DISCUSSION</td>
<td></td>
</tr>
<tr>
<td>1. POLAROGRAPHY OF STANDARD ZINC SOLUTIONS</td>
<td>51</td>
</tr>
<tr>
<td>2. AMALGAM POLAROGRAPHY</td>
<td>62</td>
</tr>
<tr>
<td>3. SUMMARY OF RESULTS</td>
<td>78</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>82</td>
</tr>
<tr>
<td>COPY 'THE USE OF DILUTE AMALGAMS IN THE DROPPING ELECTRODE'</td>
<td></td>
</tr>
<tr>
<td>by HEYROVSKY AND KALOUSEK</td>
<td>84</td>
</tr>
</tbody>
</table>
INTRODUCTORY NOTE

The division of this thesis into several parts has been found necessary to clarify presentation of the various phases involved in the work. Firstly, the equations for the polarographic diffusion current are derived. Since an equation for the diffusion current is the law required in the fundamental theory of polarography, the several derivations have been integrated for comparison. Secondly, since the literature dealing with amalgam polarography is limited it was decided to gather as much as possible under one cover. Thirdly, in order to have as much useful information as possible in one place for future investigations, a wide range of subjects is discussed herein. These subjects are the preparation, chemistry and physics of zinc amalgams described in the literature as well as closely related subjects such as the transport of metal in an amalgam during passage of the electric current. Unfortunately, some of the information is fragmentary due to the fact that the original literature was not immediately available. On the other hand, there are some subjects which were not covered due to the fact that time did not permit further literature search. Among the omissions may be mentioned the electrocapillary characteristics of mercury and dilute mercury amalgams. This subject, however, appears to be a field for separate investigation. Fourthly, the experimental methods and results of this work are presented.
Due to the considerable range of material covered some overlapping and repetition is required for continuity.

In a few instances experimental evidence is given without detail of method. In these cases, however, the results were unsatisfactory and detail was considered superfluous since the context explains the basis of the method.

It is regretted that time did not permit further investigations under the conditions which experience gained in this work had shown to be necessary.
DROPPING AMALGAM ELECTRODES IN POLAROGRAPHY

A--INTRODUCTION

During investigation for suitable methods of analysis in research on zinc anodes in chromate electrolysis the polarographic technique was considered. Lingane's note on the dropping cadmium amalgam electrode suggested that perhaps a dropping zinc amalgam electrode in the polarography of chromate solutions would afford some useful information with respect to the electrode reactions involved. Further search in the literature at that time revealed no quantitative data relating to the anodic diffusion current of dropping amalgam electrodes. Consequently, this work has been directed towards determining the characteristics of dropping zinc amalgam electrodes in polarography with respect to the feasibility of their use in investigating anode reactions. Since time did not permit the completion of the entire work in mind, it was decided that the determination of the apparent diffusion coefficient of zinc in mercury under polarographic conditions would provide the most useful data towards further investigations.
The polarographic method of chemical analysis was invented by J. Heyrovsky. The method is based on the interpretation of the current-voltage curves that are obtained when solutions of electro-reducible or electro-oxidizable substances are electrolyzed in a cell in which one electrode consists of mercury falling drop-wise from a fine bore capillary. The solution contains a minute amount of the electrochemically reacting substance in the presence of a relatively huge amount of an indifferent electrolyte. The unique current-voltage curves obtained by the method indicate both the species and concentration of the reactive substance.

On account of the smallness of the dropping mercury electrode, extreme concentration polarization occurs so that the current is determined by diffusion of the reacting substance and the area of the mercury drop. The diffusion current is thus proportional to the concentration of the reacting substance when all other factors influencing the diffusion current are made constant. That is

\[ i = KC \]

The proportionality constant \( K \) is determined by measuring the diffusion current \( i \) for a solution of known concentration \( C \). Subsequently, an unknown concentration may be determined by using the experimentally determined value for \( K \).
However, it is more desirable to calculate $\Delta K$ for any reasonable variations of the factors which influence the diffusion current. An equation for the polarographic diffusion current has been derived by Ilkovic (2) and substantiated by others (3) (4).

The general and theoretical principles of polarography have been discussed in some detail by several authors (5) (6) (7), and the reader is referred to them for a more complete treatment than is given here. In particular, the more recent publications of Lingane and Loveridge (8) and Strehlow and Stackelberg (9) have added much to the theory of the polarographic diffusion current.

Before deriving the Ilkovic equations it may be in order to present a brief summary of their development. The original Ilkovic equation reads (2):

$$i_d = 605 n D^{\frac{1}{2}} C^{\frac{2}{3}} t^{\frac{1}{2}}$$

where $i_d$ = average current in microamperes during the life of the drop.

$n$ = number of faradays of electricity required per mole of the electrode reaction.

$D$ = diffusion coefficient of the reducible or oxidizable substance in the units $cm^2 sec^{-1}$.

$C$ = its concentration in millimoles per litre.

$m$ = rate of flow of mercury from capillary in $mm sec^{-1}$.

$t$ = drop time in seconds.

Since $25.00^\circ C$ has been chosen as a standard condition for polarographic work the values of the physical constants at that temperature must be used. The Ilkovic diffusion current
equation for the standard condition $25.00^\circ$C is given

$$ id = 607n \frac{D^{1/2} C m^{3/5} \zeta^{1/4}}{\tau} $$  \hspace{1cm} (II)

By collecting the variable terms

$$ \frac{id}{C m^{3/5} \zeta^{1/4}} = 607n D^{1/2} = I $$  \hspace{1cm} (III)

where $I$ = diffusion current constant. However, Lingane and Loveridge (3) (10) have shown that $I$ varies significantly with changing values of $m^{3/5} \zeta^{1/4}$, thus demonstrating that the original Ilkovic equation, although approximately correct, is not completely satisfactory. They have also shown that the equation can be derived directly from the diffusion current equation for linear diffusion to a plane electrode. Presumably, the simplifications in intermediate mathematical operations became equivalent to a neglect of the curvature of the mercury drop in the original Ilkovic equation. By a simple artifice Lingane and Loveridge obtained a new equation (IV).

$$ id = 607n \frac{D^{1/2} C m^{3/5} \zeta^{1/4}}{\tau} (1 + 39D^{1/2} m^{-3/5} \zeta^{1/4}) $$  \hspace{1cm} (IV)

Strehlow and Stackelberg (9) have derived a similar equation (V) which differs only in the value of the numerical constant

$$ id = 607n D^{1/2} C m^{3/5} \zeta^{1/4} (1 + 17D^{1/2} m^{-3/5} \zeta^{1/4}) $$  \hspace{1cm} (V)

Their derivation from basic principles also gave the equation (VI) for the polarographic diffusion current of dropping amalgam electrodes.

$$ id = 607n D^{1/2} C m^{3/5} \zeta^{1/4} (1 - BD^{1/2} m^{-3/5} \zeta^{1/4}) $$  \hspace{1cm} (VI)

The problem involved is to calculate the diffusion of the reactant across an area which is defined by the surface area of an expanding drop. Since the diffusion current is the product of the quantity of electricity required per mole of electrode reaction and the unit flux and the area of the
electrode an equation of the form

\[ i_t = n F \frac{\partial c}{\partial r} \chi_t A \]  

might be expected where

- \( i_t \) = diffusion current at the time \( t \).
- \( F \) = the electrochemical equivalent, the faraday.
- \( n \) = the number of faradays required per mole of electrode reaction.
- \( D \) = proportionality constant for diffusion.
- \( \frac{\partial c}{\partial \chi} \) = rate of change of concentration \( c \) with change of distance \( \chi \) from a fixed origin \( \chi = 0 \) at a plane defined by \( \chi \) at the time \( t \). (since the concentration at any plane is dependant on the time).
- \( A_t \) = Area of the drop at the time \( t \).

Such an equation would give the instantaneous current at the time \( t \). However, we have a drop expanding with time which counteracts the decrease of the unit flux with time. Further, the concentration at \( \chi \) referred to a fixed coordinate \( \chi = 0 \) must be changed since the plane in question is itself moving due to the relative incompressibility of liquid. In view of these considerations it is required to replace \( \frac{\partial c}{\partial \chi} \) and \( A_t \) with the appropriate expressions.

Firstly, it has been assumed that the reactant reaches the electrode by diffusion alone. In the case of ordinary polarography this condition is adequately fulfilled. Although the electric field and the electric transport of the reactant are never nil, the effect is immeasurably small since the indifferent electrolyte is usually \( 10^3 \) to \( 10^6 \) times the concentration of the reactant. In the case of amalgam polarography, however, the assumption will be considered.
questionable pending further investigations. Here the question of electric transport of metals dissolved in mercury arises. Elsewhere there is given some evidence for the phenomena. Whether or not the effect is measurable in amalgam polarography cannot be stated here. In addition to electrical transport, a convection current could also interfere with true diffusion. Actually, a convection current of considerable magnitude does exist. According to Strehlow and Stackelberg (9), the mercury current issuing from the capillary persists so as to cause streaming at the mercury surface. This streaming, or rinsing effect, is not as strong in ordinary polarography, where the reactant is in solution, as it is in amalgam polarography. The streaming, or rinsing effect, is shown schematically in Fig. 1. Thus, the initial assumption for the derivation of the equation for the polarographic diffusion current is imperfectly fulfilled.

For linear diffusion the number of moles, \( dN \), of reactant diffusing across a cross sectional plane of area \( A \) cm\(^2\) in the infinitesimal interval of time \( d\tau \) is proportional to the concentration gradient \( \frac{\partial C}{\partial x} \) at the plane in question and is expressible by

\[
\frac{dN}{d\tau} = DA \frac{\partial C}{\partial x} d\tau \tag{VIII}
\]

where \( D \), the proportionality constant, is the diffusion coefficient. The flux at a plane distance \( x \) from the origin designated

\[
J_x = \frac{dN}{Ad\tau} = D \frac{\partial C}{\partial X} \tag{IX}
\]

In order to calculate the total amount of material that will diffuse across a given plane in a finite period, it is necessary to have a knowledge of the change in concentration with time at
FIGURE 1. — Schematic representation of current due to mercury outflow and resultant streaming or rinsing effect.
the plane in question. The change in concentration with time between two planes separated by the infinitesimal distance $d\chi$ is equal to the difference between the number of moles which enter across the plane at $\chi + d\chi$ and the number which leave across the plane at $\chi$ divided by the volume $Ad\chi$ enclosed between the planes; that is

$$\frac{dC}{dt} = \frac{f_{\chi+d\chi} - f_{\chi}}{d\chi}$$

(Since $A$ is equal to unity when we speak of the flux we also have)

$$f_{\chi+d\chi} = f_{\chi} + \frac{\partial f}{\partial \chi} d\chi$$

Since from

$$\frac{\partial f}{\partial \chi} = D \frac{\partial^2 C}{\partial \chi^2}$$

we find from equation (I) that the change in concentration with time at a given plane at a given instant is expressed by

$$\frac{dC}{dt} = D \frac{\partial^2 C}{\partial \chi^2}$$

The problem is to obtain an expression for the concentration gradient at any instant at $\chi = 0$, from which by means of equation (IX) the flux, and hence the current can be computed. At the instant the EMF is applied, ($\chi = 0$), the concentration at the electrode, ($C_0$), is equal to that in the body of the solution, ($C$). After the EMF is applied, ($\chi > 0$), $C_0$ is rapidly decreased by the electrode reaction. The initial and boundary conditions are therefore,

$$C_0 = C \quad \text{when} \quad \chi = 0$$

$$C_0 \ll C \quad \text{or} \quad C_0 = 0 \quad \text{when} \quad \chi > 0$$

These conditions hold in polarography since at an appropriate applied EMF the reactant is electrolytically reduced or
oxidized, as fast as it meets the electrode surface. Under these conditions the solution of equation (XIII) is \[ C_{2c} = C \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-y^2} dy \quad (XIV) \]

By differentiating equation (XIV) under the condition that \( x = 0 \) we obtain
\[ \left( \frac{\partial C}{\partial x} \right)_{x=0} = \frac{C}{\sqrt{\pi} \Delta t} \quad (XV) \]

Substituting in equation (VII) we have
\[ I = \mu FA C \sqrt{\frac{D}{\pi \Delta t}} \quad (XVI) \]

This is the equation for the instantaneous current at any time \( I \) after the EMF is applied, where linear diffusion to a plane electrode is considered. Lingane and Loveridge (5) derived the corrected Ilkovic equation (II) from equation (XVI) by substituting the values for \( A \), integrating to obtain the average current and multiplying by a numerical constant.

Such a derivation provided a clue to the inadequacy of the original Ilkovic equation.

However, the problem involves a spherical electrode. In the derivation it is assumed that the mercury drop is a free sphere. Later it will be shown that this is not actually the case. Here we will consider the reactant diffusing to a free spherical electrode of radius \( r_e \). The diffusion field is a spherical shell surrounding the electrode at distance \( r \) measured from the centre of the sphere. The area of the surface is \( 4\pi r^2 \).

1. See reference (5) page 21 for a discussion of this solution, equation (XIV).
The number of moles which diffuse across this surface in the
time $d\tau$ is given by the expression, analogous to Fick's
First Law,
\[ \frac{dN_1}{dt} = 4\pi n^2 D \left( \frac{\partial c}{\partial n} \right)_n d\tau \]  
(XVII)
and the flux at $n$ is
\[ f_n = \frac{dN_1}{4\pi n^2 d\tau} = D \left( \frac{\partial c}{\partial n} \right)_n \]  
(XVIII)
Similarly, the number of moles that diffuse across the surface
at $n+dn$ in the time $dt$ is
\[ dN_1 + dn = 4\pi (n+dn)^2 D \left( \frac{\partial c}{\partial n} \right)_{n+dn} dt \]  
(XIX)
and
\[ f_{n+dn} = D \left( \frac{\partial c}{\partial n} \right)_{n+dn} \]  
(XX)
The concentration gradient at $n+dn$ is related to that
at $n$ by
\[ \left( \frac{\partial c}{\partial n} \right)_{n+dn} = \left( \frac{\partial c}{\partial n} \right)_n + \frac{\partial}{\partial n} \left( \frac{\partial c}{\partial n} \right)_n dn \]  
(XXI)
and hence, equation (XIX) may be written as
\[ dN_1 + dn = 4\pi (n+dn)^2 D dt \left[ \frac{\partial c}{\partial n} \right]_n + \frac{\partial}{\partial n} \left( \frac{\partial c}{\partial n} \right)_n dn \]  
(XXII)
Expanding and neglecting the terms containing infinitesimals
of the second and third orders, equation (XXII) becomes
\[ dN_1 + dn = 4\pi D dt \left[ \frac{\partial c}{\partial n} \right]_n + 2n \frac{\partial c}{\partial n} dn + n^2 \left( \frac{\partial c}{\partial n} \right)_n dn \]  
(XXIII)
The change in concentration in the spherical shell in the time
$dt$ is the difference between the number of moles which enter
the shell at $n+dn$ and the number which leave at $n$ divided by
the volume of the shell which is $4\pi n^2 dn$; that is
\[ \Delta C = \frac{dN_1 + dn - dN_1}{4\pi n^2 dn} \]  
(XXIV)
Therefore, the rate of change of concentration with time at
given values of $n$ and $\tau$ is
\[ \frac{\partial c}{\partial \tau} = \frac{dN_1 + dn - dN_1}{4\pi n^2 L n d\tau} \]  
(XXV)
By substituting the values expressed by equations (XVII) and (XXIII) into (XXV) we obtain
\[
\frac{\partial (\mathfrak{c})}{\partial t} = D \left[ \frac{\partial^2 \mathfrak{c}}{\partial x^2} + \frac{\partial^2 \mathfrak{c}}{\partial y^2} \right] \quad (XXVI)
\]

In order to calculate the total flow through a given shell of infinitesimal thickness in a finite time it is necessary to integrate equation (XXVI). The initial and boundary conditions for linear diffusion are applicable, that is:
\[
\begin{align*}
C_0 &= C \quad \text{when} \quad t = 0 \\
C_0 &< C \quad \text{or} \quad C_0 = 0 \quad \text{when} \quad t > 0
\end{align*}
\]
Under these conditions the solution is
\[
C(t) = C(t) + \frac{2C_n}{2} \int_0^{2\pi} \mathcal{E}^{-y} dy \quad (XXVII)
\]
and
\[
\lim_{t \to \infty} C(t) = C \left( 1 - \frac{\mathfrak{c}^0}{\mathfrak{f}^0} \right) \quad (XXVIII)
\]
That is, with increasing time of diffusion the concentration at any given point in the diffusion field gradually approaches a constant value, a steady state is said to exist. The constant concentration in the steady state is a function of \( \mathfrak{f} \) and varies from zero at the electrode surface \( \mathfrak{f} = \mathfrak{f}_0 \) to \( C \) at a large distance from the electrode \( \mathfrak{f} \rightarrow \mathfrak{f}_0 \) and \( \frac{\partial \mathfrak{c}}{\partial \mathfrak{f}} = 0 \).

This is an important fundamental difference between symmetrical spherical diffusion and linear diffusion, in which latter case a steady state is theoretically unattainable.

1. See reference (5) Pages 28-29 for a discussion of this solution.
The current at any instant is governed by the flux at the electrode surface, i.e., by the concentration gradient at \( \mathbf{t} = t_0 \). By differentiating equation (XXVII) the concentration gradient at the electrode surface at any time \( \mathbf{t} \) is given by
\[
\left( \frac{\partial C}{\partial \mathbf{t}} \right)_{\mathbf{r} = 0, \mathbf{t} = t_0} = \frac{a}{\partial^2} \left( \frac{1}{t_0} + \frac{1}{\sqrt{\pi \mathbf{t}}} \right) = \frac{f_{t = t_0}}{D} \quad (XX IX)
\]
The instantaneous value of the resulting current is, therefore,
\[
\dot{C}_t = nF4\Pi \text{A}^2 f_{t = t_0} = nFADC \left( \frac{1}{t_0} + \frac{1}{\sqrt{\pi \mathbf{t}}} \right) \quad (XXX)
\]
In the case of the dropping mercury electrode the area of the diffusion field changes continuously during the life of a drop and diffusion takes place in a medium that is moving with respect to the centre of the drop, in a direction opposite to the direction of diffusion. Due to the incompressibility of a liquid a diffusion spherical shell remains the same distance from the electrode surface but the surface area increases continuously with time during the life of each drop. Therefore, the equations that describe diffusion to the dropping electrode differ from those for stationary spherical diffusion by terms which describe the increase in the area of the diffusion field with time.

It is assumed that the mercury drops are free spheres. Actually a small part is screened off by the capillary thus decreasing the diffusion field. However, the drops are deformed by gravitation and become tear shaped, thus creating a larger surface area than is possessed by a true sphere of equal volume. Thus, the screening effect and deformation oppose each other with respect to the deviation of the surface area.
It is assumed that at $t=0$ the drops have an area $=0$. In reality an area is always maintained.

It is also assumed that the rate of flow of mercury is constant. Actually, at the beginning of drop formation a very considerable counter pressure due to the curvature of the drop prevails, although it is very quickly removed. Thus, at the beginning of the drop time the rate of increase in surface area is considerably decreased for a brief interval. This compensates to some extent the maintenance of an area at $t=0$.

It is assumed that the thickness of the diffusion layer is small compared to the radius of the drop. This is not satisfactorily the case as shall be seen further on.

Further discussion is based on at least three different lines of development. Firstly, the derivation is based on that shown by Kaltof and Lingane \(^{(12)}\) from a discussion by MacGillavray and Rideal \(^{(11)}\). Secondly, Lingane and Loveridge\(^{(7)}\) derivation will be traced. Thirdly, the more rigorous derivation given by Strehlow and Stackelberg \(^{(9)}\) will be introduced.

We have seen that the fundamental differential equation for symmetrical spherical diffusion is

$$\frac{\partial c}{\partial t} = D \left[ \frac{\partial^2 c}{\partial \rho^2} + \frac{1}{\rho} \left( \frac{\partial c}{\partial \rho} \right) \right]$$

(XXVI)

in which $\rho$ is radial distance measured on a fixed coordinate system whose origin is at the centre of the spherical electrode. In order to apply this equation to diffusion at the dropping electrode the fixed coordinate $\rho$ must be replaced by a moving coordinate, $\rho$, to take into account the increase in area of the
diffusion field during the growth of the mercury drops. The moving coordinate \( \rho \) is defined as the radius of a hypothetical sphere whose volume is the same as the volume enclosed between the surface of the growing mercury drop and a spherical surface of radius slightly larger than the radius of the drop. That is
\[
\frac{4}{3} \pi \rho^3 - \frac{4}{3} \pi \rho_0^3 = \frac{4}{3} \pi \rho^3
\]  
(XXXI)
or
\[
\rho^3 = \rho_0^3 - \rho_0
\]  
(XXXII)
where \( \rho \) is the radial distance from a point in the solution to the centre of the drop, and \( \rho_0 \) is the radius of the drop at any instant.

If we assume that the mercury drop is truly spherical, then its volume at any time \( t \) measured from the beginning of its formation is
\[
V = \frac{4}{3} \pi \rho_0^3 = \frac{m}{\alpha} = \alpha t
\]  
(XXXIII)
where
- \( m \) = weight of mercury flowing from capillary per second.
- \( \alpha \) = the density of mercury.
- \( \alpha \) = proportionality constant = volume of mercury flowing from the capillary per second.

