ROSE, Michael Larry, 1942-
APPLICATIONS AND DEVELOPMENT OF THIN LAYER
ELECTROCHEMISTRY EMPLOYING TWIN DROPPING
MERCURY ELECTRODES.

The Ohio State University, Ph.D., 1970
Chemistry, analytical

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APPLICATIONS AND DEVELOPMENT OF THIN LAYER ELECTROCHEMISTRY EMPLOYING TWIN DROPPING MERCURY ELECTRODES

DISSERTATION
Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By
Michael Larry Rose, B.S., M.S.

*****

The Ohio State University
1970

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ACKNOWLEDGMENTS

The author would like to thank the Department of Chemistry for financial support. I would also like to thank Dr. Larry B. Anderson for his patient direction in the preparation of this thesis. Also, again I would like to thank my wife for all the help during my years at Ohio State.
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HISTORY

Introduction

The difficulties involved with experimentation using thin layer electrochemistry have been discussed by many authors. Most of the problems are concerned with obtaining thinner solution layers. It is the aim of this work to devise and apply new technics to thin layer electrochemistry in order to obtain solution layers thicknesses of ten microns or less. Equations describing chemical kinetic measurements have been derived for thin layer experiments. We have also derived here mathematical equations for transient signals in thin layer electrochemistry and have shown how these signals can be used to solve diffusional and kinetic problems. The particular model kinetic system we have investigated here is the Benzedine Rearrangement with azobenzene and perchloric acid.

In order to expand the areas of application of TLE we have investigated the reduction of Ni(II) complexes in aqueous and alcoholic solutions containing a variety of complexing agents. This work was undertaken to demonstrate the utility of our development of electroanalytical procedures for detecting small quantities of unstable reduction products. In addition, we have been able to unequivocally
differentiate between electrochemical reactions which produce solution soluble products from those which produce adsorbed products or products plated on or into the electrode.\textsuperscript{11,12}

To be able to take data on all of the above mentioned systems it was necessary to design and construct a general purpose electrochemical instrument.\textsuperscript{13,14,15,16} Many publications have described similar instruments, but several interesting features have been incorporated into the particular instrument built for this work making the instrument worthy of discussion.


\textsuperscript{7} McDuffie, Anderson, and Reilley, \textit{op. cit.}


\textsuperscript{9} McDuffie, Anderson, Reilley, \textit{op. cit.}


THEORY

TETLE

Twin electrode thin layer electrochemistry (TETLE) in which two independently controlled working electrodes are positioned to face each other across a thin layer of solution, is a relatively new area in analytical chemistry with a great deal of promise. TETLE has the second electrode advantage (one electrode may be used as a probe to monitor concentrations immediately adjacent to the opposing electrode) over thin film (TF) and single electrode (SETLE) technics with an inert opposing face. TETLE has a wider range of applicability to SETLE using mercury coated electrodes since TETLE can distinguish between solution soluble and mercury soluble or surface adsorbed species. This wider range of applicability also extends to homogeneous kinetic reactions which follow the electron transfer reaction. Some authors have used technics such as cyclic voltammetry and reverse ramp chrono-potentiometry to indirectly measure this type of kinetic reaction. With TETLE one electrode can be used to investigate the products produced at the surface of another electrode directly and give additional information concerning the above types of kinetic reactions.
Double Smoler Electrodes

Two dropping mercury electrodes (DME) in close proximity to each other entrap a layer of solution between them. Two possible configurations are shown in Figure 1. An additional possibility utilizes one DME together with a second solid electrode such as platinum. Two arrangements of this type of pair are shown in Figure 2. The distance separating the two electrodes in any of the pairs described above changes as the radius of the mercury sphere (or spheres) increases as shown in Figure 3.

There are two advantages in using dropping mercury electrodes. The smoothness of the liquid surface is undeniably perfect. The reproductibility of the flow rate (i.e., change in the radius of the Hg sphere) has been well proven in such areas as polarography.\textsuperscript{24} Drop time reproducibility of 0.25\% has been found for two uncontrolled Smoler electrodes.\textsuperscript{25} Drop time reproducibility of 0.01\% has been described for controlled Smoler electrodes.\textsuperscript{26} Another possible advantage in using two mercury drops to form the thin layer cell may prove fruitful in future work. As the two drops approach each other very closely the double layers of the two electrodes will penetrate each other and may lead to some interesting observations such as charge effects, adsorption, maxim, etc.

Geometric Considerations

The space between the thin layer electrodes as mentioned earlier is a function of the radius of the Hg sphere or spheres.
Figure 1.--Two Representations of Hg.-Hg. Electrode Arrangement
Smoler Electrodes

Ordinary DME'S
Figure 2.—Two Representations of Hg.-Pt. Electrode Arrangement
Pt. Wire

Glass Tube

Ordinary DME

Platinum Bead Electrode

Smoler Electrode

Flat Platinum

Pt. Wire
Figure 3.—Variation in $l$ With Change in Radius $r$
The Smoler electrodes may be placed in a fixed position so that the mercury drops will grow in size until they physically touch at some time before they are pulled from the tips of the capillaries by gravitational forces. The radius of the drops at any point in time together with the distance between the capillary tips determines the dimensions of the thin layer and the minimum electrode separation $d$. Thus it is the difference in the final radius, $r_f$, and the radius, $r$, at some previous time that determines $d$. More detailed schematic drawings and geometric descriptions corresponding to the several different electrode configurations referred to above are shown in Figures 4 through 7.

Qualitative Evaluation of Twin Thin Layer Electrodes

I-Twin Dropping Mercury Electrodes: When a DME is immersed in a solution containing a reducible, soluble material and an appropriate potential is applied a typical polarogram is observed:

![Figure 8. Current Time Curve](image)

This current, Figure 8, is described by the Ilkovic equation as proportional to $1/6$. If the product of the above reduction
\[ r_1 \propto t^{1/3} \]
\[ r_f^o \propto t_f^{1/3} \]
\[ r_f = 2r_f^o - r_1 \]
\[ r_f \propto (2t_f^{1/3} - t^{1/3}) \]

Figure 4.—Twin Smoler Electrodes
Figure 5.—Twin DME Electrodes

\[
\begin{align*}
    r_1 & \propto t^{1/3} \\
    r_f^0 & \propto t_f^{1/3} \\
    r_f & = (1+\sin \Theta)r_f^0-(\sin \Theta)r_1 \\
    r_f & \propto (1+\sin \Theta)t_f^{1/3}-(\sin \Theta)t^{1/3} \\
\end{align*}
\]
Figure 6.--DME with Platinum Bead

\[ r_1 \propto t^{1/3} \]
\[ r_f^0 \propto t_f^{1/3} \]
\[ r_f = \frac{r_f^0 + r_1}{2} \]
\[ r_f \approx \frac{1}{2} (t_f^{1/3} + t^{1/3}) \]

\[ \ell = r_f^0 - r_1 \]
\[ \ell = (t_f^{1/3} + t^{1/3}) \]
\[ r_1 \alpha t^{1/3} \]
\[ r_0 \alpha t_1^{1/3} \]
\[ t_f = 2r_0 - r_1 \]
\[ t_f \alpha (2t_1^{1/3} - t^{1/3}) \]

\[ l = r_f - r_1 \]
\[ = 2r_0^{1/3} - 2r_1 \]
\[ l \alpha 2(t_1^{1/3} - t^{1/3}) \]

Figure 7.—DME with Flat Platinum Probe
is soluble it will diffuse away from the electrode surface into the bulk solution. This electrode reaction product may be detected electrochemically by placing a second electrode (or probe) in the solution immediately adjacent to the first electrode (or generator). A particularly useful (and symmetrical) case results if the second electrode is also a DME. If the product is oxidizable at the potential of the probe a current will flow. Since the concentration of this product will be higher at the surface of the generator than at any other point in the solution (due to random diffusion) there will be a higher current response at the probe the closer it is placed to the generator. The distance between the two expanding drops decreases as a function of time and the current at the second electrode appears as shown in Figure 9. There are four regions of interest shown in the figure. The (A) region, which composes the first 75% of the signal along the time axis is a small background current. As the drops grow closer together more of the products from the generator come in contact with the probe and the current rises as shown in (B). The (C) region indicates that the drops have touched causing an electrical short in the instrument. The (D) region indicates a restabilization of the instrument after the drops have fallen off, breaking the electrical short. Since the current rises very sharply as $l$ approaches zero this indicates that $i$ is probably inversely proportional to $l$.

II-Mercury Electrodes with Platinum Probe: The overall response
of this thin layer electrode pair is identical to that of the twin DME cell. The only difference is that only one surface is moving as a function of time.

Both of these technics are potentially useful. The absolute difference in the $i$ vs. $t$ curves is seen in the relationship between $t$ and $\Delta l$ for both technics. For the twin DME system:

$$\Delta l \propto 4\left(t_f^{1/3} - t^{1/3}\right)$$  \hspace{1cm} (1)

While the Pt probe-DME system:

$$\Delta l \propto \left(t_f^{1/3} - t^{1/3}\right)$$  \hspace{1cm} (2)

Since the current at the probe is a function of $\Delta l$ and not $t$ the two current-drop time curves look like the plot in Figure 10.

![Figure 10](image_url)

Figure 10.—Pt.-DME versus DME-DME

The curve for the Pt probe-DME system indicates that it takes a longer time for $\Delta l$ to change as increment $\Delta l$ in case 2 than it does in case 1. A plot of $1/i$ vs. $t^{1/3}$ for both systems will give a factor of 4 difference in the slopes of the plots. Even though the Pt probe-DME system shows a slower rate of closure of the opposing electrode surface it has other disadvantages. First Pt can never be polished to
as smooth a surface as the liquid Hg drop. The second and more serious disadvantage appears during the actual experiment. After the Hg drop has come in contact with the Pt surface several times, mercury metal starts to adhere to the Pt causing very high background currents (due to the oxidation of Hg) at the Pt probe. Using the Pt probe does extend the range of applicability of the technic into the anodic region but the difficulties far outweigh the advantages for its use in this work.

Analysis of the Diffusional Process

Figure 11 illustrates how lines of uniform flux and circles of constant concentration are formed between two closely spaced spheres (represented by the two inner circles in the figure) with direchlet boundary condition.\textsuperscript{27} If all of the lines of flux could be shown (three dimensional representation) a watermelon shaped surface would be formed between the two spheres. In order to obtain the lines of uniform flux shown in Figure 11 it is necessary to control the surface concentration at each electrode. The control of the surface concentration is accomplished by potentiostatic methods. One of the electrodes (generator) is held at a potential sufficient to reduce an electroactive species in solution:

\[ O + ne \rightleftharpoons R. \]

The second electrode (probe) oxidizes the product from the generator electrode and reflects it back onto the generator electrode. The flux or resultant current response at the
Figure 11.—Solution Gradients Around Twin DME's
probe is then a direct observation of the products of the generator electrode.

A possible second method of controlling the surface concentration is by galvanostatic control of the generator electrode and potentiostatic control of the probe electrode. But the control of current at the twin DME electrodes offers no particular advantage over the potentiostatic experiments described above. In fact the analysis of the mass transport process is considerably complicated by the nonuniform flux that is dictated by the twin DME configuration. Using galvanostatic control of the generator electrode and potentiostatic control of the probe electrode an approximately uniform flux will be produced at the generator electrode when the electrodes are far apart (see Figure 12). As they grow close together a portion of the probe electrode will electrolyze and reflect back onto the generator electrode additional electroactive material. The current density will thus be higher on that portion of the generator nearest the probe. All hope of a simple solution to the diffusional transport problem is lost since the total current of the probe will be the sum of two complicated time dependent processes.