For a given capillary and a constant pressure \( m \) and \( \alpha \) are virtually constant and independent of the interfacial tension at the mercury-solution interface (13). However, during the formation of a single drop there is a very considerable change in pressure. Assuming \( m \) constant then the volume of the drop is directly proportional to its age, but its radius increases with the cube root of its age; that is
\[
\rho_0^3 = \frac{3\alpha}{4\pi} t = \delta t
\]  
(XXXIV)
In view of these relations, and equation (XXXII), can be expressed as a function of the age of the drop by
\[ D^3 = R^3 - \gamma t \] (XXXV)

The flux of the diffusing substance at a given instant and given value of \( \rho \) is
\[ f_n = D \frac{\partial \rho}{\partial n} = D \frac{\partial \rho}{\partial n} \frac{\partial \rho}{\partial n} \] (XXXVI)

From equation (XXXV) for a given value of \( t \)
\[ \frac{\partial \rho}{\partial n} = \frac{2n}{\rho} \] (XXXVII)

and hence, equation (XXXVI) becomes
\[ f_n = D \frac{2n}{\rho} \frac{\partial \rho}{\partial n} \frac{\partial \rho}{\partial n} = \frac{dN}{A_n dt} \] (XXXVIII)

where \( A_n \) is the area of the diffusion field at \( \rho \) at any instant, and \( dN \) is the number of moles that diffuse through \( A_n \) in the time \( dt \). Differentiating equation (XXXVIII)
\[ \frac{\partial f_n}{\partial n} = D \left[ \frac{2n}{\rho} \frac{\partial \rho}{\partial n} + \frac{\partial \rho}{\partial n} \left( \frac{2n}{\rho^2} - \frac{2n^2}{\rho^3} \frac{\partial \rho}{\partial n} \right) \right] \] (XXXIX)

Now in terms of flux of the diffusing substance equation (XXVI) may be written
\[ \frac{\partial \rho}{\partial t} = \frac{\partial f_n}{\partial n} + \frac{2n}{\rho} f_n \] (XLI)

By substituting the foregoing relations for \( f_n \) and \( \frac{\partial f_n}{\partial n} \) into this equation and simplifying
\[ \frac{\partial \rho}{\partial t} = D \frac{\partial n}{\partial n} \left[ \frac{2n}{\rho} \frac{\partial \rho}{\partial n} + 2 \left( \frac{\rho^3 - 2n}{\rho^3 + n} \right) \frac{\partial \rho}{\partial n} \right] \] (XLII)

This is the fundamental differential equation for diffusion to the dropping mercury electrode.

We are interested in the region very close to the surface of the dropping electrode and since in this region \( \rho \) is only slightly larger than \( \rho_0 \) it follows that \( D^3 \) is very much smaller than \( \gamma t \). When \( D^3 < \gamma t \) we have \( \frac{\rho^3 - \gamma t}{\rho^3 + \gamma t} = -1 \) and
\[ \rho^4 = (\gamma t)^\frac{4}{3} \]

Therefore, for this region very near to the surface of the
dropping electrode equation (XLI) becomes
\[
\frac{2c}{\gamma} = \frac{D(\partial t)^{\frac{3}{2}}}{\gamma} \left[ \rho \frac{\partial^2 c}{\partial \beta^2} - \frac{\partial^2 c}{\partial \beta^2} \right] \tag{XLI}
\]
In order to obtain a solution of this equation it is convenient to perform a substitution of variables to simplify the algebra. Let
\[ \chi = \rho^3 \quad \text{and} \quad \gamma = \tau^\frac{3}{2} \]
Then
\[
\frac{\partial \chi}{\partial \rho} = 3\rho^2 \quad \frac{\partial^2 \chi}{\partial \rho^2} = 6\rho
\]
and
\[
\frac{\partial \gamma}{\partial \tau} = \frac{7}{3} \tau^{\frac{4}{3}}
\]
In terms of these new variables
\[
\frac{2c}{\gamma} = \frac{2c}{\gamma} \frac{\partial \gamma}{\partial \tau} = \frac{3}{3} \tau^{\frac{4}{3}} \frac{2c}{\gamma}
\]
\[
\frac{2c}{\gamma^2} = \frac{2c}{\gamma^2} \frac{\partial^2 \gamma}{\partial \tau^2} = 3\rho^2 \frac{2c}{\gamma}
\]
\[
\frac{\partial^2 c}{\partial \beta^2} = \frac{\partial^2 c}{\partial \beta^2} \frac{\partial^2 \gamma}{\partial \tau^2} + \frac{\partial^2 c}{\partial \beta^2} \frac{\partial^2 \gamma}{\partial \tau^2} \left( \frac{\partial \gamma}{\partial \tau} \right)^2
\]
(XLIV)
Substituting the relations expressed by equations (XLI) and (XIV) into (XLI) leads to
\[
\frac{\partial c}{\partial \gamma} = \frac{2\gamma^{\frac{3}{2}} D}{\gamma} \frac{\partial^2 c}{\partial \beta^2} = m \frac{\partial^2 c}{\partial \beta^2}
\]
(XLVI)
where
\[ m = \frac{2\gamma^{\frac{3}{2}} D}{\gamma} \]
A solution of equation (XLVI) is
\[
\chi = K + B \int_0^{\chi} e^{-\frac{\gamma^2}{2m}} \gamma d \gamma
\]
(XLVII)
where \( \gamma \) is an integration variable, \( K \) and \( B \) are constants and the value of the integral depends only on the value of the upper limit. 1.

The initial and boundary conditions
\[
C_0 = C \quad \text{when} \quad \tau = 0
\]
\[
C_0 < < C \quad \text{or} \quad C_0 = 0 \quad \text{when} \quad \tau > 0
\]
where \( C \) is the concentration in the body of the solution, and \( C_0 \) the concentration at the surface of the mercury drops. When \( \tau > 0 \), \( \rho = 0 \) and since \( \gamma = \rho^3 \), \( \gamma \) is also equal to zero.

1. See reference (5) page 35
Hence, when \( t > 0 \) the upper limit of the integral in equation (XLVII) and the integral itself, become equal to zero. Since \( C_0 \) is also equal to zero when \( t > 0 \) it follows that \( K \) must be equal to zero. On the other hand, when \( t = 0 \) since \( y_o = \frac{C}{\sqrt{t}} \) the upper limit of the integral becomes infinity and the value of the integral becomes \( \sqrt{\pi} \). Since \( C_0 = C \) when \( t = 0 \) it follows that the constant \( B \) is equal simply to \( C \). Hence, equation (XLVII) becomes

\[
C_0 = \frac{2C}{\sqrt{\pi}} \int_0^\infty \int_0^\infty e^{-\frac{y^2}{4}} dy
\]

Since \( \gamma = \rho^3 \) and \( \chi = \frac{3}{2} \) and \( m = \frac{2}{3} \),

\[
\frac{x}{2vm} = \frac{1}{6} \sqrt{\frac{3}{2} \frac{D}{(\sigma t)^2}} = S
\]

and hence equation (XLVIII) may be written

\[
C_0 = \frac{2C}{\sqrt{\pi}} \int_0^\infty e^{-\frac{y^2}{4}} dy
\]

The resultant current at any instant during the life of a drop is governed by the flux of the diffusing substance at the surface of the drop \( (\rho = 0) \), and is given by

\[
\mathbf{I} \mathbf{t} = 4\pi \rho o m F (\mathbf{f}_1) \rho = 0
\]

From equation (XXXVIII)

\[
\mathbf{f}_1 = D \mathbf{a} \frac{\partial}{\partial \rho} (XXXVIII)
\]

By differentiating equation (I) with respect to \( \rho \), we obtain

\[
\frac{\partial C}{\partial \rho} = \frac{2C}{\sqrt{\pi}} \frac{\partial S}{\partial \rho} \frac{\partial}{\partial S} \left( \int_0^S e^{-\frac{y^2}{4}} dy \right)
\]

or in view of equation (XLIX)

\[
\frac{\partial C}{\partial \rho} = C \frac{e^{-\frac{S^2}{4}}}{\sqrt{\pi}} \left( \frac{7 \chi}{3D} \right)^{\frac{1}{2}} \frac{\partial^2}{\partial (\sigma t)^2}
\]

Therefore

\[
\mathbf{f}_1 = D \mathbf{a} \frac{\partial}{\partial \rho} \frac{2C}{\sqrt{\pi}} = \frac{DC \mathbf{a}^2}{(\sigma t)^{\frac{1}{2}}} \left( \frac{7 \chi}{3D} \right)^{\frac{1}{2}} e^{-\frac{S^2}{4}}
\]

when \( \rho = 0 \), \( e^{-\frac{S^2}{4}} = e^0 = 1 \) and \( S = S_o = (\chi \sigma t)^{\frac{1}{2}} \)
Hence from equation (LIV), the flux at the surface of the drops is given by

\[(f_{uv})_{\rho=0} = \frac{Dc}{(8\pi)^{\frac{1}{2}}(3\pi D)^{\frac{1}{2}}} = \frac{D^\frac{1}{2}c}{C^{\frac{1}{2}}(3\pi)^{\frac{1}{2}}} \]  \hspace{1cm} \text{(LV)}

and the expression for the current in equation (LI) becomes

\[i_t = 4\left(\frac{2F}{3}\right)^{\frac{1}{2}}nF D^{\frac{1}{2}}C y^{\frac{1}{2}}C^{\frac{1}{2}} \]  \hspace{1cm} \text{(LVI)}

Since \[D = \frac{3c}{4\pi} = \frac{3m}{4\pi d} \]  \hspace{1cm} \text{(LVII)}
equation (LVI) becomes

\[i_t = 0.732 nF D^{\frac{1}{2}}C m^{\frac{1}{2}} C^{\frac{1}{2}} \]  \hspace{1cm} \text{(LVIII)}

where 0.732 is simply a combination of the numerical constants. This relation was originally derived by Ilkovic.

It is more convenient to express the current in microamperes, the concentration in millimoles per liter and m as milligrams/second and on this basis when the numerical value of \(F^2\) is introduced into equation (LVIII) we have

\[i_t = 706 nF D^{\frac{1}{2}}C m^{\frac{1}{2}} C^{\frac{1}{2}} \]  \hspace{1cm} \text{(LIX)}

The average current during the life of a drop is defined as the hypothetical constant current which, flowing for a length of time equal to the drop time, would produce the same quantity of electricity as the quantity actually associated with each drop. Mathematically the average current, \(\bar{i}\), is defined by

\[\bar{i} = \frac{1}{t_{\text{max}}} \int_0^{t_{\text{max}}} i_t \, dt \]  \hspace{1cm} \text{(LX)}

where \(t_{\text{max}}\) is the drop time. In view of equation (LIX)

\[\bar{i} = \frac{706 n F D^{\frac{1}{2}}C m^{\frac{1}{2}}}{t_{\text{max}}} \int_0^{t_{\text{max}}} C^{\frac{1}{2}} C^{\frac{1}{2}} \, dt \]  \hspace{1cm} \text{(LXI)}

By performing the integration we finally obtain

\[\bar{i} = 605 n F D^{\frac{1}{2}}C m^{\frac{1}{2}} C^{\frac{1}{2}} \]  \hspace{1cm} \text{(LXII)}

1. The value for \(d\) is taken here as 13.6 g/cm\(^3\).
2. The value for \(F\) is taken here as 96500 coulombs.
When the density of mercury at 25.0°C is taken as 13.53 gm. cm\(^{-3}\) the equation becomes

\[
\tilde{I} = 607n D^{\frac{1}{2}} C m^{\frac{2}{3}} \tau^{\frac{1}{2}} \tag{LXIII}
\]

Lingane and Loveridge (8) substituted the relation for the area of a spherical mercury drop into equation (XVI) and after integrating found that the equation for the diffusion current was

\[
\tilde{I} = 397n D^{\frac{1}{2}} C m^{\frac{2}{3}} \tau^{\frac{1}{2}} \tag{LXIV}
\]

If the constant 397 is multiplied by \(\sqrt{\frac{3}{2}}\) the "Ilkovic Constant" 607 is obtained. In the Ilkovic derivation the factor represents the fact that the expansion of the mercury drops counteracts the decay of the concentration gradient at the electrode surface and, hence, the factor has theoretical significance. Therefore, this factor was substituted in the equation for the instantaneous diffusion current at a stationary spherical electrode

\[
\tilde{I} = n F DCA \left( \frac{1}{n} + \frac{1}{\tau DC} \right) \tag{XXX}
\]

Substitution and integration gave the equation for the diffusion current

\[
\tilde{I} = 607n D^{\frac{1}{2}} C m^{\frac{2}{3}} \tau^{\frac{1}{2}} + 23760n D^{\frac{1}{2}} C m^{\frac{2}{3}} \tau^{\frac{1}{2}} \tag{LXV}
\]

From equation (LXV) the true diffusion current constant, \(I_0\), is

\[
\frac{\tilde{I} D}{C m^{\frac{2}{3}} \tau^{\frac{1}{2}} (1 + 39D^{\frac{1}{2}} C m^{\frac{2}{3}} \tau^{\frac{1}{2}})} = 607n D^{\frac{1}{2}} = I_0 \tag{LXVI}
\]

Strehlow and Stackelberg have also derived a new equation for the polarographic diffusion current. Their equation is similar to that obtained by Lingane and Loveridge's somewhat

1. The publication dealing with this correction has not been located so far.
arbitrary procedure.

In the derivation shown by Kalthoff and Lingane we have

\[ n^3 = \rho^3 - \gamma \tau \]  

(XXXV)

and

\[ \frac{d\rho}{dt} = \frac{Dn^4}{\rho^5} \left[ \rho^3 \frac{d\rho}{dt} + \frac{2(\rho^3 - \gamma \tau)}{\rho^3 + \gamma \tau} \frac{d\rho}{dt} \right] \]  

(XLI)

However, the relation from equation (XXXV) \( \rho^3 + \gamma \tau = n^3 \)
was not substituted for the term \( r^4 \) in equation (XLI).

Strehlow and Stackelberg have made this substitution and obtain

\[ \frac{d\rho}{dt} = D \left( \frac{\rho^3 + \gamma \tau}{\rho^3} \right)^{1/2} \left[ \rho^3 \frac{d\rho}{dt} + \frac{2(\rho^3 - \gamma \tau)}{\rho^3 + \gamma \tau} \frac{d\rho}{dt} \right] \]  

(LXVII)

with the conditions for \( C_\rho, C_\rho = C \) and \( C_\tau > 0, C_\tau = 0 \)

Equation (LXVII) is expanded to

\[ \frac{d\rho}{dt} = D \left( \frac{\rho^3 + \gamma \tau}{\rho^3} \right)^{1/2} \left\{ 1 + \frac{1}{3} \frac{\rho^3}{\gamma \tau} + \frac{2}{3} \left( \frac{\rho^3}{\gamma \tau} \right)^2 \right\} \]  

(LXVIII)

\[ \frac{\rho^3}{\gamma \tau} \]  
is the proportion of diffusion volume to drop volume

and, under polarographic conditions, small compared to \( 1 \). Then, indicating the middle value of the diffusion layer by \( d \), so that

\[ n = n_0 + d \]

and

\[ \frac{\rho^3}{\gamma \tau} = \frac{n^3 - n_0^3}{\gamma \tau} = \left( \frac{n_0 + d}{\gamma \tau} \right)^3 - \frac{n_0^3}{\gamma \tau} = 3n_0^2 \frac{d}{\gamma \tau} = \frac{3d}{\gamma \tau} \]  

(LXIX)

Since the diffusion layer \( d \) is proportional to \( \sqrt{D \gamma \tau} \) and \( n_0 \) is proportional to \( m \left( m \gamma \tau \right)^{1/2} \), then \( \frac{\rho^3}{\gamma \tau} \) is proportional to \( D^{1/2} m^{1/2} \gamma \tau^{1/2} \).

The value of \( \frac{\rho^3}{\gamma \tau} \) is about 0.15 and therefore not to be disregarded. Hence, both terms linear in \( \frac{\rho^3}{\gamma \tau} \) are kept, the higher terms are neglected. The approximation is then

\[ \frac{d\rho}{dt} = D \left( \frac{\rho^3 + \gamma \tau}{\rho^3} \right)^{1/2} \left\{ 1 + \frac{1}{3} \frac{\rho^3}{\gamma \tau} \left[ \rho^3 \frac{d\rho}{dt} - 2(1 - \frac{\rho^3}{\gamma \tau}) \frac{d\rho}{dt} \right] \right\} \]  

(LXX)

1. See reference (9) page 56.
This equation is not exactly solvable. For an approximate solution assume that \( \frac{\partial^2}{\partial t} \) is small compared to 1 and is always positive, and during the drop time at every point has a constant average value \( \epsilon \). As \( \frac{\partial^3}{\partial t} \) grows with \( t \) the average deviation from the central value is small. Set

\[
1 - 2e = a \quad \text{and} \quad 1 + \frac{4}{3}e = \xi
\]

Then equation \((\text{LXX})\) reads

\[
\frac{\partial^2 c}{\partial t} = D \frac{\partial^2 (ct)^{\frac{3}{2}}}{\partial z^2} \left[ \rho \frac{\partial^2 c}{\partial z^2} - 2a \frac{\partial c}{\partial z} \right]
\]

Equation \((\text{LXX})\) can be transformed to an equation of the type

\[
\frac{\partial^2 c}{\partial y^2} = -M \frac{\partial^2 c}{\partial x^2} (\text{LXXI})
\]

with coordinates

\[
x = \rho \frac{1}{2} + 2a \quad \text{and} \quad y = \rho \frac{3}{2} \rho^4 (\rho - 1)
\]

If one neglects the terms that multiply with \((\rho - 1)\) and are therefore small compared to the rest then

\[
M = D \frac{\rho^4}{2} (1 + 2a)^2 (\text{LXXIII})
\]

The boundary conditions are given as before. The solution of \((\text{LXXIII})\) is then

\[
C_0 = \frac{2c}{\sqrt{\pi}} \int_0^s e^{-\xi^2} d\xi (\text{LXXIV})
\]

with

\[
S = \frac{2}{2VMY} = \frac{\rho^3}{2VM} \frac{3a}{2} (\text{LXXV})
\]

The current is given by

\[
i = \frac{4\pi \rho^2}{\sqrt{\pi}} n F D (\frac{\rho^2}{2})_{\rho=0} = \frac{4\pi \rho^2}{\sqrt{\pi}} n F D \left[ \frac{\rho^2}{2} \frac{\partial^2 c}{\partial z^2} \right]_{\rho=0} (\text{LXXVI})
\]

where

\[
\frac{\partial^2}{\partial z^2} (\text{LXXVI}) = \frac{3\rho^2 c}{(1 + 2a) \frac{3}{2} \sqrt{\pi} \gamma \frac{\partial^2 c}{\partial z^2}}
\]

Substituting in equation \((\text{LXXVI})\)

\[
i = \frac{12 \sqrt{3} \pi n F D \frac{1}{2} C \frac{3}{2} \epsilon \frac{1}{2}}{(1 + 2a) \sqrt{2}} (\text{LXXVII})
\]

Now

\[
\frac{1}{(1 + 2a) \sqrt{2}} = \frac{1}{(1 - \frac{4}{3}e) \sqrt{1 + \frac{4}{3}e}} \approx \frac{1}{3} (1 + \frac{2}{3}e) (\text{LXXVIII})
\]
If all powers of \( e \) except the first are neglected one obtains from equation (LXXVII)

\[
  i = 4 \sqrt{\frac{3}{\pi}} F D^{\frac{1}{2}} C n^{\frac{3}{2}} \tau^{\frac{3}{2}} \left( 1 + \frac{2}{3} e \right)
\]

When \( \frac{1}{\rho} \) is expressed by \( 'm' \) in mgm/sec. and \( 'C' \) in milli-moles/litre and \( 'i' \) in microamperes after compiling the constants and integrating

\[
i_d = 607 n D^{\frac{1}{2}} C m^{\frac{3}{2}} \tau^{\frac{3}{2}} \left( 1 + \frac{2}{3} e \right)
\]

From equation (LXIX)

\[
  \frac{1}{\rho} = \frac{3}{2} A D^{\frac{1}{2}} m^{-\frac{1}{3}} \tau^{\frac{1}{6}}
\]

and upon substituting in equation (LXXX)

\[
i_d = 607 n D^{\frac{1}{2}} C m^{\frac{3}{2}} \tau^{\frac{3}{2}} \left( 1 + A D^{\frac{1}{2}} m^{-\frac{1}{3}} \tau^{\frac{1}{6}} \right)
\]

From this is shown that the diffusion constant \( \frac{i}{\rho} m^{\frac{3}{2}} \tau^{\frac{3}{2}} \) which was found not to be a constant practically (10) is also not a constant theoretically.

In order to calculate the constant \( A \) we make use of the derivation of the Ilkovic equation as given by M. van Stackelberg (14). Here two diffusion layers were defined

\[
  \delta = \frac{C - C_0}{\frac{\partial C}{\partial n}} n = n
\]

and

\[
  \Delta = \frac{2}{\tau} \int_{n_0}^{n} (C - C_0) \, dn
\]

The current density is now

\[
i = \frac{n F C q D}{1000 \delta}
\]

where \( q \) is the drop area

\[\Delta\] is proportional to the decreasing parts

\[
  \Delta = \frac{2000}{\delta} \int_{n_0}^{n} Idt = \frac{2000}{\delta} \int_{n_0}^{n} \tau^{\frac{3}{2}} \theta \, dt
\]

By combining these equations

\[
  \Delta = \frac{2D}{q} \int_{0}^{\tau} q \, dt = \frac{2D}{\tau^{\frac{3}{2}}} \int_{0}^{\tau^{\frac{3}{2}}} s^{-1} \, ds
\]

then

\[
  q = \left( 607 n V \right)^{\frac{1}{3}} \tau^{\frac{2}{3}}
\]
For linear diffusion, the diffusion laws yield
\[ \Delta = \frac{D}{\pi} \]  

Substituting in equation (LXXXVII)
\[ \mathcal{S} = \frac{\pi D}{2} \int_0^\infty t^{\frac{3}{2}} e^{-t} dt \]

The solution is
\[ \mathcal{S} = \sqrt{\frac{3}{7}} \pi D t \]

By a combination of equations (LXXXV) (LXXXVIII) and (XC) and converting to the units proposed by Kalthoff and Lingane one obtains the Ilkovic equation (II).

The simplification in these derivations lies in the assumption that diffusion to a plane surface takes place. These simplifications are equivalent to the assumption that the diffusion layer is very small compared to the radius of the mercury drop. The relation \( \frac{\Delta}{\mathcal{S}} \) must also be calculated for diffusion to a spherical surface. The place and time dependance for diffusion to a sphere is given by
\[ C_0 = C_n x = C(1 - \frac{n^2}{x^2}) + \frac{2C_n}{\sqrt{\pi}} \int_0^{\frac{x}{\sqrt{D}}} e^{-y^2} dy \]

That is
\[ n - n_0 = \chi \]

\( \Delta \) is according to definition
\[ \Delta = \frac{2}{\pi} \int_{n_0}^{\infty} (C - C_n) dx = \frac{2}{\pi} \int_0^{\infty} (C - C_n) dx \]

Setting (XXVII) in (XCII)
\[ \Delta = 2 \int_{n_0}^{\infty} \frac{n_0}{n_0 + x} \left( \frac{2n_0}{\sqrt{D}x} e^{-y^2} dy \right) dx \]

This integral would solve in an approximate manner by putting the logarithmic terms in series
\[ \ln(n_0 + x) = \ln n_0 - \sum_{n=1}^{\infty} \frac{(n-1)n^{n-1} x^n}{n! n_0^n} \]

1. See equation (XCV). When \( n_0 \) becomes infinite, linear diffusion exists.
2. See equation (XCVIII)
If \( X \) is very small compared to \( \mathcal{N}_0 \) then the sum of the first two terms only applies \( \Delta \approx \frac{2 \mathcal{N}_0}{V \pi D_C} \int_0^\infty \left( \mathcal{C}_0 + \frac{X^2}{4 \mathcal{N}_0^2} \right) e^{-\frac{2 \mathcal{N}_0 X}{V \pi D_C}} \, dX - 2 \mathcal{N}_0 \mathcal{R}_0. \)  

\[
S = 4 \sqrt{\frac{D_C}{\pi}} \left( 1 - \frac{\sqrt{\pi D_C}}{2 \mathcal{N}_0} \right) 
\]

is according to definition \( S = \left( \frac{\mathcal{O}}{\mathcal{C}_0} \right) \mu \mathcal{N}_0. \)  

By inserting \( C \) from (XXVII)  

\[
S = \frac{\mathcal{N}_0 \sqrt{\pi D_C}}{\mathcal{N}_0 + \sqrt{\pi D_C}} 
\]

from (XCIII) and (XCIV)

\[
\frac{\Delta}{\delta} = \frac{4}{\pi} \left( 1 + \frac{\sqrt{\pi D_C}}{\mathcal{N}_0} \right) \left( 1 - \frac{\sqrt{\pi D_C}}{\mathcal{N}_0} \right) \approx \frac{4}{\pi} \left( 1 + \frac{\sqrt{\pi D_C}}{2 \mathcal{N}_0} \right) 
\]

Substituting (XCV) in (LXXXVII) one obtains the integral equation

\[
\left( 1 + \frac{\sqrt{\pi D_C}}{2 \mathcal{N}_0} \right) S = \frac{\pi D_C}{2 \mathcal{N}_0 \frac{2}{3}} \int_0^\infty \mathcal{C}^{\frac{3}{2}} \delta^{-1} \, d\delta 
\]

Assuming that the term \( \sqrt{\frac{\pi D_C}{2 \mathcal{N}_0}} \) as the smallest correction term in the time \( \mathcal{O} \) to \( \mathcal{C} \), a constant average value \( \mathcal{C}' \) is assumed.

Equation (XCVI) becomes

\[
S = \frac{\pi D_C}{2 (1+\mathcal{C}')} \mathcal{C}^{-\frac{1}{3}} \int_0^\infty \mathcal{C}^{\frac{2}{3}} \delta^{-1} \, d\delta 
\]

A solution is \( A \pi^n \)

Substituting

\[
2 A \mathcal{N}_0 (1+\mathcal{C}') (\mathcal{C}^{-1} - n) = \mathcal{C}^{1-2n} \]

Since the expression on the left is a constant then \( n = \frac{1}{2} \) and it follows

\[
A = \sqrt{\frac{3 \pi D_C}{7 (1+\mathcal{C}')}} \quad \text{and} \quad S = \sqrt{\frac{3 \pi D_C}{7 (1+\mathcal{C}')}} 
\]

For \( \mathcal{I} \) from equations (LXXXV) (LXXXVIII) and (XCVIII)

\[
\mathcal{I} = \sqrt{1+\mathcal{C}'} \cdot 607^- \mathcal{I}^2 \mathcal{D}^2 \mathcal{N}_0^2 \mathcal{T}^{-\frac{1}{6}} 
\]

\[
= \left( 1 + \frac{1}{2 \mathcal{C}'} \right) \cdot 607^- \mathcal{I}^2 \mathcal{D}^2 \mathcal{N}_0^2 \mathcal{T}^{-\frac{1}{6}} \quad (XCIX) 
\]
\[ l' \text{ was } \frac{\sqrt{\pi DT}}{2} \text{ and for a growing drop } l_0 = (\sqrt{\pi})^{\frac{1}{3}} \]

Then

\[ l' = \frac{\sqrt{\pi DT}}{2\left(\sqrt{\pi}\right)^{\frac{1}{3}}} = 34.1 \text{ } D^{\frac{1}{2}} \text{ } m^{-\frac{1}{3}} \text{ } t^{\frac{1}{6}} \]

Substituting for the constant \( A \) in equation (LXXXII)

\[ \dot{d} = 607 \pi D^{\frac{1}{2}} C m^{2/3} t^{\frac{1}{6}} \left(1 + 17 D^{1/2} m^{-5/3} t^{1/6}\right) \text{ (IV)} \]

The constant \( A \) may also be derived from the geometry of the mercury drop and the diffusion layer as shown in Fig. 2. \( A \) is the mercury drop, \( B \) is the cylindrical diffusion volume that is alone considered in the derivation of the Ilkovic equation. However the reactant diffuses to the curved surface \( ab \) through the region \( C \) (in cross sectional view - wedge shaped).

Instead of equation (ii) may also be considered

\[ \dot{d} = 607 \pi D^{\frac{1}{2}} C m^{2/3} t^{\frac{1}{6}} \left(1 + x\right) \text{ (C)} \]

Where \( x \) is the relation of volume \( C \) to the volume \( B \).

- \( r \) = radius of mercury drop
- \( d \) = thickness of the diffusion layer.

Volume \( B \) (for the whole drop)

\[ V_B = \frac{4}{3} \pi r^3 d \]

Volume \( B + C \)

\[ V_{B+C} = \frac{4}{3} \pi [(r+d)^3 - r^3] \]

The correction factor \( 1 + x \) is given by

\[ 1 + x = \frac{V_{B+C}}{V_B} = \frac{(r+d)^3 - r^3}{3r^2 d} = 1 + \frac{d}{r} + \frac{d^2}{3r^2} \]

Since \( d \) under polarographic conditions is small compared to \( r \) the term \( \frac{d^2}{3r^2} \) can be disregarded. \( \dot{d} \) as diffusion layer is proportional to \( \sqrt{DT} \), \( r \) as drop radius is proportional to \( (m \cdot t)^{\frac{1}{3}} \). Therefore the correction term \( \frac{d}{r} \) can be given

\[ \frac{d}{r} = A \text{ } D^{\frac{1}{2}} \text{ } m^{-\frac{1}{3}} \text{ } t^{\frac{1}{6}} \]
FIG. 2

Schematic Diagram of Mercury Drop and the Diffusion Layer
From these simple ways equation (LXXXII) is obtained.

To calculate the value of \( A \) approximately we assume a linear decrease of the concentration and set \( \frac{d}{d} = \frac{8}{77} = \sqrt{\frac{3}{\pi}} D T S T T^1 \)

\( \tau \) is given by \( \frac{4 \pi \lambda^3}{13530} = \frac{m \tau}{13530} \)

Therefore \( \frac{d^2}{d^3} = \sqrt{\frac{4 \pi 13530}{3}} D^2 m^{-\frac{1}{2}} C^6 = 44.4 D^2 m^{-\frac{1}{2}} C^6 \)

Though the closer to the surface extends the solution so

that more is contributed to the current density it must still
be averaged over \( d \). For \( A \) by linear decrease of concentration

\( A = \frac{1}{3} \quad 44.4 \quad = 14.8 \)

This value in view of the omissions in the Ilkovic derivation
is satisfactory. From the previous derivation \( A = 17 \) which is
in better agreement with experiment and, therefore, shall be
assumed valid.

For a reactant with a diffusion coefficient \( 1.0 \times 10^{-6} \text{cm}^2 \text{sec}^{-1} \)

the correction term is \( 17 \sqrt{10} 10^{-3} m^{-\frac{1}{2}} C^6 = 0.054 m^{-\frac{1}{2}} C^6 \)

Since the quantities \( m^{-\frac{1}{2}} C^6 \) with commonly used capillaries
varies perhaps about 0.5 to 1.2 the correction term amounts
to 2.7\% to 6.5\% and is by no means to be neglected.

It may be mentioned that the Lingane and Loveridge
value of \( A = 39 \) amounts to a correction factor of 6.2\% to 15\%
which appears to be somewhat larger than the experimental
variation demands. When capillaries of very small outflow, \( m \),
and very large drop times are used the Ilkovic equation is no
longer applicable since \( \frac{d}{d} \) then becomes comparable to 1 or
larger. The improved Ilkovic equation may then be written

\[ \frac{d}{d} = K m^\frac{3}{2} C^\frac{1}{2} \left( 1 + a m^{-\frac{1}{2}} C^\frac{1}{2} + a^2 m^{-\frac{3}{2}} C^\frac{1}{2} \right) \]

\( \frac{d}{d} = K m^\frac{3}{2} C^\frac{1}{2} + K^2 m^\frac{5}{2} C^\frac{1}{2} + K^3 C^\frac{1}{2} \)

1. The value 13530 is taken as the density of mercury in
milligrams per \( \text{cm}^3 \) at 25\°C.
If $\frac{\partial}{\partial t}$ then the first two terms become small compared to the third. For very long drop times the current density should be proportional to $C^{\frac{1}{2}}$ as G.S. Smith (15) found experimentally. However, with thick diffusion layers there is greater risk of convection and the assumption of linear diffusion is no longer admissible.

The dissolution of a base metal from an amalgam at the dropping electrode as anode gives a current density which is likewise expressed by the Ilkovic equation. However the expression $\rho$ used in the previous derivations must be replaced by $-\rho$. This change of sign merely results in a negative sign in the correction term. By an approximation Strehlow and Stackelberg (16) have evaluated the value of the correction factor $B$ in the term $1 - B D_{D}^{\frac{1}{2}} m^{-\frac{1}{2}} L^{\frac{1}{2}}$ to be 1.5 to 2 times the value of $A$ in the term $1 + A D_{D}^{\frac{1}{2}} m^{-\frac{1}{2}} L^{\frac{1}{2}}$. Since $A$ has been accepted as 17 then $B$ would lie in the range of values 25 - 35.

A second effect causes the value of $B$ to be larger than $A$ in that the ratio $\frac{\partial}{\partial t}$ is no longer very small. In view of the conclusions drawn with respect to the transport of metals dissolved in mercury then $\frac{\partial}{\partial t} = 1$ is not inadmissible. In reality, the streaming effect caused by the outflow current from the capillary complicates the problem considerably. Strehlow and Stackelberg have determined the value of $B$ as 28.5 when a cadmium amalgam is used as the dropping electrode.
In 1939, J.J. Lingane (1) published a note reporting the qualitative behaviour of a dropping cadmium amalgam electrode in polarography of cadmium sulfate solution. Using 0.01% cadmium amalgam dropping in air free 0.1N potassium chloride solution containing 0.04 M cadmium sulfate, he obtained cathodic and anodic diffusion currents for the reduction of the cadmium ion in solution and for the oxidation of the cadmium metal in the amalgam respectively. The two branches formed a single polarographic wave. The anodic diffusion current showed a 'maxima' which was eliminated by the addition of 0.1 ml. of 0.1% methyl red. He stated that this is evidence that the polarographic 'maxima' is a phenomena of the solution side of the solution metal interface.

In 1940, M.v.Stackelberg and H.v.Freyhold (17) included a paragraph on the dropping zinc amalgam electrode in their paper on the determination of the coordination number of metal ions in complex formation by the shift of the polarographic 'half-wave' potential. Using 0.005% zinc amalgam dropping in 0.01M zinc salt solutions with potassium chloride or potassium nitrate as supporting electrolyte, they obtained a single wave for the anodic and cathodic branches of the diffusion currents. The single wave indicated almost complete reversibility of the electrode reactions. However, with IN potassium hydroxide the anodic wave and the cathodic wave were separated thus indicating an irreversible electrode reaction.
Although no quantitative data was presented in the above papers, Kølthoff and Lingane (18) state that the anodic diffusion currents obtained with the dropping amalgams were of the order of magnitude expected on the basis of the assumption that the Ilkovic equation held good.

Late in 1940, J. Heyrovsky and M. Kalousek (19) published an account of their work with very dilute amalgams of copper, cadmium, lead and zinc. This work had been announced in 1938 thus crediting these workers with the initial investigations of amalgam polarography. (Since their paper is not immediately available a copy is included with this work). However, they added nothing to the quantitative data with respect to the anodic diffusion current. Heyrovsky's (20) continued investigations have led to an oscillographic technique for recording current-voltage curves at dropping or streaming mercury electrodes. Electrodepositions involving single electron transfers and some few 2-electron transfers show the anodic and cathodic depolarization wave at the same potential. However, for most electrodepositions involving 2-electron transfers the potential of the anodic wave is different from the potential of the cathodic wave. It may be noted that the cathodic wave is due to the reduction of the ion in solution to form a dilute amalgam. The reversal of the potential sweep is so rapid that the amalgam formed by the cathodic sweep is discharged on the anodic sweep even when a streaming mercury electrode is used. From the results obtained so far, Heyrovsky has deduced that a 2-electron transfer is a two step process. One electron is accepted in an electrolytic
process: \[ Z_{n}^{++} + e = Z_{n}^{+} \]
The other electron is acquired by dismutation:
\[ 2 Z_{n}^{+} = Z_{n}^{++} + Z_{n} \]
Unfortunately, the results are reported more or less qualitatively and the significance of Heyrovsky's deduction cannot presently be appreciated. Comparisons of the behaviour of amalgam electrodes in the polarographic and oscillographic techniques should be useful.

In 1947, J.E.B. Randles (21) used a form of the polarographic capillary electrode in his study of the kinetics of electrode reactions with alternating current. Dropping amalgam electrodes (copper, cadmium, thallium and zinc) were used where an auxiliary direct current circuit was maintained across the amalgam reservoir. The capillary was attached to a siphon from the reservoir. The purpose of the auxiliary circuit is to stabilize the dilute amalgams.

A similar technique has been used in this work and illustrations are shown elsewhere.

Also in 1947, T. Erde Graz and E. Varga (22) reported the effect of non electrolytes on the electrode potentials of amalgams. The potentials of resting and dropping amalgams of bismuth, copper, thallium, lead and zinc were determined in solutions of various isoamyl alcohol, benzyl alcohol, o-toluidine, o-cresol, p-cresol, butyric acid and valeric acid. To make the solutions electrical conductors, sodium sulfate was added and the solutions and apparatus were carefully freed of oxygen. When the amalgam concentrations were above $10^{-5}$ to $10^{-4}$ gram atoms per liter, the electrode potentials were reproducible to millivolts. The potentials are determined
partly by the adsorption of ions and neutral dipole molecules on the liquid side of the solution - metal interface, partly by the adsorption of metal ions on the amalgam side of the double layer. The adsorbed metal ions form the positive part of the double layer created within the amalgam. The negative part consists of diffusely distributed electrons. (Experimental technique and data is not available since only the abstract of their paper is presently obtainable).

In 1948, F.L. English (23) reported the drop time characteristics of copper, gold, silver, tin and zinc amalgams at polarographic electrodes. Zinc metal was dissolved in mercury and the amalgam after filtering through chamois was washed with methanol and acetone to remove grease and oil. 0.01% and 0.0001% zinc amalgams gave the usual type of drop time versus voltage curve in the negative voltage range. However, similar to pure mercury, in the voltage range +0.3 volt to -0.6 volt a high degree of discordance among repeated determinations was found. In the positive voltage range the pen oscillations per drop were exceedingly irregular in both shape and amplitude. The electrolytes used in this work were 0.1N potassium chloride and 0.1N tetramethyl ammonium chloride with sometime addition of methyl red or gelatin.

After this work had started a paper by Strehlow and Stackelberg (9) reported the diffusion current for dropping cadmium amalgam electrodes. A manual circuit was employed for accuracy. All measurements were made in 0.1N potassium chloride with 0.01% gelatin at 25.0°C ± 0.4° after the solution was swept out with nitrogen. The temperature was measured to 0.1°C and the
diffusion current corrected by calculation to 25.0°C. The values for 'm' and 't' were determined in the solution at the same time the diffusion current was measured. A cadmium amalgam 13.92 millimolar was used with different dropping capillaries where the pressure was varied from 37 cm - 110 cm of mercury. The diffusion current constant $I = \frac{4\pi D}{C m^{\frac{1}{2}}}$ so determined varies up to 2% for duplicate determinations. However, I is found to vary considerably with changing values of 'm' and 't'. For different capillaries the values of were plotted versus $y$, where $y = m^{\frac{1}{2}} C^{\frac{1}{2}}$. The curves became asymptotic to a straight line for the larger values of 'm' and 't'. From the diffusion current equation for amalgam anodes (Equation VI) can be obtained

$$\frac{4\pi D}{C m^{\frac{1}{2}}} = 607 m^{\frac{1}{2}} (1 - BD^{\frac{1}{2}} y)$$

Therefore, a plot of $I$ versus $y$ would yield the value of $607 m^{\frac{1}{2}}$ from the intercept and the value of $BD^{\frac{1}{2}}$ from the slope. Since the curves were asymptotic to a straight line, Strehlow and Stackelberg used the values of its intercept and slope for the determination of the diffusion coefficient of cadmium in mercury and the value of the numerical constant B. Their experimental value for the diffusion coefficient at 25.0°C $1.52 \times 10^{-5}$ cm² sec⁻¹ is in excellent agreement with the value reported in the literature $1.520 \times 10^{-5}$ cm² sec⁻¹ at 20.0°C. The value of B is determined as 28.5.

When the value of B is calculated from the given data it is found that the values vary considerably. For those points which lie close to the straight line B varies from 24 to 29. As the deviation increases the value for B becomes more negative and a value -90.9 has been calculated. It is shown that the
value of $B$ decreases with increasing pressure of the amalgam column. Assuming that the 'rinsing' effect is the major source of error, then as the outflow current decreases the electrical current becomes more truly related to a diffusion process alone and the value of $B$ approaches a limiting value. The limiting value lies within the range 25-35 according to theoretical approximations. Actually, a range 21-35 is obtained if one considers all the theoretical approximations given by Strehlow and Stackelberg. In our own work it will be considered that the larger values for $B$ indicate that the outflow current does not unduly disturb the diffusion process at the amalgam drop surface. It should be mentioned that Strehlow and Stackelberg do not describe the preparation of the cadmium amalgam nor do they mention any technique for overcoming the instability of the dilute amalgam.

Heyrovsky (64) noticed that there is no difference between the maximum on the current-voltage curves of cadmium amalgam and the maximum existing on the cathodic waves. An attempt is made to explain the evidence in the light of Ilkovic's theory of the polarographic maxima. This theory is based on the idea of an inhomogeneous electric field due to the charging of the dropping mercury. Since cadmium is reduced at a potential corresponding to the electro capillary zero, the maximum cannot exist according to the theory. However, the explanation is given that the electro-capillary zero is shifted by the anions, whereas the reduction or oxidation potential of cadmium remains unchanged and therefore the observed maximum.
C - ZINC AMALGAMS

(1) METHODS OF PREPARING ZINC AMALGAM

The literature (24) reports many variations of three basic methods used in the preparation of zinc amalgams. These methods may be enumerated:

1. Simple contact of zinc metal and mercury.

2. Electrolytic reduction of zinc salts at the mercury cathode.

3. Chemical reduction of zinc salts by alkali metal amalgams.

In addition, there is the method of Hulett and De Lury (25)(26) where zinc metal is in contact with the mercury cathode under a layer of distilled water which contains the platinum anode. Dissolution of the zinc metal proceeds rapidly when ten volts direct current are impressed. Preliminary experiments, reported elsewhere, showed that the method of Hulett and De Lury is by far the best for preparing standard zinc amalgams.
The solubility of zinc in mercury has been reported as 2.2199 grams of zinc in 100 grams of mercury at 25°C. No evidence of intermetallic compounds is shown by the freezing point diagram. The non existence of such compounds is confirmed by observations on the solubility, electrical resistance, specific volume, vapour pressure and various observations on the electromotive force of zinc amalgams (24). Richards and Forbes (27) suggested that the deviation of the electromotive force values from the values calculated by the Nernst equation could be explained by polymerization of the zinc atoms. Hulett and Crenshaw (24) report that in the range 0.0061N - 0.00000307N, \[ Zn \rightarrow W \], where N = mole fraction the potential difference between any two amalgams conforms to the laws of a perfect solution. However, the values reported by Richards and Forbes did not agree with the values reported by Hulett and Crenshaw. Additionally, no fault could be found in the methods used by the two groups of careful workers. Hildebrand (28) measured the vapour pressure of zinc amalgam and found that the data of Richards and Forbes conformed to the laws of ideal solutions when the presence of a diatomic molecule, \( Zn_2 \), was postulated. Pierce and Eversole (29) repeated the electromotive force measurements and found good agreement with the data of Richards and Forbes. Crenshaw (30) then showed that the data of the three papers could be made to agree by consideration of a single arbitrary constant. Liebhafsky (31) reported that the data of
all the papers were in agreement when the measurements were referred to the potential of the two phase zinc amalgam. Furthermore, he showed that the amalgams conform to ideality over the entire range of composition studied when it was postulated that zinc metal in solution was present as monoatomic, diatomic and triatomic zinc. He proposed that the concentrations of extremely dilute amalgams could be calculated accurately by means of the Nernst equation from the values of E.M.F. measurements. This proposal may find some further application in determining the concentration of the amalgams used in polarography. However, from the foregoing it has been shown that dilute zinc amalgams are unique in that they conform to the laws for ideal solutions.