One additional point to be discussed in this section is concerned with the movement of the solution around the two drops. As the drops grow toward each other the solution trapped between them will be squeezed out of the thin layer. This can possible cause serious eddy currents around the drops. If the flow of solution is laminar, and approximately along the lines
Drops Far Apart

Drops Close Together

Figure 12.--Flux Between Two DME's
of constant concentration (a likely choice) no unwanted concentration gradients will be formed. Calculations indicate an approximate solution velocity of less than 1 cm/sec. is reached when the 2 drops are 10 microns apart, thus assuming laminar flow.

Quantitative Solution of the Diffusional Process

I-Cartesian Coordinates: If parallel lines of flux are assumed (one dimensional diffusion) the solution of the diffusional problem is approachable in the following manner. Both mercury drops pictured in Figure 13 are assumed to have the same radius and to be growing at the same rate. When the distance of closest approach, \( l_a \), is small two assumptions can be made: (1) mass transfer between the drops is approximately one dimensional; and (2) the current due to molecules transported from one electrode to the other approximates a steady-state.

The first assumption becomes more valid as \( l \) gets small since the current contributed by areas near the top and bottom of the electrode are small. An average molecule in the center will "bounce" back and forth many times while one on the top or bottom may only make the trip once.

The second assumption states that an average molecule will "bounce" back and forth many times while the space, \( l \), remains essentially constant.

The time it takes a molecule to travel a certain distance, \( \bar{l} \), is given by the relationship:
Figure 13.—Twin DME's in Cartesian Coordinates
where \( D \) is the diffusion coefficient of the molecule in \( \text{cm}^2/\text{sec.} \), and \( \Delta t_1 \) is the diffusional time constant of the cell.

The radius is related to the time, \( t \), from geometric considerations as

\[
\frac{dr_1}{dt} = \left( \frac{3m}{4 \pi d^3} \right)^{1/3} \left( \frac{3m}{4 \pi d} \right)^{1/3} t^{1/3}
\]

(5)

or, as long as \( \Delta t \) is small

\[
\Delta r_1 = \left( \frac{1}{3t^{2/3}} \right) \left( \frac{3m}{4 \pi d} \right)^{1/3} \Delta t
\]

(6)

if the maximum allowable change of \( \ell \) is 1%, then the time \( \Delta t_2 \) necessary for \( r_1 \) to change \( \ell / 100 \) will be

\[
\Delta t_2 = \frac{\ell}{100} \times \frac{3t^{2/3}}{\left( \frac{3m}{4 \pi d} \right)^{1/3}}
\]

(7)

When \( \Delta t_2 \) is greater than or equal to \( \Delta t_1 \), the diffusional mass transfer is faster than the rate of change of \( \ell \) and

\[
\ell \leq \frac{6D t^{2/3}}{100 \left( \frac{3m}{4 \pi d} \right)^{1/3}}
\]

(8)

assuming \( D = 5 \times 10^{-6} \text{cm}^2/\text{sec.} \), \( m \) is 0.5 mg./sec. and \( t \) is 2.0 seconds. This means that the steady-state assumption should when

\[
\ell_0 \leq 0.23 \text{ microns}
\]
As shown in Figure 13 the steady-state current contributed by the element of area $dA$, is the ring between the radial distance $y$ and $y + dy$ will be:

$$dI_{ss} = \frac{nFDC \, dA_y}{\lambda y} \quad (9)$$

The total current will then be the sum of the contributions of all the elements of area from $y = 0$ to $y = r_1$

$$I_{ss} = nFDC \int_0^{r_1} \frac{dA_y}{\lambda y} \quad (10)$$

Substituting $dA_y = 2\pi y dy$ and $l_y = 2 \left( r_f - \sqrt{r_1^2 - y^2} \right)$

$$I_{ss} = 2\pi nFDC \int_0^{r_1} \frac{y \, dy}{r_f - \sqrt{r_1^2 - y^2}} \quad (11)$$

The resulting solution is:

$$\frac{I_{ss}}{\pi nFDC} = r_f \ln \left[ \frac{r_f}{r_f - r_1} \right] - r_1 \quad (12)$$

The conditions under which this equation is most useful is described by the following theoretical example. If the two drops are at a minimum distance $l$ microns apart (distance of closest approach, see Figure 13) the surface area of the drops can be divided into circular sections. If the sections are small they can be assumed to be planar and the area of each section can be easily calculated. With the area of a section and the average spacing, $l_a$, for each section known a number proportional to the current can be calculated for this section ($i \propto A/l_a$). To determine how the central 10% section of the electrode contributes to the total current response a
plot of this "sectional current" is shown in Figure 14. When the ratio of $r_f/l$ is 10,000 or more the central 10% of the electrode contributes essentially all of the current response and one dimensional diffusion can be assumed with no contributions from the outer edges of the drops. Table 1 also indicates that at no point of close spacing (5 microns) between the two electrodes will a planar approximation be valid under steady-state conditions.

The derivation of the transient response of the thin layer in Cartesian coordinates is thoroughly pursued is the section on Fick's law with planar approximations.

II-Bipolar Coordinates: A more general approach to unusual geometries represented by the TETLE is transformation of the coordinates. The mathematical physicist has developed systems of bipolar coordinates for use with electrostatic fields and heat and mass transport between spherical surfaces.

Figure 15 shows two spheres in a two dimensional projection of three dimensional bipolar coordinates. The single horizontal line between the two points is coordinate $\alpha = \pi$. At smaller values of $\alpha (0 \leq \alpha < \pi$) spindle shaped surfaces of revolution are formed between the same two points on the two circles. At $\alpha = 0$ the line starts to the right of the point shown on the right and goes to $\infty$. It reenters from the $-\infty$ (from the left) and connects to the other point shown on the left. The circles themselves are at $\beta = -\beta_0$ and $\beta_0$. If the circles represent two spheres a simplified version is shown in Figure 16.
Figure 14.—Illustration of Current Carried by Central Portion of Electrode as a Function of TLE Cell Dimensions
Fraction of $\frac{1}{ss}$ Carried by Central $0.1r_f$
# TABLE 1

**ILLUSTRATION OF SPHERICAL SHAPE OF DME AT CLOSE SPACING**

<table>
<thead>
<tr>
<th>Fraction of $r_f$</th>
<th>Avg.</th>
<th>Position of Drop Center</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 to 0.1</td>
<td>0.1</td>
<td>A</td>
</tr>
<tr>
<td>0.1 to 0.2</td>
<td>4.7</td>
<td>B</td>
</tr>
<tr>
<td>0.2 to 0.3</td>
<td>16.1</td>
<td></td>
</tr>
<tr>
<td>0 to 0.1</td>
<td>0.5</td>
<td>B</td>
</tr>
<tr>
<td>0.1 to 0.2</td>
<td>5.0</td>
<td>C</td>
</tr>
<tr>
<td>0.2 to 0.3</td>
<td>16.5</td>
<td></td>
</tr>
<tr>
<td>0 to 0.1</td>
<td>1.0</td>
<td>C</td>
</tr>
<tr>
<td>0.1 to 0.2</td>
<td>6.6</td>
<td>Where A is closer than B</td>
</tr>
<tr>
<td>0.2 to 0.3</td>
<td>17.0</td>
<td>closer than C.</td>
</tr>
</tbody>
</table>

Where A is closer than B closer than C.
Figure 15.—Illustration of Bipolar Coordinates
Figure 16.—Twin DME's in Bipolar Coordinates
The position of the two drops can be described at \( \beta = \beta_1 \) and \( \beta = \beta_2 \). The radius of the spheres (if they are expanding Hg drops)\(^{29}\) is expressed as:

\[
 r = \left( \frac{3m}{4 \pi d} \right)^{1/3} t^{1/3}
\]  

(13)

where \( m = \) flow rate of the DME  
\( d = \) density of mercury  
\( t = \) any time during the growth of the drop

After transformation to spherical coordinates the position of the two drops are expressed as:

\[
 \beta_1 = f(\lambda, r_1)
\]  

(14)

\[
 \beta_2 = f(\lambda, r_2)
\]  

(15)

In the general case the concentration in the region outside the spheres (\( \beta_1 < \beta < \beta_2 \)) can be described as a summation of terms:\(^{30}\)

\[
 C = 2\cosh \beta - 2\cos \alpha \left[ M_n \cosh (n + \frac{1}{2}) \beta + N_n \sinh (n + \frac{1}{2}) \beta \right] P_n(\cos \alpha) \quad n = 0, 1, 2, \ldots
\]  

(16)

where \( M_n \) and \( N_n \) are determined by the boundary conditions and \( P_n(\cos \alpha) \) is the Legendre Polynomial. In the simplified symmetrical case (\( r_1 = r_2 \)), the left hand sphere corresponds to:

\[
 \beta = -\beta^o
\]  

(17)

while the right hand sphere corresponds to:

\[
 \beta = \beta^o
\]  

(18)

and

\[
 \cosh \beta^o = (\lambda/r + 2)
\]  

(19)

If the concentration at both electrodes is given, and gradient of \( C \) in bipolar coordinates the total current may be
determined from equation 16 by integration of the flux over the entire surface of the sphere $\beta = \beta_0$.

We feel that this type of mathematical analysis would be an important next step in the development of the quantitative application of TETLE. It was, however, beyond the scope of the present analysis, and we have limited our subsequent mathematical discussion to approximate methods that can be shown to apply adequately to the application investigated in this work.

Fick's Law with Planar Approximations

As has been described by Ashley and Reilley, a general equation can be derived from Fick's Second Law for the change in concentration with time as a function of the rate of change in concentration due to one dimensional diffusion from a planar electrode and from chemical reactions as follows:

$$\frac{\partial \rho}{\partial t} = \frac{\partial^2 \rho}{\partial x^2} - k_{fr} \rho_f + \sum_r k_{rf} \rho_r (r \neq f) \quad (20)$$

where $D = \text{diffusion coefficient}$

and $k_{fr}$ and $k_{rf}$ are (pseudo-) first-order rate constants.

This is then rewritten assuming all the diffusional constants are equal:

$$D \rho_f - \sum_g k_{gf} \rho_g = 0 \quad (21)$$

where

$$D = \frac{\partial}{\partial t} - D \frac{\partial^2}{\partial x^2}$$

The general case for a series of $N$ linear combinations of $N$ equations of the above type is:
\[ \sum_{R} a_{Rh} \left[ D_{c_R} - \sum_{g} k_{gf} c_g \right] = 0 \]  

(22)

the value of the coefficient \( a_{Rh} \) is such that:

\[ \varphi_h - \lambda \varphi_h = 0 \]  

(23)

where

\[ \varphi_h \equiv \sum_{R} a_{Rh} c_R \]

and \( \lambda \) is a constant.