All of the above quoted papers as well as several others (24) (32) (33) report on the instability of dilute zinc amalgams. W.G.Horsch (32) gave up the study of the apparently anomalous behaviour of dilute zinc amalgams. He reported that between two samples of the same amalgam the E.M.F. varied in an erratic manner, falling and rising rapidly. In our own work it was impossible to find evidence of zinc from polarograms of amalgams which had been exposed to air overnight. (Although the limits of detection have not been reached at 0.1 ppm there is reason to believe that it will be found of the order 0.001 ppm. This latter figure being estimated from the waveheight shown by a very dilute amalgam and the sensitivity settings of the recording apparatus.) Richards and Forbes (27) found that when oxygen was removed from their solutions the E.M.F. values for the very dilute amalgams fitted in with
the data obtained with more concentrated amalgams. Although
this is evidence that oxygen plays some part in the reactions
leading to instability, Liebhafsky (33) states that even in the
absence of oxygen the amalgams tend increasingly to lose zinc
as they become more dilute. It is also known that hydrogen gas
is not readily evolved from dilute zinc amalgams immersed in
acid solutions (24). According to Liebhafsky, the absolute
rate of oxidation increases only slightly with increasing con­
centration of zinc. He has postulated the following reactions
to explain the experimental evidence obtained with dilute zinc
amalgams in sulfuric acid solutions. A rapid equilibrium
exists between the amalgam and amalgam surface:

\[
\text{Amalgam} \leftrightarrow \text{Amalgam surface}^\pi + n \text{electrons}
\]

The rate determining step:

\[
O_2 + 2 \text{electrons} + 2H^+ \rightarrow H_2O_2
\]

A rapid follow reaction:

\[
(\text{Amalgam surface})^{(\pi + 1)^+} = \text{Amalgam surface}^{\pi + 2} + 2Zn^{++}
\]

The electron density at the amalgam surface is regarded as a
constant depending on space and charge factors. Thus, in clean­
ing mercury the removal of zinc becomes progressively easier as
the concentration of zinc decreases. In view of this instabi­
ility, it is not surprising that few papers report investigations
of dilute amalgams at the concentrations required in the
polarographic technique.

There is some considerable literature which deals
with subjects pertaining to or applicable to this work. The
normal electrode potential of zinc has been determined by
several workers as shown in Table 1.
**TABLE 1.**

**THE NORMAL ELECTRODE POTENTIAL OF ZINC**

<table>
<thead>
<tr>
<th>INVESTIGATOR</th>
<th>E.M.F. Volts</th>
<th>REF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Horsch</td>
<td>0.758</td>
<td>(32)</td>
</tr>
<tr>
<td>Scatchard and Teft</td>
<td>0.7610 (corr.)</td>
<td>(34)</td>
</tr>
<tr>
<td>Getman</td>
<td>0.7613</td>
<td>(35)</td>
</tr>
<tr>
<td>Shrowder, Cowperthwaite and LeMer</td>
<td>0.7614 (corr.)</td>
<td>(36)</td>
</tr>
</tbody>
</table>

The corrections noted in Table 1 refer to the correction for the E.M.F. between zinc metal and the two phase zinc amalgam in zinc salt solutions. The values determined by various workers are shown in Table 2.

**TABLE 2.**

**THE ELECTROMOTIVE FORCE OF ZINC-ZINC AMALGAM**

<table>
<thead>
<tr>
<th>INVESTIGATOR</th>
<th>E.M.F. MILLIVOLTS</th>
<th>REF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cohen</td>
<td>0.570</td>
<td>(37)</td>
</tr>
<tr>
<td>Puschin</td>
<td>-2.0</td>
<td>(38)</td>
</tr>
<tr>
<td>Clayton and Vosburgh</td>
<td>0.0</td>
<td>(39)</td>
</tr>
</tbody>
</table>

For the value of the potential difference between zinc amalgams Hulett and Crenshaw found that in the range 0.006IN-0.00000307N, where \( N = \) mole fraction, the simple equation held true

\[
E = \frac{Rt}{nF} \ln \frac{C_1}{C_2}
\]

where

- \( E = \) electromotive force
- \( R = \) the gas constant
- \( T = \) absolute temperature
- \( n = \) electro equivalents per mole
- \( F = \) Faraday
- \( \ln = \) natural logarithm
- \( C_1, C_2 = \) concentrations of respective amalgams.
Richards and Forbes (27) have published a table showing the electromotive force between zinc amalgam and amalgamated zinc in zinc sulfate solution as determined by earlier workers. The only reference they give is "Lindeck 1888".

The values are shown in Table 3.

**TABLE 3.**

EMF Zinc Amalgam vs. Amalgamated Zinc in Zinc Sulfate Solution.

<table>
<thead>
<tr>
<th>% Zinc</th>
<th>E.M.F.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.860</td>
<td>0.003 volt</td>
</tr>
<tr>
<td>0.467</td>
<td>0.022 &quot;</td>
</tr>
<tr>
<td>0.064</td>
<td>0.047 &quot;</td>
</tr>
<tr>
<td>0.028</td>
<td>0.057 &quot;</td>
</tr>
<tr>
<td>0.0014</td>
<td>0.096 &quot;</td>
</tr>
<tr>
<td>0.0010</td>
<td>0.11 &quot;</td>
</tr>
<tr>
<td>0.0038</td>
<td>0.13 &quot;</td>
</tr>
<tr>
<td>0.0027</td>
<td>0.14 &quot;</td>
</tr>
<tr>
<td>0.0020</td>
<td>0.15 &quot;</td>
</tr>
<tr>
<td>0.0015</td>
<td>0.16 &quot;</td>
</tr>
</tbody>
</table>
Hildebrand, (40) from his findings on the vapor pressure of zinc amalgams plus the data published by Richards and Forbes, gives the following equation for the electromotive force between zinc amalgams.

\[ E = \frac{2.3026}{2} \frac{RT}{F} \left[ \sum \log \frac{N_i + 2}{N_i + 2} - \log \frac{N_i - 1}{N_i - 1} \right] \]

where \( N \) subscript = mole percent zinc of respective amalgam

the remaining symbols having the previously given meaning.

Pierce and Eversole (27) give the following relation

\[ E = \frac{RT}{nF} \ln \frac{A_2}{a_2} \]

where \( A_2, a_2 \) = activity of zinc in the respective amalgam.

These workers have given tabled values for the activity of zinc and of mercury in zinc amalgams as well as for free energy, entropy and temperature coefficients.

Liebhafsky (31), by recalculating previously published data, has established the relation

\[ E = 0.09922 T \log \frac{\Sigma Zn_1}{\Sigma Zn_2} \]

where \( \Sigma Zn \) sub = terms for equilibrium constants and concentration of zinc in the respective amalgams.

The log terms are based on the assumption of a rapid equilibria between monoatomic, diatomic and triatomic zinc in the amalgam.

\[ Zn \rightleftharpoons Zn_2 \rightleftharpoons Zn_3 \]

The best values of the equilibrium constants required for a solution of the equation are given in Liebhafsky's paper.

Although the electromotive force of zinc amalgam
electrodes appears to be well established, there are few reports on the behaviour of zinc amalgams during conduction of electricity. Lewis and his co-workers (41) found that alkali metals in dilute amalgams apparently migrate to the anode during the passage of electrical current. G. Mayr (42) reported a similar behaviour for all base metals. F. Skaupy (43) concluded that since the addition of zinc increases the conductivity of mercury considerable ionization occurs. He postulated that the solvent metal and solute metal are in equilibrium with a common ion, the electron. He explains that the change of electron concentration during the passage of current induces the positively charged metal ions to migrate. The positive ions apparently drag along neutral atoms. He gives an expression for transport in amalgams, 

\[ t = \frac{u}{\nu} \left( 1 + \frac{Z}{C} \right) \]

\( u \) = mobility of mercury cation
\( \nu \) = "" electron
\( Z \) = number of neutral mercury moles for each cation
\( C \) = concentration of alkali metal amalgam

According to K. Schwarz (44) and C. Wagner (45), during the passage of electricity mercury is almost completely dissociated into \( \text{Hg}^{++} \) ions but \( \text{Hg}_2^{++} \) ions cannot be excluded. Zinc is dissolved in mercury as ions. Schwarz (46) states that the ion with the greater charge density migrates to the cathode. From the transference number he has determined the diffusion constant of zinc in mercury at 25°C and 35°C as shown in Table 3. More recently, G. Bianchi (47) has presented his findings on the dissolution of metal electrodes in dilute amalgam solutions. The results he obtained indicate some similarity to the dissolution of metal electrodes in salt solutions. Anomalies are
evident - for instance at temperatures over 150°C the anode corrodes faster than the cathode, at lower temperatures the cathode corrodes faster. This result was obtained for the passage of direct current through copper electrodes in mercury. He has also found that the solubility of copper in mercury is greatly reduced when zinc is present in the mercury.

According to Meyer (49) the dissolution of zinc in mercury lowers the surface tension of mercury as some salts in water lowers its surface tension. The available data is given in Table 4. (49)

**TABLE 4**

<table>
<thead>
<tr>
<th>WEIGHT % ZINC</th>
<th>$\gamma$ dynes/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.661</td>
<td>437.1</td>
</tr>
<tr>
<td>1.221</td>
<td>440.4</td>
</tr>
<tr>
<td>1.750</td>
<td>440.0</td>
</tr>
</tbody>
</table>

The published values for the diffusion constant of zinc in mercury are somewhat confusing with respect to the units employed. The data has been recalculated for expression in the units cm² sec⁻¹ for Table 5.
### TABLE 5. DIFFUSION CONSTANT OF ZINC IN MERCURY

<table>
<thead>
<tr>
<th>INVESTIGATOR</th>
<th>TEMPERATURE</th>
<th>DIFFUSION CONSTANT</th>
<th>REF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>G. Meyer</td>
<td>150°C</td>
<td>2.42 x 10^-5 cm^2 sec^-1</td>
<td>(50)(51)</td>
</tr>
<tr>
<td>Wogan</td>
<td>11.5°C</td>
<td>2.52 x 10^-5</td>
<td>(50)</td>
</tr>
<tr>
<td>Schwarz</td>
<td>99.2°C</td>
<td>3.36 x 10^-5</td>
<td>(50)</td>
</tr>
<tr>
<td>Schwarz</td>
<td>25°C</td>
<td>2.00 x 10^-5</td>
<td>(46)</td>
</tr>
<tr>
<td>Schwarz</td>
<td>35°C</td>
<td>2.13 x 10^-5</td>
<td>(46)</td>
</tr>
<tr>
<td>Guthrie</td>
<td>15°C</td>
<td>1.15 x 10^-5</td>
<td>(52)</td>
</tr>
</tbody>
</table>

Some considerable variation is shown between the values reported. For this reason, it is somewhat doubtful that the value of the diffusion constant at 25°C has been established. Further, Samarin and Shvartsman (53) have calculated the coefficient of diffusion of several metals in mercury from atomic radii and viscosity data by Stokes - Einstein law. For the alkali and alkaline earth metals, the calculated and experimental values were in agreement to 10%. However, for gold, lead, thallium, and zinc, the discrepancies were up to 50%. This discrepancy is explained if zinc atoms in mercury solution polymerize to form diatomic and triatomic molecules.

From the foregoing, it is apparent that a solution of zinc in mercury may be considered in some ways similar to a solution of salt in water. It is an interesting analogy which, perhaps, could bear further investigation. So far as this work is concerned, the electrical transport of the solute metal is most important, since polarographic theory demands a diffusion process alone. Provided that electrical transport may be considered negligible then the determination of the diffusion.
coefficient would be still complicated by the polymerization of zinc in amalgam as postulated by several workers. In this case the diffusion coefficient would become a function of the concentration. Such a relation would explain the variation in the experimental values for the diffusion coefficient as well as the deviation of the value calculated by the Stokes-Einstein Law.
D -- EXPERIMENTAL

I - Materials and Solutions

Mercury -- The mercury used in this work was originally very dirty. The mercury was filtered at a capillary funnel and then aerated under 5% nitric acid for several days. The supernatant liquid being siphoned off and renewed three or four times for each batch. Following aeration, the mercury was passed in a fine spray through four scrubbing columns containing 5% nitric acid, 5% sodium hydroxide, 2.5% nitric acid and distilled water in that order. The mercury was then vacuum distilled at least three times. After each distillation the mercury still was cleaned with nitric acid, flushed with tap water, rinsed with distilled water and finally dried in a stream of dry air. Polarograms recorded with the final product showed no unexpected curves. The U.S. Pharmacopoeia test for mercury purity (54) was applied. In this work the mercury remained brightly metallic one minute and ten seconds to one minute and twenty-five seconds after the appearance of boiling at the surface of the solution.

Zinc -- Tadanac zinc (99.99 + %) was fractured and the loosened crystals were pried off with horn-tipped tweezers and weighed immediately. The weight was taken to be that of pure zinc.

Potassium chloride -- Reagent grade potassium chloride was recrystallized three times from doubly distilled water and finally dried overnight at 110°C.
0.1N Potassium chloride -- 14.822 gm. of recrystallized potassium chloride was dissolved in distilled water and made up to 2000 ml. Calculated 0.0994 N KCl.

Standard zinc solutions -- Zinc crystals were dissolved in 5 ml. Nichol's Hydrochloric Acid, C.P., in a covered 250 ml. beaker. Very little, if any, spraying was observed. The solution was evaporated just to dryness on a hot plate at low heat. The zinc chloride crystals were washed into a 2000 ml, volumetric flask containing 14.822 gm. of potassium chloride and made up to the mark with distilled water. Aliquots were made up to the mark with 0.1N potassium chloride solution. The zinc standards are recorded in Table 6.

<table>
<thead>
<tr>
<th>No.</th>
<th>MAKE UP</th>
<th>Molarity millimoles/liter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0809 gm. Zn in 2000 ml.</td>
<td>0.6187</td>
</tr>
<tr>
<td>2</td>
<td>0.0440 &quot; &quot; &quot; &quot;</td>
<td>0.3365</td>
</tr>
<tr>
<td>3</td>
<td>0.02695 &quot; &quot; &quot; &quot;</td>
<td>0.2061</td>
</tr>
<tr>
<td>4</td>
<td>0.0136 &quot; &quot; &quot; &quot;</td>
<td>0.1040</td>
</tr>
<tr>
<td>5</td>
<td>25.0 ml #2 to 500 ml.</td>
<td>0.0168</td>
</tr>
<tr>
<td>6</td>
<td>25.0 ml #2 to 1000 ml.</td>
<td>0.0084</td>
</tr>
<tr>
<td>7</td>
<td>10.0 ml #3 to 500 ml.</td>
<td>0.0041</td>
</tr>
</tbody>
</table>

Zinc Amalgam -- In preliminary work dilute zinc amalgams prepared by simple contact of the metals proved unsatisfactory. Whether prepared in air, in nitrogen atmosphere, in vacuum or under zinc sulfate solution a surface film was evident. In air, a black film of zinc suboxide appeared on the surface of the mercury. In nitrogen or in vacuum a crystalline metallic film appeared. The existence of these films prevents the preparation of amalgams of known concentra-
tion by simply weighing the two metals before amalgamation. Amalgams prepared under zinc sulfate solution were covered by considerable amounts of a white flocculent precipitate which is presumed to be a mixture of basic zinc salts and zinc hydroxide. Upon exposure to air the amalgam was covered with a black film almost immediately. All of these amalgams showed a marked tendency to adhere to glass. When a small globule was rolled around on a clean watch glass streaks of amalgam would be left sticking to the glass. On the whole, amalgams prepared by these methods were not suitable for use in glass apparatus nor did the method allow quantitative preparations.

Amalgams prepared by the method of Hulett and DeLury closely resembled pure mercury so long as they were not exposed to air for more than a few seconds. However, it is advisable that oxygen does not come in contact with the amalgam at any time. Unfortunately, Hulett's paper on the preparation of zinc amalgam is not immediately available. However, Hulett and DeLury have shown that cadmium metal dissolves quantitatively in mercury under the same conditions. In this work polarography of the water layer after amalgamation gave polarograms (Fig. 8C) which could not be distinguished from polarograms of distilled water. It has been found that 0.008 millimolar zinc solutions can be distinguished from distilled water by polarographic methods. Thus it can be said that the water layer after amalgamation contains less than 0.5 \( \gamma \) per milliliter. For an amalgam made up with 30 milligrams of zinc metal with a water layer of 25 cm\(^2\) in volume an error of the order of 0.1\% in concentration may be possible. The method offers the most
satisfactory results for preparation of the amalgams used in polarography.

The method for making up a standard zinc amalgam is described in the section dealing with the amalgam cell.

Calomel Electrode Paste — Mercurous chloride, C.P., was mixed with purified mercury to form a powdery paste.

Gelatin — 0.2 gm. of Knox Sparkling Gelatin was dropped into 10 ml. 0.1N potassium chloride and heated just to boiling or until the gelatin dissolved. Immediately after dissolution 20 ml. of 0.1N potassium chloride was run in. This make up is approximately 0.6% gelatin in 0.1N potassium chloride. 1 ml. diluted to 125 ml. is approximately 0.005% gelatin.

IN Potassium chloride — 75 grams reagent grade potassium chloride was made up to 1 liter.

Saturated potassium chloride — Reagent grade potassium chloride was added to distilled water until an excess remained after standing several days.

Saturated potassium chloride — zinc chloride — Approximately 100 grams of zinc chloride was added to 100 ml. of saturated potassium chloride.

Saturated potassium nitrate — zinc nitrate — Potassium nitrate, reagent grade, was added to 100 ml. distilled water until an excess remained undissolved on standing several hours. Approximately 150 grams of zinc nitrate were added to the saturated potassium nitrate.

All chemicals used were reagent grade as supplied by the University of British Columbia, Chemicals Storeroom.

Doubly distilled water was used throughout the experimental procedures.
II - Apparatus

A Sargent Model XXII Polarograph was used to record the polarograms.

A manual method was also devised which employed the recording polarograph to measure the current at constant applied E.M.F. A Leeds and Northrup Student Type Potentiometer measured the potential across the dropping electrode and the 0.1N calomel electrode. The circuit diagram is shown in Fig. 3.

Opening and closing the stabilizing circuit did not cause any deflection of the potentiometer galvanometer thus indicating that the possibility of error from this source is negligible. The effect of switching on the current recorder could not be determined. The error involved here depends on the magnitude of the current and the shunt resistances selected by the sensitivity settings. For a current of 6 microamperes and a sensitivity setting of 0.04 microamps/mm an error of the order of 0.0015 volt can be expected. Such an error is negligible in most polarographic work. The method appears to offer the same degree of accuracy as the simple manual circuit described by Lingane (55).

The amalgam cell -- The amalgam cell is shown in Fig. 4. The container was weighed filled with mercury and weighed again to determine the weight of mercury. The four hole rubber stopper contains a contact electrode, C, which extends to the bottom of the cell, a platinum wire coil electrode, B, which is positioned about 1 cm. above the mercury surface, a siphon tube, A, which extends to within 1-2 mm...
Sketch of Apparatus Showing Stabilizing Circuit and Leads to Potentiometer and Polarograph.

A - Amalgam
P - Platinum coil electrode
E - Mercury contact electrodes
W - Water layer
R - Reference electrode
S - Electrolyte
B - Anode pool
DE - Dropping electrode
Figure 4

The Amalgam Cell

A. Siphon tube
B. Platinum coil electrode
C. Contact electrode to bottom of mercury
D. Pressure tube
Figure 5.

Polarographic Cell

A. Reference Electrode
B. Platinum coil electrode in water layer
C. Polarographic cell showing anode pool container
T. Thermometer
N. Nitrogen gas line
R. Amalgam reservoir
of the bottom of the cell and a short tube, D, which is used to exert pressure for starting the siphon. After positioning the stopper, a weighed zinc crystal was dropped through the hole for the pressure tube, D. Distilled water was added till the coil electrode was covered. The pressure tube was replaced. Finally, 10 volts were impressed across the cell making the coil electrode the anode and the mercury the cathode. The cell was agitated so as to rotate the mercury at intervals. After several days electrolysis the amalgam was siphoned into the dropping electrode assembly.

Although no real evidence has been obtained in this work, it is believed that the zinc amalgam is ready for use in the dropping electrode shortly after the metallic zinc disappears.

The Polarographic Cell Assembly — The polarographic cell is shown in Fig. 5. The circuit connections are shown in Fig. 3. A 250 ml. beaker was used as the electrolysis vessel. A large rubber stopper was bored so that the dropping capillary, the contact electrode, the nitrogen line, the thermometer and the calomel electrode, A, could be inserted in the electrolyte. The contact electrode dipped into a mercury pool contained in a glass dish, C, positioned so that the falling drops did not fall into the pool. The 0.1N calomel electrode was made up with 0.1N potassium chloride, calomel paste and mercury. It was always placed in the electrolyte so that the solution flowed from the cell towards the calomel electrode before coming to the common level. The thermometer is graduated 0.1°C per scale division. The nitrogen line was a piece of 4mm glass tubing drawn to a
fine tip connected to the purification train by rubber tubing.

Dropping Electrode Assemblies -- The soft glass capillary tubing, S - 29350, supplied with the Sargent Polarograph was cut to lengths 7.0 - 7.5 cm and joined to 8 mm soft glass tubing. Fig. 6 shows the regular dropping electrode assembly for mercury alone. The mercury reservoir A, is connected to the capillary and column, B, by neoprene rubber tubing. The tubing was cleaned by passing steam through it for two hours followed by drying in a stream of air. Before connecting, a small quantity of mercury was allowed to flow through it to carry out any loose material remaining. The contact electrode, C, dips into the mercury reservoir through a rubber stopper. Air entered the reservoir and the capillary column through the attached drying tubes, D. The mercury level was controlled to 1 mm by a slot in the marker E.

The dropping electrode assemblies for use in amalgam polarography are shown in Figs. 7, 5. The capillary is connected to the reservoirs by 8 mm soft glass tubing. The reservoirs have a capacity of about 100 ml. The total height of the assemblies is about 45 cm, thus allowing an amalgam column of about 35 cm. A platinum contact electrode is set into the 8 mm glass tubing about 1 cm below the reservoirs. The assembly shown by itself had a second contact electrode about 1 cm above the capillary. The platinum coil electrode is held in the rubber stopper shown at the top of the reservoirs.

Before the mercury was siphoned into the amalgam reservoirs they were swept out for two or three hours with
Figure 6

Dropping Electrode Assembly

A. Mercury reservoir
B. Mercury column connected to reservoir by neoprene tubing.
C. Contact electrode
D. Drying tubes
E. Marker for mercury level.
Figure 7

All glass dropping electrode assembly for amalgam polarography.

C. Capillary
E. Contact electrodes
P. Platinum coil electrode (Dips into water layer in amalgam reservoir.)
nitrogen. A 4 mm glass tube was lowered till it was resting on the upper part of the capillary so as to sweep out air by the nitrogen stream. The nitrogen stream was maintained as long as possible while the mercury was siphoned in. As the thin glass tube was withdrawn it was manipulated so as to remove entrapped gas bubbles. As quickly as possible, distilled water was layered on the amalgam surface and the coil electrode inserted to close the stabilizing circuit.

Nitrogen purification -- Tank nitrogen used to sweep out dissolved oxygen was purified in a vanadous sulfate train after the method described by Meites (54). The purification train consisted of four scrubbing bottles containing 0.1N vanadous sulfate solution and a final bottle containing 0.1N potassium chloride made basic by the addition of one or two pellets of potassium hydroxide to which 1-2 grams of sodium sulfite were added.
III-METHODS

The mass of mercury flowing from the capillary was determined in air and in the electrolyte. In air the mercury drops were caught on a tared watch glass. As a drop fell the stop watch was started and the next drop was caught. The stop watch was stopped as the last drop fell into the watch glass. In the electrolyte the timing was made in the same manner, however, the mercury drops were caught in a glass ladle. The collected mercury was washed with a stream of distilled water. The excess water was decanted and the spoon and mercury dipped into acetone and swirled around. This process was repeated with fresh acetone. The excess acetone was decanted and the mercury globule tipped into a weighed watch glass. After the acetone had evaporated, the watch glass and mercury was weighed and the weight of mercury determined by difference.

For polarographic work the room was warmed to 23°C-27°C by means of a hot plate. The temperature being determined by means of thermometers distributed about the room. The mercury was filtered at a capillary funnel into the anode container and about 125 ml of standard solution added. The required amount of gelatin was then added. After setting up the dropping electrode assembly, the solution was swept out with nitrogen. The temperature of the electrolyte was brought to 25.0°C by holding the sides of the beaker by hand or rubbing with dry ice. The temperature was found to hold within 0.1°C during the run. When ready for the run the nitrogen tube was withdrawn so that it would maintain a blanket over the solution.
Usually the drop time was determined from the recording. In some cases the drop time was determined by timing with a stop watch graduated to 0.1 second. It was found that the drop times could only be reproduced in the absence of vibration. Even movements in other parts of the building seemed to have some effect. For this reason polarographic runs were made at such times outside interference was at a minimum.

In amalgam polarography the dial settings and electrode connections were set so that the potential of the dropping electrode became more positive. The dial settings for the amalgam runs are as follows: RANGE 1.500 Volts, SPAN 1.500 Volts OPPOSED, DME $\oplus$, DAMPING 1, SENSITIVITY 0.06 $\mu$amp. % RANGE was set 10.0 and zero current set at 40 mm. chart reading. The apparatus was calibrated (see manual of instructions) during zero current check. The recorder was run at E.M.F.CONSTANT until the pen reached the line chosen for the start of the polarogram then the switch was thrown to E.M.F.INCREASING.

For a manual run the Polarograph was set E.M.F.CONSTANT and the potential across the cell varied by setting % RANGE. When the chart showed steady current the recorder was switched off (the applied E.M.F. is maintained) and the potential of the dropping electrode determined vs. O.IN calomel reference electrode by the potentiometer. The potentiometer was frequently calibrated against a Weston Standard Cell.

The potentiometer reading is that setting for which the galvanometer (Leeds and Northrup CAT. NO. 330-D period 2.4 sec. sensitivity 0.35 $\mu$amp) is deflected equally from zero.
E - Results and Discussion

I - Polarography of Standard Zinc Solutions.

Determinations of the capillary constant 'm' for the regular dropping mercury electrode are recorded in Table 7. The mean value 2.595 mgm/sec.

TABLE 7.
The Rate of Mercury Flowing from Capillary into Air.

<table>
<thead>
<tr>
<th>Date</th>
<th>Mass of Hg Outflow</th>
<th>Time</th>
<th>'m'</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feb.13</td>
<td>3201.2 mgm</td>
<td>1231 sec</td>
<td>2.601 mgm/sec</td>
</tr>
<tr>
<td>Apr.16</td>
<td>442.0 &quot;</td>
<td>170.7 sec</td>
<td>2.589 &quot;</td>
</tr>
<tr>
<td>&quot; 16</td>
<td>476.5 &quot;</td>
<td>183.9 &quot;</td>
<td>2.591 &quot;</td>
</tr>
<tr>
<td>&quot; 25</td>
<td>823.7 &quot;</td>
<td>316.7 &quot;</td>
<td>2.601 &quot;</td>
</tr>
</tbody>
</table>

Mean Value 2.595 " has been used in calculations. The use of this value for 'm' is not strictly valid since 'm' varies with the potential of the dropping electrode. From rather meager data shown by Kolthoff and Lingane (.57) an error of the order of 2% is expected.

The removal of dissolved oxygen by purified tank nitrogen was tested with the regular polarographic apparatus. The results are shown in Table 8.

TABLE 8.
Removal of Dissolved Oxygen by Nitrogen Sweep
Electrolyte IN KCL EMF applied 1 volt.

<table>
<thead>
<tr>
<th>Time of N₂ Sweep</th>
<th>Sensitivity</th>
<th>Damping</th>
<th>Current</th>
<th>Pen Travel</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min</td>
<td>0.04/amp/mm</td>
<td>#1</td>
<td>5.8/amp</td>
<td>21 mm</td>
</tr>
<tr>
<td>5 &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.84 &quot;</td>
<td>2.0 mm &quot;</td>
</tr>
<tr>
<td>10 &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.24 &quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>15 &quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.25 &quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>20 &quot;</td>
<td>&quot;</td>
<td>none</td>
<td>0.25 &quot;</td>
<td>2.25mm</td>
</tr>
<tr>
<td>&quot; 0.01</td>
<td>&quot;</td>
<td>#1</td>
<td>0.245 &quot;</td>
<td>0.25 &quot;</td>
</tr>
<tr>
<td>&quot; 0.003</td>
<td>&quot;</td>
<td>#1</td>
<td>0.255 &quot;</td>
<td>0.25 &quot;</td>
</tr>
<tr>
<td>&quot; 0.04</td>
<td>&quot;</td>
<td>none</td>
<td>0.255 &quot;</td>
<td>14.0 &quot; &quot;</td>
</tr>
<tr>
<td>25 &quot;</td>
<td>&quot;</td>
<td>#1</td>
<td>0.25 &quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>lgm Na₂ S₃ added</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.18 &quot;</td>
<td>1.0 mm</td>
</tr>
</tbody>
</table>
It is seen that a fifteen minute nitrogen sweep is sufficient for practical purposes. However, traces of oxygen remain dissolved in the solution. After a nitrogen sweep of one hour a small 'wave' appeared on the polarograms at approximately -1.10 volt versus 0.1N calomel electrode when maximum sensitivity of the recording instrument was used. It is believed that this 'wave' is due to dissolved oxygen.

Oxygen is reduced stepwise at the dropping electrode. The first wave is due to the reduction of oxygen to hydrogen peroxide, equation 1. The half wave potential in 0.1N potassium chloride is given versus S.C.E.

\[
\begin{align*}
(1) & \quad O_2 + 2H_2O + 2e \rightarrow H_2O_2 + 2OH^- \quad E^\frac{1}{2} = 0.1v \\
(2) & \quad H_2O_2 + 2e \rightarrow 2OH^- \quad E^\frac{1}{2} = 0.9v.
\end{align*}
\]

It is seen that in the presence of dissolved oxygen in a neutral solution, the diffusion layer about the mercury drop becomes a basic solution containing hydrogen peroxide. The small wave noticed at -1.1 volt versus 0.1N calomel electrode in this work is presumably due to the reduction of hydrogen peroxide. The wave heights varied somewhat between 0.03/amps to 0.09/amps.

Results of a test for reproducibility of the instrument settings are shown in Table 9A. After each reading the dials were thrown off and reset before taking the potentiometer reading.
TABLE 9A

Reproducibility of Instrument Settings

Dropping mercury electrode in standard zinc solution

<table>
<thead>
<tr>
<th>Span</th>
<th>Initial</th>
<th>% Range (%)</th>
<th>Voltage</th>
<th>Reading</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 volts</td>
<td>add 0.1 volt</td>
<td>49%</td>
<td>0.8350 V</td>
<td>0.8346 V</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.8344  &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.8349  &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.8343  &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.8345  &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
<td>0.8350  &quot;</td>
</tr>
</tbody>
</table>

Since one scale division is 0.0150 volts the variation of the potentiometer readings 0.0006 volts represents 4% of one scale division. It is evident that the instrument settings can be duplicated accurately. It was found, however, that the pen position on the chart varied by as much as 0.2 chart division. That is the chart voltage reading varied from the dial setting value. This variation is due to backlash in the chart drive mechanism. Fortunately, the discrepancy is noticeable as the instrument operates and consequently the error can be estimated when the instrument is stopped. For an error of 0.1 chart division at a span setting of 1.500 volts an error in the measurement of the half-wave potential of 0.0015 volts results.

When the polarograph was used in conjunction with the potentiometer for point by point readings the applied potential was calculated from the dial settings and checked against the potentiometer reading. The results are shown in Table 9B.
TABLE 9B

Polarograph vs. Potentiometer Readings.

<table>
<thead>
<tr>
<th>Polarograph Setting</th>
<th>Potentiometer Reading</th>
<th>Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.350 volt</td>
<td>1.347 volt</td>
<td>-0.003 volt</td>
</tr>
<tr>
<td>1.005 &quot;</td>
<td>1.003 &quot;</td>
<td>-0.002 &quot;</td>
</tr>
<tr>
<td>0.900 &quot;</td>
<td>0.900 &quot;</td>
<td>0.000 &quot;</td>
</tr>
<tr>
<td>0.750 &quot;</td>
<td>0.753 &quot;</td>
<td>0.003 &quot;</td>
</tr>
<tr>
<td>0.525 &quot;</td>
<td>0.531 &quot;</td>
<td>0.006 &quot;</td>
</tr>
<tr>
<td>0.300 &quot;</td>
<td>0.309 &quot;</td>
<td>0.009 &quot;</td>
</tr>
<tr>
<td>0.015 &quot;</td>
<td>0.021 &quot;</td>
<td>0.006 &quot;</td>
</tr>
</tbody>
</table>

It is seen that the potentiometer readings become increasingly higher than the instrument setting with decreasing applied potential by an amount outside the limit of error determined from Table 9A. It is assumed that the deviation is entirely due to inherent error of the potentiometer. Consequently, a similar degree of error is expected in the determination of the potential of the dropping electrode for point by point polarograms.

In order to obtain information with respect to the reliability, reproducibility and accuracy of the method used, polarograms of standard zinc in 0.1N potassium chloride with added gelatin were recorded. The data is given in Table 10. Typical polarograms are shown in Figs. 9A, 10A, 10B.
TABLE 10

Polarographic Characteristics of Zinc Solutions

(1) Recorded with Sargent Polarograph.

Standard Zinc in 0.1N KCL with 0.0001% gelatin.

Temperature 25.2°C 0.2°C

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration</th>
<th>(\text{id(a)})</th>
<th>(t)</th>
<th>(E_i^b(b))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.6187 molar</td>
<td>4.44 mamp.</td>
<td>2.84 sec</td>
<td>1.105 volt</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>4.51 mamp.</td>
<td>2.70 &quot;</td>
<td>1.098 &quot;</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>4.89 mamp.</td>
<td>2.89 &quot;</td>
<td>1.093 &quot;</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>4.71 mamp.</td>
<td>2.70 &quot;</td>
<td>1.095 &quot;</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>4.83 mamp.</td>
<td>2.91 &quot;</td>
<td>1.095 &quot;</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>4.83 mamp.</td>
<td>3.04 &quot;</td>
<td>1.084 &quot;</td>
</tr>
<tr>
<td>7</td>
<td>&quot;</td>
<td>4.74 mamp.</td>
<td>2.98 &quot;</td>
<td>1.090 &quot;</td>
</tr>
<tr>
<td>8</td>
<td>0.3365 &quot;</td>
<td>2.68 mamp.</td>
<td>2.62 &quot;</td>
<td>1.092 &quot;</td>
</tr>
<tr>
<td>9</td>
<td>&quot;</td>
<td>2.62 mamp.</td>
<td>2.58 &quot;</td>
<td>1.090 &quot;</td>
</tr>
<tr>
<td>10</td>
<td>&quot;</td>
<td>2.63 mamp.</td>
<td>2.49 &quot;</td>
<td>1.098 &quot;</td>
</tr>
<tr>
<td>11</td>
<td>&quot;</td>
<td>2.62 mamp.</td>
<td>2.49 &quot;</td>
<td>1.095 &quot;</td>
</tr>
<tr>
<td>12</td>
<td>0.2061 &quot;</td>
<td>1.67 mamp.</td>
<td>2.95 &quot;</td>
<td>1.098 &quot;</td>
</tr>
<tr>
<td>13</td>
<td>&quot;</td>
<td>1.71 mamp.</td>
<td>2.92 &quot;</td>
<td>1.093 &quot;</td>
</tr>
<tr>
<td>14</td>
<td>&quot;</td>
<td>1.66 mamp.</td>
<td>2.70 &quot;</td>
<td>1.101 &quot;</td>
</tr>
<tr>
<td>15</td>
<td>0.1040 &quot;</td>
<td>0.828 mamp.</td>
<td>2.52 &quot;</td>
<td>1.107 &quot;</td>
</tr>
<tr>
<td>16</td>
<td>&quot;</td>
<td>0.837 mamp.</td>
<td>2.70 &quot;</td>
<td>1.105 &quot;</td>
</tr>
<tr>
<td>17</td>
<td>0.0168 &quot;</td>
<td>nil mamp.</td>
<td>2.70 &quot;</td>
<td>nil</td>
</tr>
<tr>
<td>18</td>
<td>0.0084 &quot;</td>
<td>&quot;</td>
<td>2.70 &quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>19</td>
<td>0.0041 (d)</td>
<td>0.035 mamp.</td>
<td>2.70 &quot;</td>
<td>1.113 &quot;</td>
</tr>
</tbody>
</table>

(a) Corrected to 25.0°C  (b) Applied voltage reading
(c) Oxygen present  (d) Identical wave found in 0.1N KCL alone.

Standard Zinc in 0.1N KCL with 0.0001% gelatin. plus 0.1 gm Na₂SO₄ per 100 ml.

Temperature 25.1°C 0.2°C

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration</th>
<th>(\text{id(a)})</th>
<th>(t)</th>
<th>(E_i^b(a))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1(a)</td>
<td>0.6187 mmolar</td>
<td>2.96 mamp.</td>
<td>2.95 sec</td>
<td>0.895 volt</td>
</tr>
<tr>
<td>1(b)</td>
<td>&quot;</td>
<td>2.64 mamp.</td>
<td>2.89 &quot;</td>
<td>0.877 &quot;</td>
</tr>
<tr>
<td>2(a)</td>
<td>0.2061 &quot;</td>
<td>0.67 mamp.</td>
<td>2.91 &quot;</td>
<td>0.858 &quot;</td>
</tr>
<tr>
<td>2(b)</td>
<td>&quot;</td>
<td>0.61 mamp.</td>
<td>2.95 &quot;</td>
<td>0.891 &quot;</td>
</tr>
<tr>
<td>3(a)</td>
<td>0.1040 &quot;</td>
<td>0.51 mamp.</td>
<td>2.75 &quot;</td>
<td>0.950 &quot;</td>
</tr>
<tr>
<td>3(b)</td>
<td>&quot;</td>
<td>0.44 mamp.</td>
<td>2.79 &quot;</td>
<td>0.918 &quot;</td>
</tr>
</tbody>
</table>

(a) Applied voltage reading.
(2) **Manually Recorded**

Standard Zinc in 0.1N KCl with 0.0001% Gelatin.

Temperature 25.0°C.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>( n )</th>
<th>( \text{id} )</th>
<th>( t )</th>
<th>( E'_{\text{a}} ) (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2061 mmolar</td>
<td></td>
<td>1.40 mA/amp</td>
<td>3.15 sec</td>
<td>-1.095 volt</td>
</tr>
</tbody>
</table>

(a) \( E'_{\text{a}} \) vs. 0.1N calomel electrode.
(b) oxygen indicated.

Standard Zinc in 0.1N KCl with 0.0001% gelatin plus 0.1 gm Na\(_2\) SO\(_4\) per 100 ml.

Temperature 25.2°C 0.2°

<table>
<thead>
<tr>
<th>Concentration</th>
<th>( n )</th>
<th>( \text{id} )</th>
<th>( t )</th>
<th>( E'_{\text{a}} ) (a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6187 mmolar</td>
<td></td>
<td>2.61 mA/amp</td>
<td>3.04 sec</td>
<td>-1.095 volt</td>
</tr>
<tr>
<td>0.2061 &quot;</td>
<td></td>
<td>0.65 &quot;</td>
<td>2.70 &quot;</td>
<td>-1.098 &quot;</td>
</tr>
</tbody>
</table>

(a) \( E'_{\text{a}} \) vs. 0.1N calomel electrode.

The diffusion current and drop time were measured by the method described in the Sargent Manual of Instructions for the Polarograph. The temperature coefficient 2.0% per degree (57) was used to correct the measured value to the value at 25.0°C where necessary. In most cases the correction term is negligible. The maximum correction is shown in the following calculation.

\[
\text{id measured at 25.3°C} = 4.74 \text{mA/amp.}
\]

\[
\text{id corrected} = 4.74 \text{mAmps} - 0.3 \times \frac{2}{100} \times 4.74 \text{mAmps} = 4.71 \text{ mA at 25.0°C.}
\]

The half wave potential for zinc in 0.1N potassium chloride is determined as - 1.095 volt versus 0.1N calomel electrode. The value given in the literature is - 1.084 volt (50). It is seen that the half wave potentials determined from the instrument settings agree with the value determined...
within the limit of error. On the other hand in the presence of sulfite the $E^{1/2}$ values calculated from the instrumental settings do not correspond to the determined values -- 1.095 volt and -- 1.098 volt versus 0.1N. calomel electrode.

The runs made with sulfite present were duplicates, that is run b was made immediately following run a. There is a considerable degree of discordance among the results. The only consistency is that the current decreased further during run b. The decrease of the diffusion current upon the addition of sulfite is not satisfactorily explained.

It was noted that the presence of oxygen also decreased the diffusion current for zinc. Fig. shows polarograms of 0.6187 mmolar zinc in 0.1N potassium chloride with 0.0001% gelatin. Fig. (a) was obtained with oxygen present. The pen travel before the zinc wave indicates the presence of a reducible substance. Fig. (b) shows that the oxygen has been removed to its minimal concentration. Its presence is not detectable. According to the electrode reaction of dissolved oxygen the diffusion layer becomes basic and contains hydrogen peroxide. The conditions therefore favor the formation of zincate or zinc peroxide, most likely the former. The zinc complex is not reducible except at a more negative potential and, therefore, does not contribute to the diffusion current at -1.095 volt half-wave potential. It may be noticed that the total current is approximately the same. Such behaviour could be expected on the basis that the amount of zinc removed by complex formation is proportional to the concentration of oxygen.

The disappearance of the zinc wave at a concentration
Figure 8

Polarograms of 0.6187 millimolar zinc in 0.1N potassium chloride plus 0.0001% gelatin. Sensitivity 0.04/amp/mm. Drop times (8a) 2.84 sec, (8b) 2.89 sec.

In Figure 8a the presence of dissolved oxygen is shown by pen travel preceding the current increase due to the reduction of zinc.