If a new term is defined:

\[ \Phi_h \equiv \varphi_h e^{\lambda x t} \]  

(24)

then

\[ D \Phi_h = 0 \]  

(25)

A new form of Fick's law can be written for the new term as:

\[ \frac{\alpha \Phi_h}{\alpha t} = D \frac{\alpha^2 \Phi_h}{\alpha x^2} \]  

(26)

Thus by taking the Laplace transform and adding boundary condition of \((x = 0, t)\)

\[ \Phi_h = q e^{-q x} + k \]  

(27)

where \( q = p^{1/2}/D^{1/2} \) (\( p \) being a Laplace variable)

and \( k = \Phi^0_h/p \)

The above equation then reduces to the form:

\[ \Delta \Phi_h = \Phi_h - \Phi^0_h/p \]  

(28)

After a series of algebraic manipulations are made, summarized in the Appendix, the solution to the general equation involving the change in concentration \( C \), due to diffusional and kinetic effects is expressed as:
$$\left( \overline{j}_g \right)_{x=0} = -D^2 \sum_{G} (\Delta \overline{c}_G)_{x=0} \sum_{h} k_{fgh} (p + \chi h)^\frac{1}{2} \times \left( \frac{c-q}{c-q} \right)$$

$$\left( \frac{e-q}{c-q} + e \frac{q}{c-q} \right) + D^2 \left[ (\Delta \overline{c}_G)_{x=0} \sum_{h} k_{fgh} (p + \chi h)^\frac{1}{2} \left( \frac{c-q}{c-q} \right) \right]$$

A stepwise solution is described in the appendix. The terms of the above equation are as follows:

$$\left( \Delta \overline{c}_G \right) = \text{the Laplace transform of the change in } G$$
$$D = \text{diffusion coefficient}$$
$$\overline{j}_g = \text{the Laplace transform of the flux}$$
$$K_{fgh} = \text{a combination of ratios of first-order rate constants}$$
$$P = \text{the Laplace transform variable}$$
$$x_h = \text{a constant related to the magnitude of the rate constants.}$$

The solution of the current from this equation for the non-kinetic case is:

$$i = \frac{2nFAD^2}{c^0} \sum_{n=0}^{\infty} \exp \left[ -\frac{1}{4Dt} (2n+1)^2 \right]$$

or

$$i = \frac{nFAD}{c^0} \int (1+2) \sum_{n=1}^{\infty} \left( -1^n \exp \left( \frac{-n^2\pi^2}{4D^2} \right) \right)$$

where the solutions are for different DT/\( \xi \). Equation 30 is more accurate at small values of DT/\( \xi \) while equation 31 holds best for large values of DT/\( \xi \). A comparison of the two equations is shown in Figure 17. As it is seen in the figure either equation is applicable in the region from 0.900 to 0.995 of \( t \). These equations have also been verified by using the "folding" technic. These solutions are also shown in the appendix.
Figure 17.—Comparison of Equations 30 and 31
When kinetic reactions follow the initial electrode reaction
\[ A_1 + n_e = A_2 \]
they may be one of the following types:
\[ A_2 + Z \xrightarrow{k_1} A_1 + Y \]
\[ A_2 + Z \xrightarrow{k_2} \text{inactive products} \]
where \( Z \) and \( Y \) are electroinactive at either electrode and \( A_2 \) is initially absent. The solution of the catalytic case is:
\[
1 = \frac{nFAD^2C^0}{\sqrt{\pi t}} \exp(-kt) \sum_{n=0}^{\infty} \left\{ 2\exp\left( - \frac{(2n + 1) \mu}{4Dt} \right) \right\}
\]
\[
\sqrt{\pi kt} \left[ \exp\left( - \frac{(2n + 1) \mu k}{D^2} + kt \right) \text{erfc}\left( \frac{(2n + 1) \mu t^{3/2}}{4D^{3/2}} + \sqrt{kt} \right) \right. \\
+ \exp\left( - \frac{(2n + 1) \mu k}{D^2} \right) \text{erfc}\left( \frac{(2n + 1) \mu t^{3/2}}{4D^{3/2}} - \sqrt{kt} \right) \right\}
\]
while the solution for the non-catalytic case is:
\[
1 = \frac{nFAD^0C^0}{\lambda} \exp(-kt) (1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \left( - \frac{n^2 \pi^2 D^2 t}{\lambda^2} \right) \\
(33)
\]

**Mathematical Simplifications**

All of the equations derived in this chapter are complicated enough to make the use of a small computer desirable. The alternative is to simplify the equations. Equation 30 will be used to illustrate how this can be accomplished.
\[
1 = \frac{2nFAD^2C^0}{\sqrt{\pi t}} \sum_{n=0}^{\infty} \exp\left( - \frac{(2n + 1) \mu}{4Dt} \right)
\]
Values of the SUM can be calculated for a theoretical system with arbitrary values of \( D \), \( t^* \), and \( \lambda \). The term \( \sqrt{DT/\lambda} \) is also calculated using the same arbitrary values of \( D \), \( t^* \), and \( \lambda \). The linear relationship between the SUM and \( Dt/\lambda \) is shown in Figure 18. Since the limiting slope of the plot in Figure 16 is equal \( \sqrt{\pi/2} \), equation 30 reduces to:

\[
\frac{1}{nFADc_0} = 1/\lambda \tag{34}
\]

over the region of linear dependence shown in this figure.

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18 Christensen, Anson, op. cit.

19 Anderson, Reilley, op. cit.

20 Oglesby, Anderson, McDuffie, and Reilley, op. cit.


22 Schwarz and Shain, op. cit.


28 Lebedev, Skalskaya, Uflyand, op. cit., Chapt. 7.


30 Lebedev, Skalskaya, Uflyand, op. cit., p. 233.


Figure 18.—Illustration of Simplification of Equation 30
\[ \text{SUM} = \sum_{n=0}^{\infty} \exp \left( \frac{-([2n+1]\delta)^2}{4Dt} \right) \]
INSTRUMENT

The proposed studies in thin layer electrochemistry required assembly of an instrument with the capability of independently controlling potentials and currents at two working electrodes. While maintaining such control, the instrument must also be able to measure both potential and/or current at the appropriate electrode. The potential control and current measuring electronics must respond to the diffusional time constant (~1 msec.). The accuracy of the current measurement must be greater than 1% in the region from approximately 10 nanoamperes to 10 milliamperes, and the potential must be controlled with ± one millivolt accuracy.

Multipurpose instruments have been described by several authors. A particularly advantageous design feature of several instruments is the use of modular construction, whereby a portion of the instrument may be readily expanded or redesigned without altering either the design of the instrument, or modifying other functional elements. A more recent innovation has been reorganization of the instrument controls along the line of operational classifications such as Excitation, Systems Control, and Response. It is not insignificant that we made the decision to incorporate both of these features in the construction of this instrument.
In addition, several other features were used in this work to produce a more versatile instrument. The "plug-in" feature found so useful by Tectronix and other oscilloscope companies was taken to give a modular capability to the instrument. Specifically we chose the Philbrick Q-3 modular assembly for enclosure of the instrument. Also it was decided to incorporate a programmable feature into the instrument. Many authors 39,40 have shown the advantages of programmed potential control in the areas of pretreatment of electrodes, preelectrolysis of impurities, and complicated potential reversal techniques. Finally, the choice of relay switching was made from two considerations, expense and speed of switching. Relay switching is faster than manual switching and the time response of the closure of the relay contact must be within the range of the diffusional time constant of the cell (~ 1 msec.). Relay switching is also less expensive than electronic switching. 41

In the Operational classification as stated above, Excitation refers to those signal sources that provide voltage levels and time dependent voltage functions to the Systems Control portion of the instrument. These excitations can include all waveforms commonly used in electrochemical experiments (square waves, sawtooth waves, sinusoidal waves, etc.) The System Control portion to the instrument accepts these instructions, controls the voltages applied to the electrochemical cell. The flexibility for using complicated sequences of excitation is provided by the program boards of the System Control portion. Finally the resulting cell currents are
converted to DC voltage levels and transferred via the trunk lines to the Response section of the instrument. In the Response section, AC signals may be rectified, DC signals integrated, or otherwise processed into more useful forms. These signals, analog or digital, may then be transferred out at impedance levels matching the users recording devices.

There are two areas in the specific instrument designed and built by this author that merit discussion. These are two modules housing the system control function of the instrument. The first module, or "box," contains the cell control amplifiers and current-to-voltage transducers. The circuit shown in Figure 19 schematically illustrates this box. This circuit permits independent control of the potentials of two working electrodes using one reference and one auxiliary electrode. Amplifier 3 injects into the cell that current necessary to control the potential of the reference electrode at a fixed value $E_I$ above ground.

Amplifiers 1 and 2 control the potential of the two working electrodes while measuring the current flowing at these two electrodes. Amplifier 4 computes the sum of $E_{II}$ and $E_{ref}$ and applies this voltage to amplifier 2. In this way, amplifier 4 controls the potential of the second working electrode at $E_{II}$ volts versus the reference electrode.

From this, it can be seen that the potential of any number of electrodes could also be independently controlled versus a single reference and using a single auxiliary electrode. For example, the schematic diagram for three electrode control
Figure 19.--Four Electrode Potential-Potential Control
is shown in Figure 20.

The same analogy also holds for the E-i control function of the system control module. Here the potential of one electrode and the current at the second electrode are controlled. This can be expanded as in the E-E section by duplicating the appropriate portion of the circuit to duplicate the desired control.

The advantages of using a single reference electrode in a multielectrode cell are many. An early use of multi-electrodes was in electrolysis at two closely spaced electrodes in a moving stream. This author used two reference electrodes and two auxiliary electrodes in the two working electrode cell to maintain potential control. With the instrument described earlier the authors mentioned above would not have needed two separate potentiostats. Nor would they have needed to match two reference electrodes since only one is necessary. Also in this area of electrochemistry (flowing stream analysis) paraphernalia in the cell compartment.

Although the underlying principles are identical, a slightly different control problem is created by efforts to compensate for extraneous signals by dummy cell technics. Thus, galvanostatic and potentiostatic control and compensation have been described. Both areas could be simplified by the use of a single reference electrode.

Measurement and control problems in the presence
Figure 20.--Five Electrode Potential Control
of electrode potential gradients on macro electrodes are very important and their effects in dummy cell technics must be considered. Studies have been made in this area with a cell containing five working electrodes.45

A final area for application of multiple electrode control technics has appeared in rotating ring disk methods.46 Independent control of the ring and disk is essential in order to follow the rapid mass transport of electrode reaction products from the disk to the electrically isolated ring. This technic is very similar to thin layer cell technics47 in that the rate of mass transfer may be varied over a wide range without varying the potential of the two electrodes. For ring-disk cells this is accomplished by varying the speed of rotation of the disk. In TLE the space between the two electrodes is the variable.

The second area of specific interest is the programable function of the instrument. As mentioned earlier several authors have shown the need for such a feature. Complex potential step, and ramp reversal experiments are best handled with an automatic potential control feature. All of the events are set initially and the instrument is programed to initiate these events in a prescribed manner. In this work all of the excitation potentials are initiated with the aid of mercury wetted relays. The relay power connections are wired to a program switching matrix. The appropriate sequence of events is then programed into the program switch-
ing matrix. As the program initiator button or switch is
activated the program is followed step by step and the pre-
scribed sequence of events is carried out. At this partic-
ular stage in the development of this instrument the initiator
switch is an eight position, single pole, ceramic wafer
switch. Each position on the switch is connected to a column
in the switching matrix. The relay power connections are
wired to the rows in the switching matrix. The program board
connects the columns and the rows to give any desired sequence
of events. The switch is then turned successively from posi-
tion one to eight to initiate the proper relays at the proper
time. At a later date a timing circuit will replace this
eight position switch so that accurate time intervals between
the events can also be programmed.

Basic Instrument Features

In order for an instrument to be of maximum value
to the research electrochemical chemist it must have the
following characteristics:

A - Precision
  1 - fast time response
  2 - accurate current and voltage measurement
  3 - low noise level

B - Flexibility

C - Simplicity of Operation
  1 - modular design with interchangeable parts
  2 - compact in size
  3 - simple to operate
D - Ease of repair

The instrument built by the author can be used to carry out a broad range of electrochemical experiments. When the appropriate excitation functions are completed such experiments as polarography, chronopotentiometry, amperometry, cyclic voltammetry, A. C. polarography, reverse ramp chronopotentiometry, etc. can be carried out with this instrument. The accuracy of the measurement of currents and potentials will only depend on the quality of the interchangeable electronic components used throughout the instrument. The basic layout of the instrument is shown in Figures 21 through 29. Each section of the instrument is shown in block diagram with simple schematics added for clarity.

The enclosure for the instrument utilized the Philbrick Researches, Inc. Q-3 modular assembly. The 3 x 3 matrix shown in Figure 30 holds nine basic modules. The rear of the 3 x 3 assembly shows (Figure 31) that each section of the nine section case has two 24-pin AMP connectors. Except for the top left and the lower left sections (seen from the rear), which are used for D. C. power supplies, all of the corresponding sections are wired together. The sketch in Figure 32 will illustrate this point:
Figure 21.—Basic Instrument Layout
Figure 22.—Block Diagram of Excitation Box A
Step Potentials

Ramp Potentials

Integrator

Excitation Potentials

Integrator

Step Potential

Ramp Potential
Figure 23.—Block Diagram of Excitation Box B
Integrator

Ramp Potential

Step Potential

Step Potential

(See Figure ??)

(See Figure ??)

Integrator

Step Potential

Ramp Potential

(2)

(3)

(Relay Switches)
Figure 24.—Block Diagram of Cell Control Box Function - 1
Current Generator Type - 1

Inverter

Current Generator Type - 1

Non-Inverting Adder-Subtractor

Cell

Current to Voltage Transducer

Current to Voltage Transducer

(Rf. Electrode)

(Aux. Electrode)

Current Generator Type - 1

Non-Inverting Adder-Subtractor

(Metal Electrode)

Current to Voltage Transducer

Inverter
Figure 25.—Block Diagram of Cell Control Box Function - 2
(Input) 

Current Generator Type - 2 → Cell → Follower → (Output)

(See Figure 25)

(Ref. Electrode)

Current Generator Type - 2 → Follower

Figure 26.—System Control; Function - 3
Figure 27.—System Control; Function - 4
Figure 28.— Program Control Module
Subtractor Function Selector Integrator

3-pole; 3-position Non-Shorting Switch

Figure 29.—Data Processor Module
Figure 30.—Front View of 3 x 3 Matrix
Figure 31.—Rear View of 3 x 3 Matrix
This means that the remaining seven sections can be used by any instrumental functional module. This eliminates the need for assigning a specific section to a specific module.

An illustration of the individual basic modules is shown in Figure 33. With these basic modules and numerous P-0, 10-pin plug-in units, and SP-0, 15-pin plug-in units (purchased from Philbrick Researches, Inc.) the entire instrument was constructed. The single power supply for operating the amplifiers and other low current D. C. circuitry was a Philbrick Researches, Inc. QPR-300 power supply with \( \pm 15 \) volts at 0.1% regulation and a 300 ma current output.

With a general idea of the basic instrument in mind a detailed description of each function can be presented.

**Excitation Functions**

There are at present two excitation modules or boxes in use in this laboratory. From the first excitation
Figure 33.—Basic Module as Purchased
From Philbrick Researches, Inc.
box, labeled A, shown in Figure 34 signals of two types are available:

1 - Single step potential from -2.000 volts to +2.000 volts D. C. (Figure 35 below)

2 - Ramp D. C. potential from +10 to -10 volts D. C. at variable slope or sign (Figure 36 below)

\[ E = \frac{-V}{RC} \Delta t \]

where \( E \) = volts out

\( V \) = volts in
Figure 34.—Schematic Diagram of Excitation Box A

- $R_1 = 500$ ohms
- $R_2 = 5.9$ kohms
- $R_3 = 13.3$ kohms
- $R_4 = 147$ kohms
- $R_5 = 3.24$ kohms
- $R_6 = 100$ kohms
- $R_7 = 100$ meg. ohms
- $R_8 = 1$ kohm

- $C_1 = 1$ uf
- $C_2 = 0.1$ uf
- $C_3 = 0.01$ uf

Note: $\bigcirc =$ Trim Pot.
Figure 37.---Front Panel of Excitation Box A

---

Figure 39.---Front Panel of Excitation Box B
Excitation Module A

Initial

-2v to +2v

Ramp

0 to 1 mv

10Q

10

A

Ramp Mult.

1

10

20

100

(-)

(+)

Ramp Direction

Excitation Module B

Step -1

-2v to +2v

Ramp

0 to 1 mv

Step -2

-2v to +2v

Ramp Mult.

20

50

100

200

500

1000

Ramp Direction
R = resistance in megohms
C = capacitance in microfarads
Δt = time interval in seconds

The slope of the ramp potentials (E vs t) that are generated by this module is controlled by variation in V and RC and goes from 0.011 to 10 volts per second.

The step potentials are produced by adding a small resistor in parallel to the capacitor, C. This in effect makes the integrator into a simple inverter. If the added resistor is small in value and a small capacitor is used, very fast step potentials can be obtained.

This module or box will be referred to subsequently as the single-step excitation box since it only has the one step potential pre-set capability.

The second type of excitation box, labeled B, is very similar to the first as is seen in Figures 39 and 40. The major difference between this module, B, and the previous one, A, is in the double step feature. Two step potentials can be pre-set and activated when needed. The advantage to this is to allow the experimenter to switch between two potentials rapidly. The usefulness of this will become apparent in the discussion of the Potential - Step technic in the Experimental chapter of this work.

In addition to these two types of excitation boxes other more complex modules could be constructed. Some examples are square wave generators, cyclic voltammetry or triangular
Figure 40.—Schematic Diagram of Excitation Box B

\[ \begin{align*}
R_1 &= 500 \text{ ohms} \\
R_2 &= 1.47k \text{ ohms} \\
R_3 &= 5.9 \text{ ohms} \\
R_4 &= 13.3 \text{ ohms} \\
R_5 &= 28 \text{ ohms} \\
R_6 &= 147 \text{ ohms} \\
R_7 &= 3.16 \text{ ohms} \\
R_8 &= 100 \text{ ohms} \\
R_9 &= 10 \text{ meg. ohms} \\
R_V &= 1k \text{ ohm} \\
C &= 0.1 \text{ uf}
\end{align*} \]
Note: φ = Trim Pot.
wave generators, and sinusoidal wave generators. Any of these signal sources could be easily incorporated into the basic instrument. It would only be necessary to insure that the amplifiers in the following circuits (control section) be able to handle the magnitude (voltage limits) and time response (amplifier slow rate) of the incoming signal.

System Control

I-Cell Control:

The first subdivision to be discussed under system control is the cell control portion of the instrument. The four basic functions of the instrument are shown in Figure 41. They are three electrode potential control, three electrode current control, four electrode potential-potential control, and four electrode potential-current control. In addition to these elements there is an elaborate switching system for changing the cell control from one of these four functions to another. The schematic diagram for this switching matrix is shown in Figure 42. The four control functions, shown in Figure 41, can be used in electrochemical experiments involving the following:

A - Three electrode

1 - current measurement at controlled potential
2 - potential measurement at controlled current

B - Four electrode

1 - current measurement at both electrodes with potential control at both
Figure 41.—Schematic of Cell Control Module
Figure 42.—Schematic Diagram of Switching Matrix of Cell Control Module
2 - potential measurement with current control at one electrode with current measurement at controlled potential at the other electrode

The basic electronic design for this module can be explained by analyzing one portion. The remainder of the module will follow the same analysis.

Function 1 has the ability to control the potential of two working electrodes independently of each other and versus the same reference electrode. The amplifier marked 1 and connected to \( W_1 \) is a current-to-voltage transducer. The equation for the ideal response of this type of electronic circuit is as follows (Figure 43):

\[
E/R = i
\]

Figure 43.— I-to-V Transducer

The amplifier marked 3 is essentially a follower where current is injected into the cell from the output of the amplifier until the potentials of the two inputs are equal (E of the reference electrode vs. gnd. is equal to \( E_1 \)). This potential, \( E_1 \) vs. gnd., is opposite in sign to E of \( W_1 \) vs. the reference electrode. An inverter has been placed between the excitation box and input at \( E_1 \) to invert the
incoming signal before it is applied to the spot marked $E_I$. In this way the voltage that comes out of the excitation box is equal in sign and magnitude to $E$ of $W_I$ versus the reference electrode.

The amplifier marked 4 is a control amplifier. With the resistors that are shown it controls the entire circuit in such a way that the potential $E$ of the $W_{II}$ versus the reference electrode is equal to $E_{II}$. The remaining amplifier is also a current-to-voltage transducer but of a slightly different type since the positive input is not grounded. The solution of the current is as follows (Figure 44):

$$\Delta E/R = i$$

Figure 44.— I-to-V Transducer Type 2

The front of the cell control module, shown in Figure 45, contains the current sensitivity switches for the two working electrodes, the four inputs from the cell (Ref., Aux., $W_I$, and $W_{II}$), and the four position function selector switch.

II-Program Control:

This module is the central control unit for the entire instrument. All the settings such as ramp slope, step
Figure 45.—Front Panel of Cell Control Module

Figure 46.—Front Panel of Program Module
System Control Module

Current Multipliers

8 10
6
4
2
7 9
5
3

Function Selector

1
2
3
4

Program Control Module

Function Selector

(1,4) (2,3)

3
5
7
1
9

Program Steps

W1-Ref.-Aux. W2

Cell Inputs
magnitude, integration rate, etc. are made on the fronts of the respective modules but the activation of these modules is controlled from the program control module. The schematics for this module are shown in Figures 46 and 47. As is shown this module consists of only a few major parts. They are the AMP connectors and a single pole, eight position switch. The "Y" axis (or rows) on the AMP connectors is a bank of relays which are located in the other modules for activating the step potentials, integrators, etc. The "X" axis (or columns) is connected to the eight position switch along row 1. Figure 48 shows how the lower part or "program switching matrix" of the AMP connectors is wired. Rows 2 through 10 on the program switching matrix are wired as shown in Figure 47 to nine different relays throughout the instrument. Columns 1 through 8 in row 1 are wired to the positions on the switch. (Column 1 to switch position 1, column 2 to switch position 2, etc.) The top part of the AMP connectors is the "program board". It has a matrix identical to the program switching matrix (8 columns with 10 rows). Both the program board and the program switching matrix are fitted with gold contacts (purchased from Philbrick Researches, Inc.) which interlock with each other when the two connectors are interconnected (see Figure 49).
Figure 47.—Schematic Diagram of Program Module

Diodes = IN485A

T = RCA-40409

R = 1 k ohm
Figure 48.—Lower View of Program Switching Matrix Showing Wiring of Diodes
Figure 49.—Gold Contacts

The program board is then programmed by connecting a wire from row 1 to any other row or rows in a single column. An example is shown in Figure 50. If the power switch is in position 2 then the relay connected to row 4 will be activated. If the power switch is in position 6 the relay in row 7 will be activated. Figure 51 shows exactly how the activation is accomplished:

Figure 51.—Relay Activation

The +V is applied by the power switch to row 1 and is transferred to the row in question (see above examples). It then passes down the gold contacts from the program board to the
Figure 50.—Picture of Typical Program
program switching matrix and through the diode to the respective relay coil. The purpose of the diodes becomes apparent when more than one relay is wired in a single column. When column 6 is activated then row 7 receives the +V and passes it along as described above. But a careful look at the program switching matrix shows that the diodes prevent this same +V from activating the relay in row 8. When the current passes down the gold contacts in row 7, column 1, it passes through the diode and along the wire under column 4. If the diodes were not there the current would pass up column 4 (as well as on along the wire to the correct relay) to the program board. It would then pass back along the wire on the program board (see Figure 50 again) and down the gold contact in row 8 or column 4, thus activating the relay in row 8 at the wrong time.