<table>
<thead>
<tr>
<th></th>
<th>8a</th>
<th>8b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residual current plus oxygen current at $E_1$</td>
<td>0.92 amp</td>
<td>0.36 amp</td>
</tr>
<tr>
<td>Zinc current at $E_2$</td>
<td>4.44 &quot;</td>
<td>4.88 &quot;</td>
</tr>
<tr>
<td>Total current at $E_2$</td>
<td>5.36 &quot;</td>
<td>5.24 &quot;</td>
</tr>
</tbody>
</table>
Polarogram of supernatant water layer from amalgam cell with added potassium chloride, A, compared with polarogram of 0.1N potassium chloride, B. Both solutions swept out with nitrogen. Sensitivity 0.003 μamp/mm without damping. Both polarograms are similar to polarograms of 0.0041 millimolar zinc in 0.1N potassium chloride plus 0.0001% gelatin swept out with nitrogen.

Voltage - 1.15 volt versus 0.1N calomel electrode read from instrument settings.
0.0168 mmolar zinc is believed due to the fact that the oxygen remaining in solution tied up most of the zinc in complex formation. The polarograms of 0.0084 mmolar zinc resembled those of 0.0168 mmolar zinc in that a reducible substance was indicated to be present by the pen travel during drop formation. However, polarograms of 0.0041 mmolar zinc could not be distinguished from polarograms of 0.1M potassium chloride alone. These latter were found to correspond to the polarograms of the supernatant water from the amalgam cell after a small amount of potassium chloride had been added for the polarographic analysis. Thus it is evident that the supernatant water contained less than 0.0084 mmolar zinc.

A plot of diffusion current vs. concentration is linear in the range of concentration 0.1040-0.6187 mmolar zinc. The straight line passes extremely close to the origin upon extrapolation. Fig. 9B

The diffusion current constant and the apparent polarographic diffusion coefficient of zinc in 0.1M potassium chloride have been calculated by the Ilkovic equation

\[ i_d = 6.07nD^{1/2}Cm^{2/3}C^{1/2} \]  (III)

The value so determined for \( D^2 \) has been substituted in the second terms of the equations proposed by Lingane and Loveridge, and Strehlow and Stackelberg and the value for \( D^2 \) in the first term redetermined. The results are shown in Table 11.

Theoretically the 'D' values should correspond to the value of the diffusion coefficient of zinc at infinite dilution, \( 7.2 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1} \) (11).
The calculations have been performed in the manner suggested by Lingane and Loveridge (8). These authors state that a knowledge of $D$ is necessary for the practical use of their new equation. Late in this work it was realized that the equation is a simple quadratic and it is difficult to understand why the authors have disregarded this fact in their paper.

The solution of the equation of Lingane and Loveridge is

$$\sqrt{D_L} = \frac{-1 + \sqrt{1 + 0.04952 \cdot \text{cc}}}{56.76 \cdot t^\frac{1}{2}}$$

when $m = 2.595 \text{ mgm sec}^{-1}$ as in this work, and of Strehlow and Stackelberg's

$$\sqrt{D_S} = \frac{-1 + \sqrt{1 + 0.02140 \cdot \text{cc}}}{24.74 \cdot t^\frac{1}{2}}$$

The following values calculated from these formulae may be compared with those shown in Table 11.

<table>
<thead>
<tr>
<th>No.</th>
<th>$D_L \times 10^6$</th>
<th>$D_S \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>7.03 cm$^2$ sec$^{-1}$</td>
<td>7.71 cm$^2$ sec$^{-1}$</td>
</tr>
<tr>
<td>4</td>
<td>6.78 &quot;</td>
<td>7.32 &quot;</td>
</tr>
<tr>
<td>5</td>
<td>6.85 &quot;</td>
<td>7.51 &quot;</td>
</tr>
<tr>
<td>6</td>
<td>6.75 &quot;</td>
<td>7.40 &quot;</td>
</tr>
<tr>
<td>7</td>
<td>6.57 &quot;</td>
<td>7.26 &quot;</td>
</tr>
<tr>
<td>Average</td>
<td>6.79 &quot;</td>
<td>7.44 &quot;</td>
</tr>
</tbody>
</table>

The values of $D_L$ here are about 0.10 cm$^2$ sec$^{-1}$ higher than those shown in Table 11. The values $D_S$ are about 0.03 cm$^2$ sec$^{-1}$ higher.

It should have been stated that the general solution is

$$\sqrt{D} = \frac{-1 + \sqrt{1 + \frac{4A_{ld}}{607mCm}}}{2A m^{-\frac{1}{3}} t^\frac{1}{2}}$$
Figure 9A

Polarograms of zinc in 0.1M potassium chloride plus 0.0001% gelatin swept out with nitrogen showing wave-height versus concentration. Sensitivity 0.04 μamp/mm. Compare polarogram of 0.0168 millimolar zinc with Figure 8a. The presence of oxygen is not indicated here by pen travel as in Figure 8a.
CONCENTRATION VS. DIFFUSION CURRENT

STANDARD ZnCl₂ IN 0.1N KCl, 0.0001% GELATIN, N₂ SWEEP
SARGENT POLAROGRAPH RECORDING

A MEASURED AT E₀.

+ ± MEAN VALUE OF SEVERAL DETERMINATIONS
AND ITS SIZE INDICATES VARIANCE.
Figure 10A

Polarogram of 0.1040 millimolar zinc in 0.1N potassium chloride plus 0.0001% gelatin swept out with nitrogen.

Sensitivity 0.006 $\mu$amp/mm.

Diffusion current 0.83 $\mu$amp.
Polarogram run immediately after that shown in Figure 10A after addition of sodium sulfite.
Concentration 0.1040 millimolar zinc in 0.1N potassium chloride plus 0.0001% gelatin plus 0.1 gm sodium sulfite /100 cc.
Sensitivity 0.006 $\mu$ amp/mm.
Diffusion current 0.44 $\mu$ amp.
TABLE 11

The Diffusion Current Constant and the Apparent Diffusion Coefficient of Zinc in 0.1N Potassium Chloride

<table>
<thead>
<tr>
<th>No.</th>
<th>Concentration</th>
<th>I</th>
<th>( D \times 10^6 ) ( \text{cm}^2 \text{sec}^{-1} )</th>
<th>( D \times 10^6 ) ( \text{cm}^2 \text{sec}^{-1} ) (a)</th>
<th>( D \times 10^6 ) ( \text{cm}^2 \text{sec}^{-1} ) (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.6187 mmolar</td>
<td>3.51</td>
<td>8.34</td>
<td>6.92</td>
<td>7.68</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>3.42</td>
<td>7.92</td>
<td>6.61</td>
<td>7.31</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>3.46</td>
<td>8.12</td>
<td>6.75</td>
<td>7.48</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>3.43</td>
<td>8.00</td>
<td>6.66</td>
<td>7.37</td>
</tr>
<tr>
<td>7</td>
<td>&quot;</td>
<td>3.38</td>
<td>7.76</td>
<td>6.47</td>
<td>7.16</td>
</tr>
<tr>
<td>8</td>
<td>0.3365</td>
<td>3.59</td>
<td>8.75</td>
<td>7.25</td>
<td>8.05</td>
</tr>
<tr>
<td>9</td>
<td>&quot;</td>
<td>3.52</td>
<td>8.41</td>
<td>7.00</td>
<td>7.75</td>
</tr>
<tr>
<td>10</td>
<td>&quot;</td>
<td>3.56</td>
<td>8.57</td>
<td>7.13</td>
<td>7.90</td>
</tr>
<tr>
<td>11</td>
<td>&quot;</td>
<td>3.54</td>
<td>8.51</td>
<td>7.08</td>
<td>7.80</td>
</tr>
<tr>
<td>12</td>
<td>0.2061</td>
<td>3.58</td>
<td>8.71</td>
<td>7.19</td>
<td>8.00</td>
</tr>
<tr>
<td>13</td>
<td>&quot;</td>
<td>3.68</td>
<td>9.16</td>
<td>7.54</td>
<td>8.40</td>
</tr>
<tr>
<td>14</td>
<td>&quot;</td>
<td>3.61</td>
<td>8.87</td>
<td>7.33</td>
<td>8.14</td>
</tr>
<tr>
<td>15</td>
<td>0.1040</td>
<td>3.61</td>
<td>8.90</td>
<td>7.34</td>
<td>8.15</td>
</tr>
<tr>
<td>16</td>
<td>&quot;</td>
<td>3.61</td>
<td>8.86</td>
<td>7.32</td>
<td>8.13</td>
</tr>
</tbody>
</table>

Average Values

<table>
<thead>
<tr>
<th>Concentration</th>
<th>I</th>
<th>( D \times 10^6 ) ( \text{cm}^2 \text{sec}^{-1} )</th>
<th>( D \times 10^6 ) ( \text{cm}^2 \text{sec}^{-1} ) (a)</th>
<th>( D \times 10^6 ) ( \text{cm}^2 \text{sec}^{-1} ) (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6187 mmolar</td>
<td>3.44</td>
<td>8.03</td>
<td>6.68</td>
<td>7.40</td>
</tr>
<tr>
<td>0.3365</td>
<td>&quot;</td>
<td>3.55</td>
<td>8.56</td>
<td>7.11</td>
</tr>
<tr>
<td>0.2061</td>
<td>&quot;</td>
<td>3.62</td>
<td>8.91</td>
<td>7.35</td>
</tr>
<tr>
<td>0.1040</td>
<td>&quot;</td>
<td>3.61</td>
<td>8.88</td>
<td>7.33</td>
</tr>
<tr>
<td>(c) 1.00</td>
<td>&quot;</td>
<td>3.41</td>
<td>7.91</td>
<td></td>
</tr>
</tbody>
</table>

(a) \( D_1 \) from equation by Lingane and Loveridge
(b) \( D_2 \) " " " Strehlow and Stackelberg
(c) Values reported in literature

The values for \( D \) are seen to increase with decreasing concentration of zinc. Kolthoff and Lingane (62) mention that similar deviations have been reported for other metals. They themselves found no such behaviour when the work was repeated. However, their published data for lead in 0.1N potassium chloride shows some evidence of this deviation. Such a deviation can be easily explained, in fact, such a deviation is expected when the current in the mercury drop is considered. According to Strehlow and Stackelberg (63), Antweiler has shown evidence of the current
and resultant streaming of the drop surface when a dye and water are used at a dropping capillary. Consequently, such behaviour is presumed to be characteristic of the dropping mercury. Under polarographic conditions it may also be presumed that the current along the axis of the capillary is constant for a given set of conditions of temperature, mercury head and back pressure. However, surface streaming would be governed by the surface conditions. One of these conditions would be the concentration of the amalgam formed by reduction to a mercury soluble metal. Assuming that the surface streaming is reduced by increasing concentration of amalgam then the ratio \( \frac{1d}{C} \) or the values for \( D \) would increase with increase in rate of streaming, that is with decrease in concentration of the reducible ion. Such behaviour has been denied apparently because the ratio \( \frac{1d}{C} \) has again decreased at very low concentrations. The nature of this decrease at very low concentrations could be explained by the effect of the minimal oxygen concentration.

The foregoing explanation appears valid for the rather limited number of papers studied so far. On the other hand, the phenomena is directly related to the occurrence of current maxima which are still the subject of controversial papers(64). Further review of reported data should assist in the establishment of an adequate explanation.

If, as reported by Kolthoff and Lingane, the relation \( \frac{1d}{C} \) is strictly linear then this work agrees with published data to within 15%. If the ratio \( \frac{1d}{C} \) actually increases with decreasing concentration of zinc the agreement is within 5%. The maximum deviation is considered in both cases.
It is evident that the method does not produce gross deviations and for this reason it is assumed that the same order of accuracy can be obtained in amalgam polarography. Provided, of course, that it can be shown that a dropping amalgam has the same dropping characteristics as pure mercury. According to English (23) the properties mentioned do agree over the range of potential necessary for polarographic measurements.
II - Amalgam Polarography.

A few tests were made to show that the dilute amalgam behaved similarly to mercury at the dropping capillary and that the stabilizing circuit had no effect on the recorded polarograms. The data from these tests is given in Tables 12 - 14.

TABLE 12

The Rate of Amalgam Flowing from the Capillary into Various Media

<table>
<thead>
<tr>
<th>No.</th>
<th>Media</th>
<th>Time</th>
<th>Amalgam Collected</th>
<th>'m'</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Air</td>
<td>162.2 sec</td>
<td>287.7 mgm</td>
<td>1.773 mgm/sec</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>161.1 sec</td>
<td>284.9 mgm</td>
<td>1.768 &quot;</td>
</tr>
<tr>
<td>3</td>
<td>Water</td>
<td>113.2 &quot;</td>
<td>200.9 &quot;</td>
<td>1.775 &quot;</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>113.2 &quot;</td>
<td>201.1 &quot;</td>
<td>1.777 &quot;</td>
</tr>
<tr>
<td>5</td>
<td>Sat KCL</td>
<td>107.7 &quot;</td>
<td>191.4 &quot;</td>
<td>1.777 &quot;</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>107.5 &quot;</td>
<td>190.6 &quot;</td>
<td>1.773 &quot;</td>
</tr>
<tr>
<td>7</td>
<td>Air</td>
<td>174.0 &quot;</td>
<td>306.8 &quot;</td>
<td>1.763 &quot;</td>
</tr>
<tr>
<td>8</td>
<td>&quot;</td>
<td>166.2 &quot;</td>
<td>290.8 &quot;</td>
<td>1.750 &quot;</td>
</tr>
<tr>
<td>9</td>
<td>Sat KCL Zn Cl₂</td>
<td>108.9 &quot;</td>
<td>191.2 &quot;</td>
<td>1.756 &quot;</td>
</tr>
<tr>
<td>10</td>
<td>&quot;</td>
<td>128.4 &quot;</td>
<td>224.8 &quot;</td>
<td>1.751 &quot;</td>
</tr>
<tr>
<td>11</td>
<td>Sat KNO₃ Zn(NO₃)₂(a)</td>
<td>124.3 &quot;</td>
<td>216.0 &quot;</td>
<td>1.738 &quot;</td>
</tr>
<tr>
<td>12</td>
<td>&quot;(a)</td>
<td>119.0 &quot;</td>
<td>207.5 &quot;</td>
<td>1.744 &quot;</td>
</tr>
<tr>
<td>13</td>
<td>Air</td>
<td>68.4 &quot;</td>
<td>120.8 &quot;</td>
<td>1.757 &quot;</td>
</tr>
<tr>
<td>14</td>
<td>&quot;</td>
<td>159.0 &quot;</td>
<td>275.4 &quot;</td>
<td>1.732 &quot;</td>
</tr>
</tbody>
</table>

(a) Swept out with N₂ for 15 minutes.

The successive values for 'm' determined for air show the effect of the decreasing amalgam head - about 2 mm during the test. Comparison with a similar table for the rate of mercury flow(15) is strong evidence that the rate of amalgam flow is independant of the media in which the drops form.

The determination of 'm' at the capillary electrode is shown in Table 13.
Table 13

The Rate of Amalgam Flowing from the Capillary Electrode

Amalgam 0.0042 gm Zn in 1457.7 gm Hg.
Stabilizing circuit closed

<table>
<thead>
<tr>
<th>Group</th>
<th>Media</th>
<th>Applied Voltage</th>
<th>Time</th>
<th>Amalgam Collected</th>
<th>'m'</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Air</td>
<td>nil</td>
<td>173.5 sec</td>
<td>301.6 mgm</td>
<td>1.738 mgm/sec</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>175.2</td>
<td>303.1</td>
<td>1.730</td>
</tr>
<tr>
<td></td>
<td>O.1N KCL</td>
<td>-0.45 v</td>
<td>176.8</td>
<td>297.4</td>
<td>1.682</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>178.7</td>
<td>299.6</td>
<td>1.677</td>
</tr>
<tr>
<td>2</td>
<td>Air</td>
<td>nil</td>
<td>179.8</td>
<td>306.3</td>
<td>1.704</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>178.4</td>
<td>303.9</td>
<td>1.704</td>
</tr>
<tr>
<td></td>
<td>O.1N KCL</td>
<td>-0.22</td>
<td>179.3</td>
<td>301.9</td>
<td>1.684</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>179.4</td>
<td>304.1</td>
<td>1.695</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>177.2</td>
<td>301.9</td>
<td>1.704</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>177.0</td>
<td>301.5</td>
<td>1.703</td>
</tr>
</tbody>
</table>

Here the data is not extensive enough to warrant any conclusions with respect to the variation of 'm' with the potential of the dropping electrode. However, it is seen that the value for 'm' determined in air may be used in the calculations since the variation appears to be about \(+\ 3\%\). The value of 'm' should be determined in the electrolyte at the appropriate potential of the dropping electrode. In the case of amalgam the dissolution of the amalgam itself is an additional complication to the variation of 'm' with potential.

The effect of the stabilizing circuit was tested by determining the drop time with the circuit open and closed. The drop time is a function of surface tension which in turn is a function of the electrocapillary potential. If the stabilizing circuit had any effect there should be some deviation of the drop times on open and closed circuit. The data is recorded in Table 14.
TABLE 14
Drop times with Stabilizing Circuit Open and Closed.
Amalgam 0.0148 gm Zn in 791.9 gm Hg. Electrolyte IN KCl.
Stabilizing circuit 10 volts applied.

<table>
<thead>
<tr>
<th>Dropping Electrode Potential (a)</th>
<th>Stabilizing Circuit Open</th>
<th>Stabilizing Circuit Closed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00 volts</td>
<td>5.98 sec</td>
<td>5.98 sec</td>
</tr>
<tr>
<td>&quot;</td>
<td>5.99 &quot;</td>
<td>6.01 &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>5.99 &quot;</td>
<td>6.08 &quot;</td>
</tr>
<tr>
<td>-0.40 &quot;</td>
<td>6.08 &quot;</td>
<td>6.08 &quot;</td>
</tr>
<tr>
<td>-1.60 &quot;</td>
<td>4.24 &quot;</td>
<td>4.21 &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>4.22 &quot;</td>
<td>4.24 &quot;</td>
</tr>
<tr>
<td>&quot;</td>
<td>4.24 &quot;</td>
<td></td>
</tr>
</tbody>
</table>

(a) Applied potential reading across dropping electrode and external S.C.E.

The drop times on open and closed circuit are seen to coincide within the limit of determination.

A more extended range of potential vs drop time determinations is shown in Fig. 1. In the positive voltage range and at potentials more negative - 1.80 volts vs. S.C.E. the drop time was highly erratic.

A polarogram obtained manually is also shown in Fig. 1. It is seen that the inflection in the drop time versus potential curve coincides with the inflection in the current-voltage curve. In both cases oxygen was present in the solution.

By breaking and closing the stabilizing circuit during a polarographic run it was found that the effect on the recorded polarogram is negligible. At a sensitivity setting 0.003 A/amp/mm with no damping the average current was decreased 0.0022 A/amps., a negligible quantity compared to a total diffusion current of
Fig. 12

Recordings of diffusion current of 0.000288% zinc amalgam at constant E.M.F. values. The stabilizing circuit was opened and closed to determine effect on instrument reading. Sensitivity 0.06 μAmp/mm. At 0.600 volt applied E.M.F. the current is decreased 0.06 μAmps when the stabilizing circuit is closed. Total current 6.45 μAmps. This is the maximum deviation shown by several tests. In most cases the deviation was indeterminate.
the order of even 0.1mAmp. In the working range of sensitivity settings with damping no deviation of the diffusion current could be detected when the stabilizing circuit was opened and closed. (Fig. 2). The breaking of the circuit, however, does cause an immediate deflection of the recording pen which then drifts back to the original value.

To sum up, the data so far indicates that dropping amalgam electrodes behave similarly to dropping mercury electrodes in capillary outflow and droptime characteristics. The stabilizing circuit has no appreciable effect on the recording circuit nor on the capillary characteristics. In short, the conditions are such that accuracy of the same order obtained in ordinary polarography could be expected in amalgam polarography.

By adding increments of gelatin solution and comparing the polarograms it was found that a concentration of about 0.005% was optimum for amalgam polarography. For different amalgam concentrations and different capillary characteristics it is possible that the optimum gelatin concentration may vary.

Polarograms of 0.0003% zinc amalgam are shown in Figs. 13, 14. Fig. 13 is a polarogram obtained before the addition of gelatin. The maxima is seen to be very considerable. Fig. 14 is a polarogram after the addition of gelatin. The data obtained for this amalgam is recorded in Tables 15 and 16.
Figure 13

Polarogram of 0.000288% zinc amalgam in 0.1N potassium chloride swept out with nitrogen.

Sensitivity 0.06 \mu \text{amp/mm}.

Diffusion current 11.6 \mu \text{amps}.

The rapid decrease in current starting at 50% span may be due to a change in drop time. The dropping electrode was almost streaming from 70% span to end of run. For this reason it is difficult to determine whether or not a maxima exists.
Figure 14

Polarogram of 0.000288% zinc amalgam in 0.1N potassium chloride plus 0.005% gelatin swept out with nitrogen.

Sensitivity 0.06 μamp/mm

Diffusion current 5.5 μamp.

The addition of gelatin has a marked effect on the current -- compare with Figure 13.
Figure 15
Polarogram of 0.000288% zinc amalgam in 0.1N potassium chloride plus 0.005% gelatin with oxygen present in solution. There is no clear distinction between the current due to reduction of oxygen or hydrogen peroxide and the current due to oxidation of the zinc in amalgam.
Figure 16

Zinc Amalgam Polarogram

0.0042 g/nl in 1/5767 g/ml Hg

Electrolyte 0.1 M KCl, 0.005% gelatin, N2 sweep

Recorded manually.

Diffusion Current (mamp)

Dropping Electrode Potential vs. O.H. Calelne Electrode

0.50 0.70 0.90 1.00 1.10 1.20 1.30 1.40 1.50
TABLE 15
Polarographic Characteristics of Zinc Amalgam

(1) Recorded with Sargent Polarograph
Amalgam: 0.0042 gm Zn in 1457.7 gm Hg

Electrolyte: 0.1 N KCl 0.005% gelatin.