With this system of AMP connectors with diodes a set of nine relays can be activated one at a time, all nine at once or any combination of the nine.

The program of events can easily be varied by removing the previous set of gold contacts with connecting wires from the program board and replacing them with a new set of gold contacts with connecting wires to produce a different program.

The second major portion of this module is found in the Power Switch referred to earlier. Activating a relay (closing the contacts) is accomplished by a D. C. voltage applied to the coils of the relay which become magnetic and
in turn pull one contact down against the other. There is one serious problem in this simple looking switch. When the current surges through the coil as the relay is turned either on or off, a spike signal is transferred to the relay contacts. To eliminate this difficulty a simple damping circuit was added to the power voltage to reduce this "kick" in the relay coils. The circuit is shown below in Figure 52.

![Diagram of Relay Damping Circuit](image)

Figure 52.--Relay Damping Circuit

When the voltage, $+\overline{V}$, is large enough to turn the transistor on then the relay will also turn on but without the usual "kick".

As explained earlier in the section on cell control there is another part to this module. It is an inverter for the cell control module. It is located here rather than in the cell control box because of space limitations in the control box.

It is also important at this time to describe the $+6$ VDC power supply that was built to activate the relays. The circuit diagram is shown in Figure 53. Since each relay requires at least 6 VDC at 0.1 amperes the power supply was designed to regulate between 6 and 6.5 volts with a peak
Figure 53.—Schematic Diagram of 6 V.D.C. Power Supply

- **Trans.** = P-5015
- **R** = 25 ohms
- **T** = 2N3055
- **D** = 1N1805

- **C**<sub>1</sub> = 1000 µf, 15 VDC
- **C**<sub>2</sub> = 1000 µf, 15 VDC
- **C**<sub>3</sub> = 1000 µf, 15 VDC
current of one ampere.

Response

This module receives the signals from the cell control module via the trunk lines and processes them in any manner desired. This could include anything from a simple interface between the cell control module and a recorder to a complex square rooter, integrator or differentiator. The one designed and built at the present time is shown in Figures 54 and 55. It has two basic capabilities. The first is to receive the voltages from the electrodes being used and converts them into a form for display on an oscilloscope. The second part consists of an integrator to integrate the currents from either of the electrodes. The output signals were made available at the front of this module for easy access. There is a single function switch on the face of this module which selects between the following alternatives:

(a) both currents available directly
(b) $i_I$ available directly with integration of $i_{II}$
(c) reverse of (b)

Repairs

It has been the experience of this author that the modular arrangement of this instrument lends itself to ease of repair. Some typical problems will be covered to illustrate this point.

P - One signal generator will not step or will
Figure 54.—Schematic Diagram of Response Box

\[ R_1 = 10 \text{ k ohm} \quad C = 1 \text{ uf} \]
\[ R_2 = 100 \text{ k ohm} \]
\[ R_3 = 1 \text{ meg. ohm} \]
\[ R_4 = 100 \text{ meg. ohm} \]
\[ R = 100 \text{ k ohm} \]
\[ R_f = 50 \text{ ohm} \]
Figure 55.--Data Processor Module
step only sluggishly.

A - Relay contacts are defective, remove defective relay and replace with premounted new one.

P - One or both current amplifiers oscillates.

A - Contact between the cell and the control unit may be broken for any of the electrodes.

A - Impedence of the solution may contain too much capacitance. Try reducing the resistance of the current-to-voltage transducer. Another solution is to increase the capacitance of the current-to-voltage transducer.

P - All the relays are inoperative.

A - Relay power supply is inoperative.

A - Transistor damping circuit is inoperative.

As can be seen from these examples the use of modules inside of modules lends itself to quick repairs. When a small portion of a circuit becomes defective only that small portion needs to be replaced. In most instances this only requires removal of one circuit board and replacement by another.

As the instrument stands now particular points in a single module cannot be checked easily. A set of cables was prepared so that the two rear AMP connectors could be connected while the single module was out of the basic unit as shown in Figure 56:
Figure 56.—Repair Cables
Later these cables will be replaced by a special module that could be plugged into the basic 3 x 3 module. It would have the cables inside it and would allow a module that needed to be checked to be plugged into it as shown in figure below:

Figure 57.—Repair Module

Time Response Measurements

I-Dummy Cell Technic:

With the instrument in the four electrode potential control mode several measurements were made with a dummy cell. The response of the two excitation boxes was found to be 1 volt/millisecond when the potential-step mode was chosen. Also the two current amplifiers followed the
response of the excitations exactly. The fluctuations of the current amplifier (I) when excitation, $E_{II}$, was applied was found to be less than 0.5%. The same was found for current amplifier (II) when $E_I$ was applied.

II-Real Cell Technic:

A sample of Eu(III)-EDTA in acetate buffer solution was prepared and placed into the TLE cell. The response of current amplifier (I) was observed when $E_I$ was applied and the response of both current amplifiers (I) and (II) were observed when $E_I$ was applied (see Figure 58). The potentials of the two working electrodes are adjusted so that the reduction of Eu(III) to Eu(II) occurs at $W_I$ and the oxidation of Eu(II) back to Eu(III) occurs at $W_{II}$ when $E_I$ is applied.

Data Processing

There is one final portion to the instrumentation used in this research. A system of computer processing of the data was assembled to alleviate the time consuming process of removing data from the Polaroid pictures. The picture to be processed was placed on an X-Y recorder. The zero controls on the recorder were used to follow the tracing on the picture while the signals from the zero controls (e.g., slide wire signals) were fed into a digital voltmeter. The voltmeter converted the analog data in binary code which in turn was punched onto paper tape with the aid of a Digitec Punch Control unit and a Paper Punch. The X and Y components of points along the tracing on the picture were punched onto
Figure 58.—Current and Voltage Response of the Cell
Current of Generator versus Potential of Generator

Current of Probe versus Current of Generator
paper tape. The tape along with an appropriate program was taken to a Wang computer which has a teletype, punched paper reader. The data was then processed to give the desired result (i vs. t) on the output of the teletype. A block diagram of the data processing apparatus is shown below in Figure 59.

A sample piece of data, punched paper tape, and teletype output are shown in Figure 60.


Figure 60.— Illustration of Data Processing Technic
(a) - Polaroid Picture of Data
(b) - Punched Paper Tape of Data
(c) - Computer Output of Processed Data
(a) 

Graph showing a curve with zero current and a line indicating 20 milliseconds per division.

(b) 

Graph showing data points.

(c) 

Table showing data:

<table>
<thead>
<tr>
<th>T</th>
<th>T^{1/3}</th>
<th>1/i</th>
<th>1/i</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2027 sec</td>
<td>1.3011 sec^{1/3}</td>
<td>0.0506 ua</td>
<td>19.74 ua^{-1}</td>
</tr>
<tr>
<td>2.2392</td>
<td>1.3083</td>
<td>0.0780</td>
<td>12.81</td>
</tr>
<tr>
<td>2.2663</td>
<td>1.3135</td>
<td>0.1099</td>
<td>9.09</td>
</tr>
<tr>
<td>2.2933</td>
<td>1.3187</td>
<td>0.1605</td>
<td>6.23</td>
</tr>
<tr>
<td>2.3172</td>
<td>1.3233</td>
<td>0.2299</td>
<td>4.35</td>
</tr>
<tr>
<td>2.3353</td>
<td>1.3267</td>
<td>0.3176</td>
<td>3.15</td>
</tr>
</tbody>
</table>
EXPERIMENTAL

After the design and construction of the instrument was completed preliminary tests of the thin layer technic were made. Two serious problems were discovered. The first involved random 60 cycle noise from the thin layer cell and electrode arrangement. If capacitors were used to filter out the 60 cycle noise at the instrument the time response of the instrument would be greatly reduced. Therefore the problem was solved by placing the entire cell arrangement inside a large Faraday cage and grounding the cage.

The second problem appeared to be while noise of a random type (as opposed to the 60 cycle type). This appeared to be caused by vibration of the two mercury drops as they approached each other. This problem was solved by placing the cell arrangement and the Faraday cage surrounding it on a vibration-free bench. The bench consisted of a large concrete table top (about 200 lbs.) placed on two partially inflated inner tubes (see Figure 61).

The thin layer in this work was formed by two Smoler electrodes. The geometric and mathematical consideration for this cell geometry are covered in the Theory chapter. The tips of the Smoler electrodes were tapered to prevent the glass edges from interfering with each other as illustrated in Figure 62.
Figure 61.—Noise Isolation Apparatus
Figure 62.—A - Untapered DME's

Figure 62.—B - Tapered DME's
Electrodes and Cell Description

Simplified operation of this thin layer technic is obtained if the flow rates of the two Smoler electrodes are approximately equal (see Theory chapter). Therefore the flow rate of each DME was measured in a 0.1M KCl solution as a function of column height and is shown in Figure 63. A suitable common flow rate was chosen (0.5mg./sec.) and the column heights for the right and left hand electrodes were set at this value for every experiment.

The cell was all glass and "square" in design to provide maximum visibility for positioning the electrodes. The two Smoler electrodes, a Pt. auxiliary electrode, the salt bridge of an SCE reference electrode, and a fritted gas dispersion tube were positioned in the glass cell as shown in Figure 64. The top of the cell was covered with a cotton plug to prevent eddy currents from bringing air into the argon filled cell. No rigid form of closure was as effective as the cotton plug since the positions of the Smoler electrodes had to be altered during an experiment.

Characteristics of the Thin Layer

The thin layer of solution was created by positioning the two Smoler electrodes very close to one another. They were positioned in such a way that the two drops were in the exact same X-Y and X-Z planes along the same X axis (Y is the vertical axis, the Z axis projects above and below the paper, while X is the horizontal axis).
Figure 63.—Variation in Flow Rate With Variation in Column Height
FLOW RATE (mg./sec.)

- LEFT ELECTRODE
- RIGHT ELECTRODE

COLUMN HEIGHT (cm)
Figure 64.—Cell Diagram with Illustration of Electrode Arrangement
Gas Dispersion Tube

Salt Bridge

Glass Frit

Pt.

Glass Cell

DME's

Argon

Cotton

Glass Cell

Salt Bridge

Pt.

Rubber Stopper

Beaker

Satd. KCl Solution

KCl

Hg/Hg₂Cl₂

Hg

Front View

Side View
The space between the two electrodes, will vary during the drop life from $4r_f$ to zero (see Theory chapter) where $r_f$ is the final radius of each drop. The dependence of the thin layer dimensions and mathematical approximations necessary to obtain an expression for the current are discussed in the Theory chapter.

**Positioning of the Smoler Electrodes**

**Method 1:** It was discovered very quickly that the positioning of the two very small Hg. drops in close proximity to one another was not an easy task. Two technics are required. First the two electrodes could be clamped to two separate ring stands so that their capillary tips were close together on the X-axis and exactly opposite in the X-Y and X-Z planes. Then a screw device was attached to the two electrodes so that they could be pulled together along the X-axis by rotating the screw as shown in Figure 65. The difficulties of this method are evident when actual adjustments are made with the screw device. Many times in making this adjustment the position of the two drops is changed irreproducibly in either the Y- or Z-axis.

**Method 2:** The second solution to the positioning problem was more often used in this laboratory. This consists of first fastening one of the electrodes firmly to a ring stand. The second entire electrode assembly was also clamped to a ring stand which in turn was screwed to the top of an X, Y, Z translational stage. This translational stage was purchased
Figure 65.--Apparatus for Positioning Electrodes Method - 1
from Lansing Research Corporation and had the following specifications. Two type TR-132 Lansing Research Corporation Translational stages and one TR-183 Translational stage are stacked to give the X, Y, Z translation. The TR-132 and TR-183 stages have a minimum travel of 0.0001 inches and a maximum travel of one inch. The TR-183 stage has a maximum load of 10 lbs. while the TR-132 stages have a maximum load of 100 lbs. For further details consult Product Bulletin 65-2, Lansing Research Corporation, 705 Willow Avenue, Ithaca, New York, 14850. The diagram of the final electrode assembly is shown in Figure 66. The electrode on the left was positioned by hand (movement of the ring stand and clamp) to a position fairly close to the electrode on the right. Final positioning was accomplished with the X, Y, Z adjustment.

**Experimental Procedure**

The standard procedure followed for each experiment was as follows. A sample was prepared and placed in the cell. The two Smoler electrodes were inserted and the cell raised to a height sufficient to immerse the tips of the electrodes in solution. An agar-KCl salt bridge from an SCE reference electrode, a platinum auxiliary electrode, a gas dispersion tube, and a cotton plug are added to the cell in a manner so that they do not interfere with free movement of the Smoler electrode. After 10 to 15 minutes of deaeration with argon the thin layer electrochemical experiment is carried out.

Many different experiments can be accomplished with
Figure 66.—Apparatus for Positioning Electrodes Method - 2
clamp

Ring Stand

Ring Stand Base

Y' Trans. Stage

Y' Translational stage

Z' Trans. Stage

micrometer spindle

X' Trans. Stage
the Twin DME Thin Layer cell. The experiments used by this
author are discussed below and labeled with titles so that
they can be easily referred to in subsequent chapters.

**Potential Step Technic**

The thin layer cell is prepared as described earlier. The
instrument is connected to the cell with the cell leads.
Two Tektronix 564 storage oscilloscopes are connected to the
output of the current amplifier connected to the probe working
electrode. The entire $i$ vs. $t$ curve is recorded as one scope
while only the last 25% or less of the curve is recorded on
the second scope. In this way the entire signal as well as
an expanded version of the final portion is recorded for the
same drop cycle. This is done to eliminate effects of irre­
producible growth characteristics of the two DME's on the
measurement of $t_r$ and $t_k$. The potential of the probe is adjusted
to a value to give a minimum background current when the gener­
ator is held at a value on the foot of the polarographic wave
of the substance in solution that is to be studied. As the
drops grow toward each other the potential of the generator
is stepped to a value on top of the polarographic wave. A
polaroid picture is then taken of the expanded scale data.

**Potential-Drop Technic**

The thin layer is prepared and the data is recorded
as described above. The only difference involves when the
potential of the generator is stepped from the foot to the
top of the polarographic wave. In the Potential-Step technic
this is done during the growth of the drops before they touch. In this method (Potential-Drop technic) the potential is applied continuously throughout the drop life.

The thin layer cell is prepared and the data is taken by either the Potential-Step technic or the Potential-Drop technic. The position of the tips is altered (moved closer or farther away) so that the time it takes for the drops to touch is altered \( t_f \) is varied.

**Chemicals and Reagents**

All the chemicals in this work were of ACS approved reagent chemicals. All of the glassware was of Kimax grade A quality volumetric glassware. The preparation of solutions followed standard analytical practices.

The aqueous nickel solutions were prepared by taking aliquote of a stock 0.1M NiCl\(_2\) solution that was not standardized. The aliquot of the nickel solution was then added to a 100ml volumetric flask. If a buffer was used an aliquot of a stock buffer solution was added and the final pH of the 100ml solution checked for accuracy of dilution. If a separate supporting electrolyte or complexing agent was needed it was added as a solid and dissolved before dilution to 100mls.

The nonaqueous nickel solutions were prepared differently. The complexing agent was dissolved in the appropriate amount of organic solvent. The supporting electrolyte was added and dissolved. If a buffer was needed it was also added.
as an aliquot from a stock solution. This solution was then transferred to a 100 ml volumetric flask and diluted to the mark. The 100 mls was then transferred to the cell and the background signal was observed. Then an aliquot of the 0.1M NiCl₂ solution was added. This causes an approximately 10 to 20% uncertainty in the concentration of all the electroactive species since it is impossible to quantitatively transfer the 100mls from the volumetric flask. The amount of error was believed to be justifiable since this portion of the research is of a qualitative nature. We were only interested in determining if these solutions would produce solution soluble reduction products and we were not interested in quantitatively how much would be produced.

The azobenzene solutions were prepared somewhat more accurately. An aliquot of 95% ethyl alcohol was added to a 100ml volumetric flask. Then 1 ml of a stock solution of 40mM azobenzene was added. The appropriate amount of dry NaClO₄, and an aliquot of 6M HClO₄ were also added. After the NaClO₄ was dissolved the solution was diluted to the mark with water and added directly to the electrochemical cell.

The europium solutions were prepared in the same manner as the aqueous nickel solutions but with the Eu(III) was added before dilution to the mark. Here also it was not necessary to run a background sample every time.
RESULTS AND DISCUSSION

Technic Verification

In the Theory chapter several alternatives were presented in solving the diffusion problem concerned with the use of twin DME's in TLE. The analysis of the problem of spherical diffusion to spherical electrodes indicated that a rigorous solution was too difficult for a preliminary analysis of this technic (twin DME's in TLE). The simplest equation (34) derived in the Theory chapter was arrived at when planar approximations were made (assuming the two DME's are two planar electrodes). In order to verify equation 34 the Nu(III)/Eu(II) - EDTA couple was chosen as a model system with both oxidation states soluble in the solution phase. Solutions were prepared as described in the experimental chapter and a polarogram was taken to establish the diffusion current, $i_d$, and the half wave potential, $E_1$. Then a series of thin layer electrograms was taken using the Potential-Step technic to verify the above mentioned equation.

Examples of data taken under three different circumstances are plotted in Figures 67 through 69. Figure 67 shows how this type of plot ($1/i$ vs $l$) appears when the potential is stepped late in the growth of the drop ($t_f - t_s = 1$sec.)
Figure 67.—Current vs Time Plot
Figure 68.—Current vs Time Plot
Figure 69.--Current vs Time Plot
\[ \frac{1}{i} \text{ (microamperes}^{-1}) \]

\[ (t_f - t_s) = 6 \text{ minutes} \]

\[ t^{1/3} \text{ (seconds}^{1/3}) \]

\[ \lambda \text{ (microns)} \]
while Figure 69 shows how the plot changes when the potential
is stopped many cycles \((t_f - t_s = 6\text{min.})\) before the data is
recorded. The "loss" of data along the linear portion of the
plot is probably due to some type of diffusion layer collapse.
The non-linear portion where the DME's are widely separated
is due to the hydrodynamics of the solution between the two
drops. At some point as the drops approach each other the
space between them is disturbed by a flow of material (stream­
ing) from the bulk solution down through the thin layer
causing a loss of oxidizable product in the thin layer. The
non-linear region of the \(1/1 \text{ vs } l\) plot in the region of close
spacing between the two drops is due to one of several reasons.
One of the most significant reasons is that the planar approp­xi­mation does not hold at very close spacing. As mentioned in
the Theory chapter the steady state approximation to the cur­rent will only hold at electrode spacings of about 0.3 microns
or less but obviously there will be a region in which a com­bination of the planar approximation and the steady state
approximation will hold. The same data that was used with
the planar approximation was taken and used with equation 12
derived for the steady state approximation. The resulting
plot is shown in Figure 70. The figure illustrates that the
current is approaching a steady state but never quite reaches
that point before the thin layer collapses.

Another possible reason for a decrease in the current
at close spacing is due to electrostatic repulsion or attraction
(depending on the charge on the two drops) of the drops toward
Figure 70.—Plot of Current as it Approaches Steady-State
$\frac{1}{i}(\text{microamperes}^{-1})$

$0$ $1.0$ $2.0$ $3.0$

$0$ $0.1$ $0.2$

$\frac{i+\frac{i^2}{i}}{i^2}$

$\text{I}$

$138$
each other. But this does not occur except at distances of 0.1 to 0.2 microns. Also hydrodynamics might effect the drops at close spacing. Convection interaction counter-balanced by resistance to sheer or adjacent layers of ions near the surface of the drops combine to slow the approach of the two drops as well a flattening type of distortion of the drops as they grow together.

The slope of the plots of Figures 67 through 69 give an area of $5 \times 10^{-6}$ cm$^2$ (assuming an average diffusion coefficient of $0.4 \times 10^{-5}$ cm$^2$/sec. and with known values of $m$ and $n$). A quick calculation of the total surface area of the probe electrode gives:

$$A_T = 4\pi r^2$$

$$= 1 \times 10^{-2} \text{ cm}^2$$

This means that only 1/2000th of the total surface area of the drops is involved in the thin layer cell. With this fact in mind it is easily understood why the planar approximation does hold in this region of $\theta$.

An attempt was made to relate the area term, $A$, in equation 34 to the drop time, $t_r$. With the use of the DME-Tip Adjustment technic a series of TLE's was taken at different $t_r$ values. A plot of the data is shown in Figure 71. Due to the large scatter observed in the plot it is difficult to
Figure 71. -- Plot of Electrode Area vs Drop Time
draw any firm conclusions. It is reasonable to assume that since the total surface area of the probe is related to the radius of the drop (or $t_f$) then that area comprising the thin layer should also be proportional to $t_f$. Either the relationship is more complex than a simple power function or the reproduceability of the experiment is very poor. The only thing that can be concluded from this data is that the area seems to decrease as $t_f$ decreases.

Equation 34 is further verified when a series of experiments is made by varying the bulk concentration of Eu(III). The equation indicates that a plot of $1/\lambda$ vs. $1/C^0$ should give a slope which is inversely proportional to $C^0$, the bulk concentration of the oxidized species. Figure 72 shows a plot of $C^0$ (the Eu(II) concentration) versus $1/\lambda$. The expected behavior is observed from 0 to 5mM Eu(III) with a zero-zero intercept. The data is summarized in Table 2. The current at the generator electrode was also checked to insure that the current was diffusion controlled. The resulting data is shown in Figure 73.