<table>
<thead>
<tr>
<th>Date</th>
<th>No.</th>
<th>Diffusion Current</th>
<th>Droptime</th>
<th>Mercury Outflow</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 5</td>
<td>1</td>
<td>5.37 amp</td>
<td>2.64 sec.</td>
<td>1.750 mgm/sec.</td>
</tr>
<tr>
<td>&quot; 6</td>
<td>2</td>
<td>5.55 &quot;</td>
<td>4.12 &quot;</td>
<td>1.734 &quot;</td>
</tr>
<tr>
<td>&quot; 6</td>
<td>3</td>
<td>5.64 &quot;</td>
<td>4.12 &quot;</td>
<td>1.734 &quot;</td>
</tr>
<tr>
<td>&quot; 7</td>
<td>4</td>
<td>4.88 &quot;</td>
<td>2.03 &quot;</td>
<td>1.703 &quot;</td>
</tr>
<tr>
<td>&quot; 7</td>
<td>5</td>
<td>4.98 &quot;</td>
<td>2.42 &quot;</td>
<td>1.703 &quot;</td>
</tr>
</tbody>
</table>

(a) The concentration of zinc is calculated from the molecular weight of zinc, 65.38, and the density of mercury at 25.00°C, 13.53 gm/cm³, to be 0.5963 millimolar on the assumption that the zinc lost in making up the amalgam was negligible. Polarograms of the supernatant water layer could not be distinguished from polarograms of distilled water (Fig. 8°C).

(2) Manually Recorded.

<table>
<thead>
<tr>
<th>Date</th>
<th>No.</th>
<th>Diffusion Current</th>
<th>Droptime</th>
<th>Mercury Outflow</th>
</tr>
</thead>
<tbody>
<tr>
<td>June 7</td>
<td>6</td>
<td>5.23 amp</td>
<td>2.75 sec</td>
<td>1.703 mgm/sec</td>
</tr>
<tr>
<td>&quot; 7</td>
<td>7</td>
<td>5.27 &quot;</td>
<td>2.75 &quot;</td>
<td>1.703 &quot;</td>
</tr>
</tbody>
</table>

Due to distortion of the wave where the current increases rapidly the measurement of the diffusion current was not made in the same manner as in ordinary polarography. Instead the vertical distance between the average current at a point before and following the current increase was taken as a measure of the diffusion current. Provided the same relative points are chosen on different polarograms the values are as consistent as those determined at the half-wave potential. The resultant values, however, are slightly larger than those taken at the
half-wave potential. The difference in values is less than 5% if the variation of 'm' and 't' is neglected. A comparison may be made with the values shown in Table 15 which gives the data obtained by the method used in ordinary polarography. These results were obtained from polarograms where distortion of the wave form did not interfere with an accurate determination of the half-wave potential. It is seen that the two methods of measurement give results which vary by 2%-5%. However, when 'm' and 't' are also measured at the potential of the current measurements, the results by either method should agree within 2%.

**TABLE 16**

<table>
<thead>
<tr>
<th>No.</th>
<th>Diffusion Current (a)</th>
<th>$E_0$</th>
<th>Droptime</th>
<th>Mercury Outflow</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>5.46 Aamp</td>
<td>1.070</td>
<td>4.12 sec</td>
<td>1.750 mgm/sec</td>
</tr>
<tr>
<td>6</td>
<td>5.13 &quot; (b)</td>
<td>1.072</td>
<td>2.75 &quot;</td>
<td>1.703 &quot;</td>
</tr>
<tr>
<td>7</td>
<td>5.06 &quot; (b)</td>
<td>1.068</td>
<td>2.75 &quot;</td>
<td>1.703 &quot;</td>
</tr>
</tbody>
</table>

(a) measured by method described in "Sargent Manual of Instructions for the Polarograph".

(b) note order of difference from Table 14.

It is noted that the order of difference for the diffusion currents of No.6 and 7 is opposite in Table 16. This result has been shown to illustrate that the measurement itself may be somewhat in error. Unless the polarogram has an ideal form there is a certain amount of choice in the extrapolation of the average current as determined from the midpoint of the pen travel during the formation of each drop. Since it has been shown that the drop time varies considerably (Fig. 11) over short potential ranges there is little likelihood of obtaining an ideal polarogram. This fact is evidence that the method for
measuring the diffusion currents as given in the book of instructions has been chosen for strict accuracy. Actually, measuring the current at potentials preceding and following the wave as well as 'm' and 't' at the same potentials and calculating the value of the residual current by the Ilkovic equation appears to offer a more accurate method for the determination of the diffusion current.

Before using the values shown in Table 15 for calculations it should be shown that the conditions under which the diffusion current equations can be applied have not been violated to a degree greater than expected. Firstly, a rough approximation of the order of \( \frac{d}{r} \), where \( d \) is the diffusion layer and \( r \) is the radius of the amalgam drop, may be obtained. From Table 14, No. 1, \( id = 5.37 \text{amp}, \ t = 2.64 \text{sec}, \ m = 1.750 \text{mgm sec}^{-1} \) where the amalgam is 0.5963 millimolar zinc. From this data is obtained the number of moles reacting in a finite period,

\[
\frac{5.37 \text{amp.} \times 2.64 \text{sec}}{2 \text{ equivalents/mole} \times 96500 \text{ coulombs/equivalent}} = 7.52 \times 10^{-11} \text{ moles.}
\]

and the number of moles of zinc contained in the drop.

\[
\frac{1.750 \text{ mgm/sec} \times 2.64 \text{ sec}}{13530 \text{ mgm/cm}^3} \times \frac{1}{1000} \text{ cm}^3/\text{molar} \times \frac{0.5953}{1000} \text{ molar} = 20.4 \times 10^{-11} \text{ moles.}
\]

That is approximately one third of the amalgam in each drop reacts electrochemically. Thus it is shown that there is no gross discrepancy.

Assume that the reacting zinc is contained in a layer \( d_0 \) at the outer surface of the drop.
\[
\frac{4}{3} \pi r^3 = V \\
\frac{4}{3} \pi (r - d_0)^3 = \frac{2}{3} V
\]
from which \( \frac{d_0}{2} = 1 - \sqrt[3]{\frac{2}{3}} = 0.13 \)

The volume of the drop can be calculated from the value of 'm' and thus the value of 'd' may be found

\[
d_0 = 0.13 \sqrt[3]{\frac{3}{4 \pi}} \frac{1.750 \text{ mgm/sec} \times 2.64 \text{ sec}}{13.53 \text{ mgm/mm}^2}
\]

\[
= 0.055 \text{ mm} \quad \text{and} \quad r = 0.43 \text{ mm}
\]

This value for \( d_0 \) agrees with the value for the thickness of the diffusion layer around the mercury drop in ordinary polarography. The ratio \( \frac{d}{r} \) does not equal 1.

The diffusion current constant 'I' has been calculated to show the order of precision. The values of I are shown in Table 17.

**TABLE 17**

<table>
<thead>
<tr>
<th>No.</th>
<th>( I ) = ( \frac{1d}{cm \times 2 \times \frac{1}{3}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.28</td>
</tr>
<tr>
<td>2</td>
<td>5.09</td>
</tr>
<tr>
<td>3</td>
<td>5.17</td>
</tr>
<tr>
<td>4</td>
<td>5.10</td>
</tr>
<tr>
<td>5</td>
<td>5.06</td>
</tr>
<tr>
<td>6</td>
<td>5.20</td>
</tr>
<tr>
<td>7</td>
<td>5.24</td>
</tr>
</tbody>
</table>

Average value 5.16 ± 0.03

The variation between extreme values is less than 5% which is slightly greater than the variation between the extreme values for I for the 0.6187 millimolar zinc solution where the extremes

1. See Ref. 5, p. 144.
vary by less than 4%.

In order to show the accuracy of the method it is necessary to know the value of the diffusion coefficient of zinc in mercury. However, the values reported in the literature (see Table 5) show considerable variation. From Wogan's and Schwarz values temperature increments $0.0096 \text{ cm}^2 \text{ sec}^{-1} \text{ deg}^{-1}$ and $0.013 \text{ cm}^2 \text{ sec}^{-1} \text{ deg}^{-1}$ are calculated. The temperature increments are such that a temperature coefficient 0.01 would not introduce any gross error in determining the value of the diffusion coefficient at $25.00^\circ \text{C}$ from the tabled values. The resultant values are shown in Table 18

**TABLE 18**

The Diffusion Coefficient of Zinc in Mercury at $25.00^\circ \text{C}$

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Reported Value</th>
<th>Value Calculated for $25.00^\circ \text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>G. Meyer</td>
<td>$15^\circ \text{C} - 2.42 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$</td>
<td>$2.52 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$</td>
</tr>
<tr>
<td>Wogan</td>
<td>$11.5^\circ \text{C} - 2.52 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$</td>
<td>$2.65 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$</td>
</tr>
<tr>
<td>Schwarz</td>
<td>$25^\circ \text{C} - 2.00 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$</td>
<td>$2.39 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$</td>
</tr>
<tr>
<td>Mean Value</td>
<td>$2.39 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$</td>
<td>$2.39 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$</td>
</tr>
</tbody>
</table>

According to the findings of Strehlow and Stackelberg streaming at the amalgam surface results in large deviations from calculated values for different values of 'm' and 't'. However, they found that a plot of $I$ vs. $y$, where

$$I = \frac{2x}{Cm^{3/2}t^{1/2}}$$

produced curves which were asymptotic to a straight line. From the intercept of the line they determined the value of the diffusion coefficient of cadmium in mercury since

$$I = 607mD^{1/4}(1 - BD^{1/4}y)$$

From the slope of the line they calculated the value of $B$ to be 28.5. This value is in agreement with the theoretical
approximation that the value of B is about 30.

Assuming that the diffusion coefficient of zinc in mercury is $2.4 \times 10^{-5} \text{ cm}^2/\text{sec}$ the value of the numerical constant 'B' may be calculated directly. The values are shown in Table 19.

**TABLE 19**

Approximation of the Numerical Constant 'B' in the Strehlow-Stackelberg Equation for the Diffusion Current of a Dropping Amalgam Electrode

<table>
<thead>
<tr>
<th>No.</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.4</td>
</tr>
<tr>
<td>2</td>
<td>23.1</td>
</tr>
<tr>
<td>3</td>
<td>20.9</td>
</tr>
<tr>
<td>4</td>
<td>25.4</td>
</tr>
<tr>
<td>5</td>
<td>26.4</td>
</tr>
<tr>
<td>6</td>
<td>26.0</td>
</tr>
<tr>
<td>7</td>
<td>24.7</td>
</tr>
<tr>
<td>Average</td>
<td>23.6</td>
</tr>
</tbody>
</table>

Since the values for B lie within the range of theoretical approximation it is assumed that the surface streaming of the amalgam drop was no more serious than that at the mercury drop in regular polarography.

According to the calculations shown in Table 11 the diffusion current equation after Lingane and Loveridge gave values of 'D' best in agreement with $D_0$, the diffusion coefficient of zinc at infinite dilution. For amalgam polarography the equation merely requires a change of sign in the second term thus

$$I = 607nD^{1/2}(1 - 39D^{1/2}m^{-1/3}C^1)$$

The value for D may be determined in the manner used previously. The results are shown in Table 20.
After completion of this work it was realized that the new equations for the diffusion current were simple quadratics with $D^s$ as the unknown quantity. From the Lingane-Loveridge equation

$$\sqrt{D} = \frac{1 - \sqrt{1 - 0.1285 \frac{m}{m - t}}}{78 m^{-\frac{1}{2}} t^2}$$

The values of $D$ computed by this formula are given in Table 21.

**TABLE 21.**

The Apparent Polarographic Diffusion Coefficient of Zinc in Mercury at 25°C.

<table>
<thead>
<tr>
<th>No.</th>
<th>$D \times 10^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.01 cm$^2$ sec$^{-1}$</td>
</tr>
<tr>
<td>2</td>
<td>1.59 &quot;</td>
</tr>
<tr>
<td>3</td>
<td>1.65 &quot;</td>
</tr>
<tr>
<td>4</td>
<td>2.69 &quot;</td>
</tr>
<tr>
<td>5</td>
<td>2.68 &quot;</td>
</tr>
<tr>
<td>6</td>
<td>2.93 &quot;</td>
</tr>
<tr>
<td>7</td>
<td>2.99 &quot;</td>
</tr>
</tbody>
</table>

There is considerably more discordance among these values than among those shown in Table 20. Here the term $t^1$ occurs in the denominator only and consequently has a larger influence. However, the value of 'm' was not determined in the solution as it should be. Actually $t$ and $m$ should be determined simultaneously for accuracy.

The solution of the quadratic is the most acceptable method for determining the value of the diffusion coefficient. The method also provides a better indication of the precision obtained.

In view of the discordance among the values shown in Table 21 it is evident that further work under carefully controlled conditions is necessary to establish the technique used in this work.
TABLE 20

The Apparent Polarographic Diffusion Coefficient of Zinc in Mercury at 25°C.

<table>
<thead>
<tr>
<th>No</th>
<th>I</th>
<th>$D \times 10^5$</th>
<th>$D_1 \times 10^5(a)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.28</td>
<td>1.89 cm$^2$sec$^{-1}$</td>
<td>2.70 cm$^2$sec$^{-1}$</td>
</tr>
<tr>
<td>2</td>
<td>5.09</td>
<td>1.76 &quot;</td>
<td>2.56 &quot;</td>
</tr>
<tr>
<td>3</td>
<td>5.17</td>
<td>1.81 &quot;</td>
<td>2.66 &quot;</td>
</tr>
<tr>
<td>4</td>
<td>5.10</td>
<td>1.77 &quot;</td>
<td>2.47 &quot;</td>
</tr>
<tr>
<td>5</td>
<td>5.06</td>
<td>1.74 &quot;</td>
<td>2.45 &quot;</td>
</tr>
<tr>
<td>6</td>
<td>5.20</td>
<td>1.83 &quot;</td>
<td>2.63 &quot;</td>
</tr>
<tr>
<td>7</td>
<td>5.24</td>
<td>1.86 &quot;</td>
<td>2.68 &quot;</td>
</tr>
<tr>
<td>Average 5.16</td>
<td>1.81 &quot;</td>
<td>2.58 &quot;</td>
<td></td>
</tr>
</tbody>
</table>

(a) $D_1$ from Lingane-Loveridge equation. = $D_0$

The mean value is agreement with the values reported by Wogan and Meyer rather than the value reported by Schwarz.

It is difficult to draw any conclusions with respect to the accuracy of these results since the available values reported in the literature vary by an amount greater than the experimental error involved. Further, it is only assumed that the experimental error in amalgam polarography is of the same order as that found in ordinary polarography. Unfortunately, time did not allow further experimentation under the conditions required to establish the technique.

It has been shown that a dilute amalgam can be stabilized for polarographic measurements. The amalgam used to obtain the data shown in Tables 14 and 15 was used from June 4-7, 1950, or over a period of 85 hours. Polarograms obtained in the first hour were approximately duplicated in the last hour. Due to a decrease in the height of the mercury column small differences were observed. The differences, however, were of the same order as the variations shown in Table 14. This amalgam was made up 0.000288% Zn. Heyrovsky and
Kalousek (19) found that amalgams less than 0.005% were too unstable for use. Strehlow and Stackelberg have obtained measurements which are in better agreement for duplicate determinations than have been obtained in this work. They used 13.93 millimolar cadmium amalgam or 0.01157% Cd. Their method of preparing the amalgam has not been given and presumably it was not protected from the atmosphere since no special technique is mentioned. Unfortunately, their tabled results (44) do not show the time that each measurement or each group of measurements was made. That is they have not shown that the concentration of the amalgam remained constant. Therefore the deviation of I vs y could be due in part to a decrease in concentration.

Early in this work an amalgam 0.000127% Zn gave more or less consistent results at the beginning and end of a 120 hour period, March 4-9, 1950. At that time, however, considerable trouble was experienced with the capillary becoming clogged thus causing highly erratic drop times which varied from a drop time of 14 seconds to constant streaming under the same conditions at different times. This clogging has since been presumed due to the presence of zinc oxide which resulted from the interaction of zinc in amalgam with oxygen which remained adsorbed on the glass walls of the electrode assembly.

According to the manufacturers, the Sargent Polarograph Model XXII is accurate to 0.1% when the temperature is controlled 25.00°C±0.05°C at the polarographic cell and room temperature is 25°C±10°C. It is suggested that temperature control be extended to include the entire apparatus, recorder, dropping electrode assembly, polarographic cell and potentiometer.
The mercury column should be controlled to ± 0.5 mm by a convenient marker and a screw device to raise or lower the mercury reservoir. It is essential that the mercury column is not subject to vibration. In order to control the mercury column it is advisable to immerse the capillary tip to a marker.

For consistent results the external electrode appears to be better than the internal anode pool.

The electrolyte should be essentially oxygen free. There is no doubt that traces of oxygen seriously interfere with the determination of the diffusion current at low concentrations.

The measurement of the diffusion current is perhaps more convenient by the method described. However, it is believed that accuracy can be best obtained by measuring the current at definite potentials before and after the half-wave potential. Mercury is collected at the same potential to determine 'm' while 't' may be determined from pen travel on the recorded chart. Then 'm' and 't' are determined again at the half-wave potential. The current measurements are then calculated to refer to the values of 'm' and 't' at the half-wave potential.

The variance among duplicate determinations with standard zinc solutions in this work is within the limits of experimental error reported by others (p. 51). However, it must be obvious that there was considerable latitude in the exercise of control.

In amalgam polarography there are other factors which must also be considered. Firstly, the amalgam must be stabilized as described herein. No other method was found to prevent the formation of a surface film and consequent decrease in concent-
tration. The amalgam reservoir and dropping capillary must be clean and free of adsorbed oxygen. Prolonged sweeping with purified nitrogen or hydrogen appears necessary. The possibility of interaction of the amalgam with glass appears negligible, although over a long period of time some effect may occur. This possibility is suggested by the filmy appearance of originally clear glass after impure mercury has been stored for some time. This film is permanent. In preliminary work, filming was observed after an amalgam had stood for several hours with the stabilizing circuit applied. The filming was partly removed by increasing the stabilizing voltage. However, the amalgam - glass interface appeared to become wetted further from the amalgam - water interface with increasing potential. Care must be exercised to prevent wetting at the capillary. Under 10 volts stabilizing E.M.F. the wetting extended about 1-3 cm from the amalgam - water interface. Under 25 volts E.M.F. the wetting extended 8-10 cm. The filming observed in these instances was easily removed by dilute nitric acid - different from the filming mentioned previously.

It was observed that at low pressures of mercury there was no flowing from the capillary. Upon increasing the mercury column the mercury thread moved slowly along the bore and finally began dropping. This suggests that the amalgam can be made up in apparatus resembling those shown in Figs. 17. The apparatus is swept out with nitrogen. Nitrogen pressure is maintained at the capillary while a weighed amount of mercury is run into the reservoir. The approximate amount being previously determined by experiment. The water layer is formed and
Figure 17
Dropping Electrode for Amalgam Polarography
a weighed sample of the solute metal added. While the metal is dissolving under the influence of the applied stabilizing potential an occasional bubble of nitrogen is forced into the reservoir to ensure a homogeneous amalgam. When ready for polarography the nitrogen pressure can be removed from the capillary and pressure applied to force the amalgam through the capillary. The pressure can be maintained constant by means of a manometer with due consideration to the variation of the mercury pressure.

Other methods for handling the amalgam present difficulties. In the siphon method described in this work entrapped gas bubbles presented a difficult problem. The method of Handles (21) appears feasible except for the uncertainty as to whether the mercury originally in the siphon becomes homogeneous with the larger body of amalgam. Here too the possibility of entrapping gas bubbles in the dropping electrode column appears rather large.

In order to prevent wetting by the overlay of water or entrainment of gas bubbles by the amalgam column rather elaborate apparatus appears to be required. However, from experience gained in this work the simple apparatus shown in Figs 17, supplies the requirements. Here the mercury head must be determined so that it does not flow through the capillary initially nor must it be so low that wetting at the amalgam-glass interface extends to the capillary.

As mentioned by Heyrovsky and Kalousek (17) and confirmed in this work, the anodic current of an amalgam is much greater than the cathodic current of a metal salt in solution by polarographic measurement. In this work it is shown, but not
confirmed that quantitative measurements are possible. For analytical work with a known weight of mercury in the reservoir a supernatant solution may be subjected to controlled potential (7) electrolysis followed by polarography of the amalgam. The solution can then be recovered and by a similar procedure another amalgam could be determined. The method could be useful for determining traces of ions which reduce to mercury soluble metals in the presence of large amounts of materials which do not.

The application of amalgam polarography to practical analysis, however, must await establishment of the technique and also systematic investigation of the interactions of the mercury soluble metals.
III - Summary of Results

Polarograms of standard zinc in 0.1N potassium chloride plus 0.0001% gelatin were recorded in the manner proposed for amalgam polarography. The straight line plot of diffusion current versus concentration over the concentration range 0.6187-0.1040 millimolar zinc passes very close to the origin. The diffusion current constant was found to increase with decreasing concentration.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Diffusion current constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6187 millimolar</td>
<td>3.44</td>
</tr>
<tr>
<td>0.3365 &quot;</td>
<td>3.55</td>
</tr>
<tr>
<td>0.2061 &quot;</td>
<td>3.62</td>
</tr>
<tr>
<td>0.1040 &quot;</td>
<td>3.61</td>
</tr>
</tbody>
</table>

The value reported in the literature for 1 millimolar zinc in 0.1N potassium chloride plus 0.005% methyl red is 3.42. Since the variation of I with concentration appears to be controversial the agreement is considered satisfactory.

When oxygen was present the diffusion current for zinc was decreased although the total current was the same after oxygen was removed. This effect is explained by the removal of zinc by precipitation or complex formation in the diffusion layer with the hydroxyl or peroxide products of the oxygen electro reduction. The total current is not affected since the amount of zinc removed is electrochemically equivalent to the amount of oxygen reduced to hydroxyl.