The variation in current at the probe with variation in the bulk concentration of Eu(III) shows that this technic can be used to determine concentrations. The apparent limitation of the technic (determination of concentrations of materials that have solution soluble products) can also be a liability. For example, if it was necessary to determine small amounts
Figure 72.—Plot Showing Linear Relationship Between Current and Concentration in Thin Layer
\[ \frac{1}{s} \propto c^0 \]
<table>
<thead>
<tr>
<th>1/Slope</th>
<th>C°(EuIII)</th>
<th>1/Slope/C°</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.9x10^-3 ua-sec^1/3</td>
<td>0.95mM</td>
<td>0.95x10^-3ua-sec^1/3mM^-1</td>
</tr>
<tr>
<td>1.84x10^-3</td>
<td>1.90</td>
<td>0.97x10^-3</td>
</tr>
<tr>
<td>2.70x10^-3</td>
<td>2.80</td>
<td>0.96x10^-3</td>
</tr>
<tr>
<td>3.63x10^-3</td>
<td>3.70</td>
<td>0.98x10^-3</td>
</tr>
<tr>
<td>4.83x10^-3</td>
<td>4.60</td>
<td>1.05x10^-3</td>
</tr>
</tbody>
</table>

Average = 0.98±0.03x10^-3
Figure 73. -- Plot of Polarographic Current vs Concentration
of Eu(III) in the presence of large amounts of Cd(II) it would be difficult by such methods as polarography since the half wave potentials for the reduction of the two metal ions are very close to one another. But with TLE the concentration of Eu(III) could be determined by observing the oxidation current of Eu(II) at the probe after the reduction of Eu(III) to Eu(II) and Cd(II) to Cd(Hg) at the generator. The accuracy of the measurement is about 0.5% at the 1mM concentration level and about 2 to 5% in the 0.1mM concentration level. As the concentration gets smaller the error gets larger due to the fact that the current response at the probe is about 0.1 to 0.5ua (for 1mM) while the noise level is a constant 5 to 10 nanoamperes.

**Kinetic System**

Several different systems were investigated in order to find a model (pseudo-) first order kinetic reaction to study and compare with the literature. The reactions of the desired system had to follow the schemes shown below:

\[ A + \text{ne} \quad \text{fast} \quad B \]  \hspace{1cm} \text{(Electrode Reaction)}

\[ B + C \quad k \quad D \]  \hspace{1cm} \text{(Kinetic Reaction)}

or

\[ B \quad k \quad E \]  \hspace{1cm} \text{(Kinetic Reaction)}

\[ B \quad \text{fast} \quad A + \text{ne} \]  \hspace{1cm} \text{(Electrode Reaction)}

A is reduced to B at the generator electrode followed by a kinetic reaction of B in the solution phase. The probe electrode is then used to measure either the amount of unreacted B after the reaction has progressed for a certain length of time or the
amount of product D or E formed during that length of time. Obviously one strict requirement is that either the product B of the electrode reaction or the product D or E of the kinetic reaction must be electro-inert at the potential of the probe. The reaction rate must be relatively fast since the kinetic window is limited to one drop time cycle. Therefore for maximum sensitivity the half life of B should be less than 2 - 3 seconds.

Two kinetic reactions were attempted using Fe(III) as the starting material, A. One reaction is coupled with H₂O₂ and the other is coupled with NH₂OH:

$$\text{Fe(III)} + n \text{e} \rightarrow \text{Fe(II)} \quad \text{(Electrode Reaction)}$$

$$\text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} \quad \text{(Kinetic Reaction)}$$

$$\text{Fe(II)} + \text{NH}_2\text{OH} \rightarrow \text{Fe(III)} \quad \text{(Kinetic Reaction)}$$

References concerning these reactions indicated that the reactions indicated that the reactions may be feasible on the slow end of the kinetic window but preliminary studies indicated that only additions of 5 to 10 M in H₂O₂ or NH₂OH would speed up the reaction rate enough to make measurements with this technic (TLE) useful.

The exchange reaction of Ca(II) with Eu(II)-EDTA seemed to be a model system to study also:

$$\text{Eu(III)}\text{-EDTA} + e \rightarrow \text{Eu(II)}\text{-EDTA}$$

$$\text{Eu(II)}\text{-EDTA} + \text{Ca(II)} \rightarrow \text{Eu(II)} + \text{Ca(II)}\text{-EDTA}$$
It was thought that the potential could be set at a value to oxidize all the unreacted Eu(II)-EDTA and not oxidize any of the free Eu(II). When the experiment did not give the desired result it was believed that the following reaction was occurring at the probe:

\[ \text{Eu(II)} + \text{EDTA} + e \longrightarrow \text{Eu(III)-EDTA} \]

thus altering the rate of the kinetic reaction and defeating the purpose of the experiment.

The final model system to be studied was the benzidine rearrangement of hydrazobenzene with perchloric acid. The products of the kinetic reaction were found to be inert to the potential of the probe electrode and the rate constant was adjusted to the kinetic window by increasing the H\(^+\) concentration.

Figure 74.—Overall Kinetic Reaction

The above chemical equation (Figure 74) shows the two major reactions involved. The first part of the reaction (the reduction) occurs at the generator electrode. The hydrazobenzene then diffuses away from the surface of the generator.
electrode and the second part of the above reaction occurs. All of the hydrazobenzene that has not reacted when the surface of the probe is reached is immediately reoxidized back to azobenzene.

The conditions found for this experiment are as follows: 25 wt.% ethanol, 0.25 to 0.90 M perchloric acid, ionic strength of 1.24 adjusted with sodium perchlorate, and 0.4 mM azobenzene. An example of the current-time curves taken with the Potential-Step technic are shown in Figure 75. The time, $t_k$, during which the kinetic reaction occurs was varied by stepping the potential of the generator at different times during the growth of the drops. If the potential is stepped early in the growth of the drops the hydrazobenzene has a long time to react before it reaches the surface of the probe and the resulting anodic current is small. If the potential is stepped late in the growth of the drop the reaction has less time to occur so that the current at the probe is higher.

The data was then fitted to the model kinetic reaction described in the Theory chapter with the use of equation 33. A plot of a representative set of data is shown in Figure 76. The shape of the curves is explained as follows. In the absence of kinetics (Eu-EDTA) the shape of the $1/i$ vs $i$ plot gave two non-linear portions around a linear portion. The $\ln (1/i)$ vs $t$ of this data would give a plot like that shown below in Figure 77.
Figure 75.—Illustration of Current Response of the Probe for Different Kinetic Times, $t_k$
100 nanoamperes/division
Figure 76.—Typical Plot of Kinetic Currents

vs Kinetic Times
Figure 77.—Diffusion Controlled Current with no Kinetics

The y-axis goes to a minimum for some portion of the data and is preceded and followed by two non-linear portions. The kinetic plots (like the one shown in Figure 26) are shaped exactly like the non-kinetic plots except that there is less linear area to the plot. The kinetic plot still goes through a minimum and it is this minimum that is plotted versus $t_k$. This is valid since the minimum of the plot of $\ln(i/\lambda)$ vs $t_k$ (or the slope of the plot of $1/i$ vs $\lambda$) is proportional to the concentration of the unreacted reduced species in the thin layer at that time.

Table 3 shows a series of data on this kinetic system (hydrazobenzene) and a plot of this data is shown in Figure 78. The two proton dependence of the rate found by other authors is observed in the slope of this plot. Figure 79 illustrates how the rate is affected by the change in the ionic strength of the solution. At the concentration level used here (> 0.6M) the usual quantitative theories cannot be applied but a qualitative discussion is warranted. Since the rate of the reaction increases with increasing ionic strength the charges
TABLE 3
25 WT. 90 ETHANOL; 1.24M TONIC STRENGTH; 0.4mM AZOBENZENE

<table>
<thead>
<tr>
<th>$c_{HClO_4}$</th>
<th>log $k$</th>
<th>$-\log (H^+)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.24M</td>
<td>-0.33</td>
<td>0.62</td>
</tr>
<tr>
<td>0.48</td>
<td>0.22</td>
<td>0.32</td>
</tr>
<tr>
<td>0.60</td>
<td>0.50</td>
<td>0.22</td>
</tr>
<tr>
<td>0.78</td>
<td>0.57</td>
<td>0.11</td>
</tr>
</tbody>
</table>
Figure 78. -- Variation in k vs Concentration of Perchloric Acid in 25 wt. % Ethyl Alcohol
Figure 79.—Illustration of Ionic Strength
Effects of the Rate Constant 0.4 mM
Azobenzene; 0.60 M HClO₄;
25 Wt. % Ethanol
Ionic Strength vs. Log (k)
on the primary reacting species must be the same. This means that the slow step in the reaction must be something like the following (Figure 80):

\[ \text{Figure 80.—Primary Kinetic Step} \]

The solvent effect on the rate of the reaction was very small as shown in Figure 81. One author's explanation for this type of behavior goes as follows. As the ethanol concentration increases the dielectric constant of the solution decreases causing a decrease in the rate of the reaction. This decrease is counter-balanced by the fact that \( \text{CH}_3\text{CH}_2\text{OH}^+ \) is a "better acid" than \( \text{H}_3\text{O}^+ \) and therefore an increase in the ethanol concentration increases the rate of the reaction.

One final check of the technic was made by duplicating two samples reported by Schwartz and Shain. The comparison of the data obtained on these two samples is shown in Table 4.

The use of TLE to measure kinetic reactions similar to those presented here appears to be a favorable method over indirect methods of the type used by Schwartz and Shain. Those authors used a technic (potential reversal) which was inherently less accurate than TLE due to the greater number of measurements that were required to obtain the rate constant. Other authors due to the limitations of their technics were
Figure 81.—Solvent Effect on Rate Constant at I=1.24 and 0.6M HClO₄
<table>
<thead>
<tr>
<th>CHClO₄</th>
<th>$k_{Shain}$</th>
<th>$k_{Rose}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1M</td>
<td>3.0 sec.⁻¹</td>
<td>3.4±0.5 sec.⁻¹</td>
</tr>
<tr>
<td>1.2M</td>
<td>4.5 sec.⁻¹</td>
<td>4.2±0.2 sec.⁻¹</td>
</tr>
</tbody>
</table>
only able to measure rate constants of up to 0.1 sec.\(^{-1}\)
while in this work rate constants of 50 times that have been
measured with only preliminary refinements to the technic.
Future refinements of the technic of TLE will be longer drop
times for measurement of slower reactions, faster drop times
and more accurate measurements of \(t_k\) for faster rate constants.