Since a nitrogen sweep only reduces the concentration of oxygen to a minimal value there could be some considerable effect on the development of the zinc wave at very low concen-
trations of zinc. In this work 0.0168 millimolar zinc failed to develop a wave form. 0.0042 millimolar zinc solutions gave polarograms which could not be distinguished from polarograms obtained with 0.1N potassium chloride alone. Further investigation is required at these extremely low concentrations.

The apparent diffusion coefficient of zinc in 0.1N potassium chloride was computed from the equations for the diffusion current as given by Ilkovic, Lingane and Loveridge, and Strehlow and Stackelberg. Theoretically the value is that of the diffusion coefficient of zinc at infinite dilution, \( D_0 = 7.2 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1} \). The Ilkovic equation gave values for \( D \) within 28\%, that of Lingane and Loveridge within 12\% and that of Strehlow and Stackelberg within 17\%. The deviations are of approximately the same degree as reported in the literature.

Contrary to Lingane and Loveridge's statement a knowledge of the value of \( D \) is not entirely essential to the use of their new equation. The equation is a simple quadratic and the solution is

\[
\sqrt{D} = \frac{-1 + \sqrt{1 + \frac{4A}{\delta^2nCm}}}{2A n^{-1} \tau^{-1}}
\]

where \( A \) = the numerical constant in the correction term. The values computed from this formula were 0.4\% - 2.5\% larger than the values computed by the method suggested by the authors mentioned.

The results were found to agree within 15\% of previously recorded data reported in the literature even when the most controversial points were allowed. Some individual results were in complete agreement. The agreement is used as evidence that the method proposed for amalgam polarography is equally satisfactory.
Within the limits of determination, very dilute zinc amalgams were found to behave like pure mercury in their dropping characteristics. The amalgam stabilizing circuit is shown to have no effect on the droptime or recording apparatus which will introduce an error greater than 0.1%. Thus, the agreement with theoretical or other data should be attained as in ordinary polarography.

When oxygen was present in the solution a deviation of the drop time versus potential curve was found to occur over the same potential range as the anodic zinc wave developed on the current versus potential curve.

Polarograms of zinc amalgam, 0.5963 millimolar zinc or 0.000288% zinc by weight, dropping in 0.1N potassium chloride plus 0.005% gelatin were recorded. The diffusion current constant, according to the Ilkovic equation is 5.16 ± 0.07 at 25°C.

Assuming that the diffusion coefficient of zinc in mercury is \(2.4 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}\), the values of \(B\), the numerical constant in the second term of the Strehlow-Stackelberg equation for the diffusion current of amalgam electrodes, range from 19.4 to 26.0 with an average value of 23.6. This is taken as evidence that the streaming current in the mercury drop did not introduce serious error.

Computation by the Lingane-Loveridge diffusion current equation gave the value \(2.52 \times 10^{-5} \text{ cm sec}^{-1} ± 0.09\) at 25°C. in excellent agreement with the values reported by Wogan, \(2.52 \times 10^{-5} \text{ cm sec}^{-1}\) at 11.5°C., and by Meyer, \(2.42 \times 10^{-5} \text{ cm sec}^{-1}\) at 15°C. Schwarz gives a value \(2.00 \times 10^{-5} \text{ cm sec}^{-1}\) at 25°C.

Computation by the solution of the quadratic equation from Lingane and Loveridge

\[
\sqrt{B} = \frac{1 - \sqrt{1 - 0.1285 \frac{D_d}{C_m}}}{78 m^{-\frac{1}{2}} T^{-\frac{1}{2}}}
\]
gave rather discordant results which, however, are of the correct degree of magnitude with a range $1.59 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ to $3.01 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$.

The most important result is the maintenance of the diffusion current over a period of several days as shown by the relatively consistent values of the diffusion current constant.

The results show that the method used for stabilizing the amalgam was successful. Such a device now enables the application of amalgam polarography to analysis. However, it remains to completely establish the method and then to investigate the behaviour of multicomponent systems, say sodium, zinc and lead in mercury. It would be interesting to investigate the behaviour of several solute metals together or to investigate selective amalgamation by reduction from salt solution.
BIBLIOGRAPHY

(1) J.J. Lingane, J.A.C.S., 61, 976 (1939).
(12) Ref. 5, pp. 32-37
(13) Ref. 5, p. 64.
(14) M. Von Stackelberg, Z. Elektrochem., 45, 466 (1939).
(16) Ref. 9, p. 56.
(18) Ref. 5, p. 148.
(20) J. Heyrovsky, Discussions of the Faraday Society, 1, 212 - 222 (1947).
(21) J.E.B. Randles, ibid, 1, 15 (1947).
(22) T. Erde Gruz and E. Varga, Chem. Abs., 42, 8676g (1948).


(31) H.A. Liebhabsky, J.A.C.S., 57, 2657 (1935).

(32) W.G. Horsch, ibid, 41, 1791 (1919).

(33) H.A. Liebhabsky, ibid, 59, 452 (1937).

(34) Scatchard and Teft, ibid, 52, 2280 (1930).


(36) Shrowder, Cowperthwaite and LeMer, J.A.C.S., 56, 2348 (1934).


(39) Clayton and Vosburgh, J.A.C.S., 58, 2093 (1936) (see also Garner, Gran and Yost, ibid, 57, 2056 (1935)


(41) Lewis, J.A.C.S., 37, 2656 (1915).


(47) G. Bianchi, Chem. Abstr., 41, 2631a, 7281c (1947)

(48) G. Meyer, Chem. Abst., 6, 446 (1912) Ber. physik Geo., 793 (1911)
(see Physik Z. 12, 975 - Q C p.51).

(49) International Critical Tables, II, 591,
McGraw Hill, New York (1933)

(50) Landolt Barnstein p.136


(52) Smithsonian Physical Tables 6th Ed. p.140
Smithsonian Institution, Washington

(53) Samarin and Shvartsman, Chem. Abst., 42, 7593a (1948)

(54) Squires' Companion to the British Pharmacopoeia,


(57) Ref.5, Table 8 p. 64, Table 11 p. 72.

(58) Ref.5, p.307.

(59) Ref.5, Table 13 p. 76.

(60) Ref.5, p. 487.

(61) Ref.5, p.79.

(62) Ref.5, p.60, Table 6 p.59.

(63) Ref.9, p. 60.

(64) J. Heyrovsky, Chem. Abst. 44, 1834a (1950)

(65) Ref.5, Table 8, p.64.

(66) Ref.9, Table 4, p.59.

POLAROGRAPHIC STUDIES WITH THE DROPPING MERCURY ELECTRODE. - PART XI. - THE USE OF DILUTE AMALGAMS IN THE DROPPING ELECTRODE.

by J. Heyrovsky and M. Kalousek.

THEORETICAL.

The dropping mercury electrode acquires in a mixture of a reducing agent (denoted "red") and an oxidizing agent (denoted "oxy") a potential, \( \Pi \), which is that of a reversible "redox" electrode and is thus given as

\[
\Pi = \Pi_0 - \frac{RT}{2F} \ln \frac{[\text{RED}]}{[\text{OXY}]}.
\]

According to the nature of the reducing or oxidizing agent and the phase in which they are placed, we may distinguish three typical cases.

1. The agent "oxy" (i.e. the higher stage of oxidation) consists of kations in the solution around the dropping mercury cathode, which on their electro-deposition form an amalgam furnishing thus the agent "red" (i.e. the lower stage of oxidation).

2. The agent "oxy" is a compound of oxidizing properties (like a titanic salt or quinone), which is placed in the solution around the dropping mercury cathode and gets reduced there to a reducing agent (i.e. the titanous salt or hydroquinone), yielding thus the agent "red".

The same potential is reached, however, when the reducing agent (e.g. a titanous salt or hydroquinone) is oxidized at the dropping mercury anode to the oxidizing agent (i.e. the titanic salt or quinone).

3. Similarly as in the latter case also the reducing agent of case 1. may be oxidized, if in the dropping electrode an amalgam is used instead of pure mercury and the electrode is made the anode, sending the ions of the base metal dissolved in mercury into the solution. These ions then furnish the substance "oxy".

\(^{0)}\) A communication published in "Chemické Listy" 35, p. 47-50 (1940), to the occasion of the 60th birthday of Professor J. Milbauer.
II.

The redox system 1, is realized in the electrodeposition of kations at the dropping mercury cathode, about which many studies are published. To the redox system 2, belong the reversible polargraphic reductions and oxidations in the solution, such as are described by H.O. Muller and J.P. Baumberger, E. Kodicek and K. Wenig, R. Strubl, M. Spalenka and K. Schwarz. The case 3 has not yet been treated fully: an account of it has been given by one of the present authors and a note was published by J. J. Lingane in 1939. The experimental work here described was, however, started in 1937.

Before going into the experimental details and the discussion of the results, let us deduce an equation of the current-voltage curve obtained with the dropping electrode in case 3, viz. when using instead of pure mercury an amalgam. This case is closely allied with case 1 as the anodic process of case 3 is the reversed one to that in case 1. so that a general solution would express the procedure in either direction of the reversible process involved, i.e. the anodic dissolution of the metal dissolved in mercury as well as the cathodic formation of the amalgam.

Let us denote the concentration of kations in the solution surrounding the dropping electrode by \( C^+ \) and the concentration of the metal in the amalgam by \( c^+ \). The potential of the dropping electrode is given by the concentration prevailing closely at the electrode interface: there the concen-

0) In a public lecture of J. Heyrovsky at the Faculty of Science, Masaryk University, Brno, April 26th, 1938: compare also the Dissertation of M. Kalousek in 1939.
tration of kations is $C_0^+$ and the concentration of the baser metal in mercury $c_0^-$. We assume the presence of an indifferent electrolyte in the solution in a concentration sufficient to furnish the total transference of the current, so that the kations of the dissolved metal practically do not take part in the migration.

We take the view, used in the previous deductions\(^9\) of the mathematical equations for the polarographic current-voltage curves due to reversible processes, that the transference of the current across the electrode is given strictly by diffusion of the depositing or dissolving particles. The anodic current thus depends on the diffusion rate of the metallic atoms from the interior of the amalgam drop to its surface and on the diffusion rate of the metallic ions from the electrode surface into the solution. These two diffusion rates must be equal during the formation of each drop of the amalgam otherwise an accumulation or insufficiency of particles would grow at the electrode interface and would change the potential, as it depends on $\log \frac{C_0^-}{c_0^+}$. Experiments, however, show that during the formation of the mercury drop its electrode potential in reversible electrode processes remains constant, which is only possible, if $C_0^+$ as well as $c_0^-$ are constant (at a certain applied E.M.F.).

Then the intensity of current, $i$, is given by the rate with which the metallic atoms are furnished to the surface
of the amalgam drops; this is expressed by the equation
\[ i = \frac{A}{A_1} (C^a - C^b) \]

The same intensity, however, is also determined by the rate with which the metallic ions, formed by the anodic dissolution of the metal, diffuse from the surface of the anode; hence also
\[ i = \frac{A}{A_2} (C^a - C^b) \]

From these equations we obtain for

\[ \frac{[RED]}{C^a} = \frac{C^b}{\frac{A}{A_1} \text{ and } \frac{[Ox]}{C^b} = \frac{C^a}{C^a + \frac{A}{A_2}} \]

which substituted into the original formula for the reversible "redox" electrode potential, lead to

\[ \Pi = \Pi_0 - \frac{RT}{nF} \ln \frac{C^a - \frac{i}{A_1}}{C^a + \frac{i}{A_2}} \]

This may be also written

\[ \Pi = \Pi_0 - \frac{RT}{nF} \ln \frac{A_2}{A_1} \frac{A_1 C^a - i}{A_2 C^a + i} \]

The intensity of the anodic current will reach its limit, when the surface of the amalgam drops will become exhausted from the metal dissolved, i.e. when \( C^b = 0 \); hereby the anodic limiting current, \( i_d \) is given as

\[ i_d = \frac{A}{A_1} C^a \]

Similarly the cathodic limiting current, \( i_d_2 \) is reached, when the solution surrounding the dropping electrode becomes exhausted of the kations of the electro-deposited metal. This condition is that \( C^b = 0 \), or

\[ i_d_2 = -\frac{A}{A_2} C^a \]

Substituting for \( k_1 C^a \) and \( k_2 C^b \) values \( i_d_1 \) and \( -i_d_2 \), we obtain the final equation of the current-voltage curve, which expresses the course of electrolysis including anodic and cathodic polarization:

\[ \Pi = \Pi_0 - \frac{RT}{nF} \ln \frac{A_2}{A_1} \frac{i_d_1 - i}{i - i_d_1} \]
The curve (fig.1) representing this equation, in which the polarization, \( \Pi \), varies and the current, \( J \), accordingly changes, has the form of a typical "polarographic wave"; the only difference from the curves hitherto deduced is that there is an anodic as well as a kathodic limiting current. The "half-wave" of this curve occurs when

\[ J = \frac{id_1 + id_2}{2} \]

and hence the potential, \( \Pi_{1/2} \), at which the current reaches the "half-wave" value is

\[ \Pi_{1/2} = \Pi_0 - \frac{RT}{\eta F} \ln \frac{\frac{ld_1}{ld_2}}{\frac{id_1 + id_2}{2}} \]

or

\[ \Pi_{1/2} = \Pi_0 - \frac{RT}{\eta F} \ln \frac{\frac{ld_2}{id_1}}{2} \]

\[ \begin{array}{c}
\text{ANODIC} \\
\ldots \\
\text{KATHODIC} \\
\end{array} \]

\( E = 0 \)

Fig. 1.
The shape of the continuous polarographic anodic-kathodic wave.

The latter formula shows that this "half-wave potential" is a characteristic constant, independent of the concentrations of the agents "red" or "oxy", and given only by the type of the reduction and oxidation process. This value is
very near to the "normal redox potential", $E^\circ$, at which red-"oxy differ from it only by the ratio of the diffusion constants of the electrode process.

EXPERIMENTAL

An older type of polarograph, made by Dr. V. Nejedly, was used. The contacts leading to the potentiometric wire were furnished with mercury joints, as described by J. V. Novak\textsuperscript{10}). The continuous change of the external E.M.F. effecting the anodic and the cathodic polarization of the dropping electrode was produced by the adjustment of J. Hoekstra\textsuperscript{11}). For the same purpose also a simpler arrangement has been found convenient viz. that shown in Fig. 2.; in this one of the electrodes (e.g. the unpolarizable) is joined to the middle terminal of a pair of accumulators whilst the other electrode (i.e. the dropping one) is connected to the sliding contact on the potentiometric wire.

The latter arrangement was used only for approximative measurements, as the two accumulators have rarely an identical E.M.F. so that the sliding contact at the middle point of the potentiometric wire does not exactly branch off zero voltage.

\[ \text{Fig. 2: The scheme of connections for continuous anodic-kathodic polarization.} \]
One of the above schemes has to be applied, when the amalgam is used both in the dropping electrode as well as in the large unpolarizable electrode at the bottom of an ordinary conical electrolytic vessel. However, the change from the anodic to the cathodic polarization can also be effected, if instead of the layer of the amalgam a separate standard electrode is used for the unpolarizable electrode. The potential of this standard electrode has to be considerably more positive than that of the amalgam in order that the applied E.M.F. may be increased from zero in one direction only (i.e. making the potential of the dropping electrode more negative), for which the ordinary polarographic connection suffices.

The vessel, which has the separate standard electrode affixed to the vessel with the dropping electrode, is shown in Fig. 3.

The solution containing the kations of the metal used in the amalgam is placed in the vessel B, into which the capillary electrode (C) is introduced through a rubber stopper. The side tubes of this vessel serve for passing an indifferent gas (in this case nitrogen) through the solution in order to free it from atmospheric oxygen. The amalgam accumulated by dropping is let out from time to time through the tap E. The unpolarizable electrode is placed in the vessel A, where it keeps—in the form of a mercury layer--its standard potential. The current passes to this electrode through a platinum wire sealed to a side contact, which is filled with mercury.

During the polarographic investigation the broad tap D is kept open, so as to offer least electrolytic resistance
between the vessels A and B. The tap F serves for the exchange of the electrode solution.

Fig. 3 Electrolysis vessel for amalgam polarography.

The electrolyte in the standard electrode was either 0.1N potassium sulfate saturated with mercurous sulfate or in potassium chloride saturated with calomel to match the anion of the electrolyte surrounding the dropping electrode.

The amalgams applied were those of copper, cadmium, lead and zinc in concentrations not exceeding 0.005%. More concentrated amalgams were found to adhere to the walls of the glass capillary.

The C-V curves obtained were all of the type theoretically deduced. Fig. 4 represents the curves polarographically recorded with lead amalgam used in the dropping electrode. Similar curves were obtained also with other amalgams.

1. Pb amalgam in 0.1N KCl
2. " " " " " " + 0.001N PbCl₂
3. Pure Hg " " " " " "

4V ACC. SENSITIVITY $\frac{1}{30}$
The straight line passing through the middle of the polarogram denotes the 0 position of the galvanometer, i.e. the zero current. At the beginning of the curves in their lower branch the dropping amalgam electrode is the anode, i.e. Pb atoms are transferred to the solution as Pb\(^{2+}\) ions. The upper branch of the curve above the zero line shows where the dropping amalgam electrode acts as cathode, i.e. deposits Pb\(^{2+}\) from the solution. Curve 1 has been obtained with amalgam dropping into a solution free from Pb\(^{2+}\), hence, there is only the anodic current shown. The cathodic one being practically zero (the small current above the zero line is due to traces of oxygen in the solution). Curve 2 has been obtained with a more dilute lead amalgam in a solution 1 millimoles in Pb\(^{2+}\). This curve shows the anodic branch due to the electrolytic dissolution of Pb from the amalgam as well as the cathodic branch caused by the electrodeposition of Pb\(^{2+}\). Curve 3 is simply due to the electrodeposition of Pb\(^{2+}\) at the dropping mercury electrode. It is remarkable that \(E\) of all three waves coincide closely (corresponding to - 0.46 V from the potential of the reference electrode N.C.E.).

The curves obtained with the same amalgams but at various times were not coinciding as far as the height of the limiting anodic current is concerned. This is explainable by the instability of the amalgams which are easily oxidized and thus lower their content of the dissolved metal. After shaking the amalgam a considerable decrease of the anodic current was produced.

Interesting is the shift of the \(E\) of the anodic
wave observed when the electrolytic dissolution of the amalgam takes place in a solution in which the metallic ion forms complexes. According to the general theory the $E^\circ$ should shift to more negative potential values if the respective ion enters in a complex. The same must of course hold also in the case of the anodic wave.

To investigate this relationship the dropping lead amalgam electrode was surrounded by solutions of electrolytes with which Pb$^{+\,+}$ form complexes. Fig. 5 shows the influence of the formation of complexes on the value of $E^\circ$. Curve 1, lead amalgam with free Pb$^{+\,+}$,

![Fig. 5](image)

Curve 2, obtained with the same amalgam in alkaline plumbite. Curve 3, effect of citrate. All three curves referred to N.C.E., and the distance between two abscissal is 0.2 V. The values of $E^\circ$ are therefore, (1)-0.46 V. (2)-0.72 V. (3)-0.53 V. These $E^\circ$ potentials coincide with those measured in the cathodic electrodeposition of Pb$^{+\,+}$ from (1) Free Pb$^{+\,+}$ ions (2) alkaline plumbite (4) lead salt in excess citrate.

Less regular are curves obtained when amalgam drops
in a solution in which the anodically formed cations are precipitated, e.g. if the dropping amalgam electrode (Pb) is surrounded by dilute alkali or cadmium amalgam by dilute ammonia. However, these irregularities are removed if the concentrations of the precipitating agents are increased so as to redissolve the precipitated hydroxides (Pb, concentrated alkali added, Cd concentrated ammonia added). The $E_{\text{p}}$ values are hereby again shifted to more negative values.

The polarographic investigation of the anodic dissolution of dilute amalgam is likely to lead to practical applications as far as qualitative and quantitative analysis of trace metals contained in mercury is concerned. We may imagine even a possibility of an analysis of alloys in which the alloy would not be dissolved in an aqueous solution but directly in mercury and the amalgam would be polarographically investigated with the dropping anode. The metallic components would be indicated by corresponding anodic waves of the $C-V$ curve. Here an advantage over the ordinary polarographic analysis of metallic constituents in solution even presents itself since in the anodic dissolution traces of baser metals (Alkali metals or zinc) may be shown with great sensitivity also in the excess of the nobler metals (Cd, Pb, Bi, Cu, Au, Ag, Hg) whereas in the cathodic polarographic investigation - just to the contrary - as a rule only the nobler constituents are more precisely estimated.

How far amalgams may be prepared and successfully used for such an analysis with the dropping mercury anode remains to be specially investigated. Here we mean just to
hint to an interesting counterpart to the analysis of solutions with the dropping mercury cathode, viz. to the polarographic analysis of amalgams by means of the dropping mercury anode.

SUMMARY

If the solution contains ions of the metal present in the amalgam, the c- curve has an anodic and cathodic branch and the equation of the curve is

\[ \Pi = \Pi_0 - \frac{RT}{nF} \ln \frac{k_2}{k_1} \frac{i_{d1} - i}{i} \]

where, \( i_{d1} \) is the anodic and \( i_{d2} \) is the cathodic limiting current, \( k_1 \) = diffusion coefficient of metal atoms in mercury and \( k_2 \) = diffusion coefficient of metallic ions in solution.
LITERATURE.

2. H.O. Muller, Chem. Rev. 24, 95-124 (1939)
5. M. Spalenka, ibid, 11, 146 (1939)
8. J.J. Lingane, J.A.C.S., 61, 976-977 (1939)