**Lower Valence Nickel Species**

Due to the interest exhibited by numerous authors
in the existence of lower valence metal ions, the reductions
of various Ni(II) complexes were studied. The solutions of
Ni(II) in saturated CaCl\(_2\), 0.15M NaCN, 0.1M pyridine/pyridinium
chloride, and 90% pyridine with 0.1M NH\(_3\)/NH\(_4\)NO\(_3\) were prepared
as described in the Experiment chapter. The polarographic
data for these four solutions are summarized in Table 5, while
sample polarograms are shown in Figures 82 through 85. With
the aid of the Potential-Step technic TLE data on the four
solutions was also taken. No anodic current was observed at
the probe electrode in the two pyridine solutions when the
potential of the generator was stepped to a value cathodic
enough to reduce the Ni(II) pyridine complex. This indicated
that the reduction proceeded as follows:

\[
\text{Ni(II)} + 2e \rightarrow \text{Hg} \rightarrow \text{Ni(Hg)}
\]

Small anodic currents (about 10\(\text{a}\)) were recorded at the probe
in the Cl\(^-\) media at all potentials of the probe less cathodic
than the reduction of Ni(II) (Figure 86). This indicated that
a very small amount of lower valence nickel was present in the
<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{1/2}$</th>
<th>$i_d/C_{Ni}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>satd' CaCl$_2$</td>
<td>-0.410 volts</td>
<td>0.66na/mM</td>
</tr>
<tr>
<td>0.15M NaCN</td>
<td>-1.284</td>
<td>2.50</td>
</tr>
<tr>
<td>0.1M py./py.Cl</td>
<td>-0.549</td>
<td>2.60</td>
</tr>
<tr>
<td>90 % py. in 0.1M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH$_3$/NH$_4$NO$_3$</td>
<td>-0.737</td>
<td>1.40</td>
</tr>
</tbody>
</table>
Figure 82.—Polarogram of Ni(II) in CaCl₂
5 mM NiCl₂; 6 M CaCl₂
Figure 83.—Polarogram of Ni(II) in NaCN
5 mM NiCl₂; 0.5 M NaCN
Current (microamperes)

-0.800
-1.200
-1.600

Volts vs SCE
Figure 84.—Polarogram of Ni(II) in Aqueous Pyridine
5 mM NiCl₂; 0.1 M Pyridine/Pyridinium Chloride
Current (microamperes)
Figure 85.—Polarogram of Ni(II) in Nonaqueous Pyridine 5 mM NiCl₂; 90% Pyridine
Figure 86.—TLE of Nickel in CaCl₂ Probe Potential -0.3 Volts
solution near the generator but due to the "large" noise level (about 5na) it was impossible to make any further conclusions about the identity of these lower valence species. The one conclusive fact discovered by this experiment is that the large evidence found by some authors$^{60,61,62,63,64,65,66,67,68}$ for the existence of solution-soluble lower valence species or major reduction products is not found here. Those authors used Kalousek commutators$^{69}$ to study the reduction process. The commutator switches the potential of the DME from the top of the reduction wave to values less cathodic than the reduction wave and observe the resulting currents. In this way not only the reduction current is recorded but also the reoxidation of the products is also observed. The only disadvantage to the technic is that no distinction can be made between solution soluble and Hg soluble reduction products. It is now evident from our experiments in TLE that the anodic current observed with the Kalousek commutator is due mainly to the reoxidation of the nickel in the mercury and not to the reoxidation of solution-soluble Ni(0) in saturated CaCl$_2$ media.

The reduction of Ni(II) in cyanide media has been studied extensively by Vlcek.$^{66,67}$ He reported that the overall reduction of Ni(II) in solutions which contained more than 4(CN)'s per Ni(II) involves two electrons. This is consistent with our data since the reduction of Ni(II) in pyridine must involve two electrons$^{65}$ and the good agreement between $i_d/C_{Ni}$ for the aqueous pyridine and cyanide solutions verifies that an equal number of electrons is involved in both reactions.
With the use of the Kalousek commutator, Vleck reported one continuous two electron redox wave at about -1.2 volts vs SCE and a separate anodic wave at about -0.8 volts. He stated that the cathodic wave at about -1.2 volts is due to the following:

\[
\text{Ni(CN)}_4^{2-} + 2e \rightarrow \text{Ni(CN)}_4^{4-}
\]

and the anodic portion at -1.2 volts was:

\[
\text{Ni(CN)}_4^{4-} \rightarrow \text{Ni(CN)}_4^{2-} + 2e
\]

He concluded that the more anodic wave at -0.8 volts was due to the oxidation of a species formed by the dimerization of a reduction intermediate, monovalent nickel:

\[
\text{Ni}_2\text{(CN)}_6^{4-} + 2\text{CN}^- \rightarrow 2\text{Ni(CN)}_4^{2-} + 2e.
\]

He made this conclusion after producing the dimer in solution by the reduction of Ni(II) with sodium amalgam. The anodic wave for the dimer formed by Na(Hg) reduction appeared only 50 mv more anodic than the proposed dimer formed in the Kalousek experiment.

With the use of TLE a small anodic current (Figure 87), equivalent to 1/200 the Ni(II) reduced, was recorded at the probe when the potential of the probe was held at -1.0 volts. When the potential of the probe was moved to -0.6 volts a very large anodic current was recorded (about 3 micro-amperes). It follows then that the current observed at -0.6 volts which accounts for more than half the Ni(II) reduced
Figure 87.—TLE of Nickel in NaCN Probe Potential -1.0 Volts
10 nanoamperes/division

20 milliseconds/division
is probably the reoxidation of a nickel zero complex to divalent nickel. This means that Vlcek's data must follow the scheme:

$$
\begin{align*}
\text{Ni(Hg)} & \longrightarrow \text{Ni(II)} + 2e \quad \text{at -1.0 volts} \\
\text{Ni}(0) & \longrightarrow \text{Ni(II)} + 2e \quad \text{at -0.6 volts.}
\end{align*}
$$

A coulometric determination at a stirred Hg pool of the overall reduction of Ni(II) followed by an analysis of the Hg for Ni content would show how much of the nickel goes into the Hg and how much of the nickel undergoes further reaction in the solution phase (such as dimer formation). This naturally assumes that the coulometric reaction will proceed exactly like the TLE reaction.

Reduction in the Presence of Organic Ligands

It was decided to investigate the reduction of nickel in the presence of some multicyclic organic ligands due to the reported evidence of lower valence nickel reduction products formed in the presence of these ligands.\textsuperscript{61-68} Two typical multicyclic ligands were chosen for this work, 2,2'-bipyridine and 1,10-phenanthroline. Table 6 shows the polarographic data for the two ligands in the absence and presence of nickel in both buffered and unbuffered media. The TLE data for the solutions listed in Table 6 was found to be very complex. Some typical responses were as follows:

1) No current response --- adsorption

2) Large currents --- either streaming or large catalytic effects

3) Irradic currents --- gaseous evolution causing disruption
### TABLE 6

**90% ETHANOL, 0.1M NH₂/NH₄NO₃, 20mM LIGAND, 5mM METAL**

<table>
<thead>
<tr>
<th>Solution</th>
<th>E₁/₂</th>
<th>i₂d</th>
</tr>
</thead>
<tbody>
<tr>
<td>2, 2'-bipyridine</td>
<td>-1.2 volts</td>
<td>-46ua</td>
</tr>
<tr>
<td>+ Nickel</td>
<td>-1.2</td>
<td>23</td>
</tr>
<tr>
<td>1, 10-phenanthroline</td>
<td>-1.2</td>
<td>23</td>
</tr>
<tr>
<td>+ Nickel</td>
<td>-1.3</td>
<td>19</td>
</tr>
<tr>
<td>Nickel alone</td>
<td>-0.75</td>
<td>12</td>
</tr>
</tbody>
</table>

**90% ETHANOL, 0.5M LiCl, 20mM LIGAND, 5mM METAL**

<table>
<thead>
<tr>
<th>Solution</th>
<th>E₁/₂</th>
<th>i₂d</th>
</tr>
</thead>
<tbody>
<tr>
<td>2, 2'-bipyridine</td>
<td>-1.8</td>
<td>80</td>
</tr>
<tr>
<td>+ Nickel</td>
<td>(a)-1.3</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>(b)-1.6</td>
<td>40</td>
</tr>
<tr>
<td>1, 10-phenanthroline</td>
<td>-1.6</td>
<td>100</td>
</tr>
<tr>
<td>+ Nickel</td>
<td>(a)-1.25</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>(b)-1.55</td>
<td>20</td>
</tr>
<tr>
<td>Nickel alone</td>
<td>-1.05</td>
<td>9</td>
</tr>
</tbody>
</table>
of the thin layer (see Figure 88).

It was impossible to make any conclusions about the reduction of nickel in the presence of these two ligands due to the inability of the probe to distinguish between the many substances formed in the overall reduction process.

In conclusion it is believed from the polarographic data alone that the reduction of the nickel ion itself does not account for the overall reduction behavior. The ligands alone both reduce to give radical anions which apparently reduce the H_2O to form H_2. The fact that the \( E_{1/2} \) values for the reduction of the ligands do not shift appreciably when Ni(II) is added indicates that the reduction is of the ligand even when nickel is present. This is especially so since the \( E_{1/2} \) for the reduction of the Ni(II) tris complex of the ligands should be reduced at a less cathodic value (-1.0v) that is found here.

\[
E_{1/2} = E_0 - \frac{2.3RT}{nF} \log (K_f)
\]

The diffusion currents are all too large to be related to only the reduction of nickel (see Table 5 for Ni(II)/NH_3 complex). On the basis of this analysis we do not believe it necessary to postulate lower valence nickel species in order to describe the polarographic and TLE behavior of Ni(II)bipyrr.3 and Ni(II)o-phen.3 complexes.
Figure 88.—Typical Current vs Time Response of Organic Ligands
Adsorption

Streaming

Hydrogen Evolution
Prewave Phenomenon

One additional area of interest was studied to see if TLE could give additional information about the reduction processes involved. The reduction of nickel in thiourea yields three separate polarographic waves. One author attributed the first two waves to surface adsorbed species such as:

$\text{Ni(H}_2\text{O)}_5\text{Tu}^{2+}$

and kinetics of formation of such adsorbed species. A TLE experiment on this system yielded no indication of any solution soluble species from any of the three reduction waves. This seems to support the conclusions found by the above authors in that the nickel is adsorbed on the surface of the electrode and the reduced nickel species upon further reduction are more likely to go into the electrode rather than away from the electrode.

Evaluation of the TLE Technic

We have applied twin electrode thin layer electrochemistry to several areas of chemistry in an attempt to show how this technic can be useful in studying electron transfer reactions. We have shown the quantitative utility of TLE in determining concentrations with the Eu(III)/Eu(II)-EDTA couple at the 0.1mM concentration level. The technic also produced good quantitative results when applied to kinetic reactions which follow electron transfer reactions (benzidine rearrangement). Our kinetic data agreed with
literature values which were found by separate technics and also indicated that TLE can measure first order rate constants as fast as 5 to 10 sec.\(^{-1}\) with the present electrodes and cell arrangement. When applied to the study of electron transfer reactions which may or may not produce unstable products TLE has given information about the quantity of unstable product formed as well as an estimate of the maximum lifetime. In two examples it was firmly established that no lower valence solution soluble products were formed (both pyridine solutions). In two other examples it was established that there were at least some solution soluble lower valence species formed (Cl\(^{-}\) and CN\(^{-}\) media). Further investigation into the electron transfer reactions of these latter two examples was not pursued since the purpose of this work was to qualitatively investigate a variety of systems in order to establish the breadth of the application of this technic. Further experiments were described but they were not believed to be within the scope of this work.

When TLE was applied to the reduction of nickel in the presence of organic ligands this technic was found to give qualitative evidence concerning such physical phenomenon as streaming, adsorption, and catalytic reduction of H\(_2\)O. Since these observations lead to the conclusion that the reduction of nickel ions had little to do with the overall electron transfer reaction further experiments could be
made in an apodic solvent in an attempt to eliminate some of these physical phenomenon. This also was not believed to be within the scope of this work.


58 Schwarz, W. M., and Shain, I., op. cit.


APPENDIX

Derivation of the general expression for the flux at an electrode from page 38.

\[ \frac{d \Phi}{dx} = -q \alpha e^{-qx} + q \beta e^q \]

\[ \frac{d \Phi}{dx} \bigg|_{x=0} = -q \alpha + q \beta \]

\[ \frac{d \Phi}{dx} \bigg|_{x=l} = -q \alpha e^{-ql} + q \beta e^{ql} \]

\[ \alpha = \beta - \frac{1}{q} \left( \frac{d \Phi}{dx} \right) \bigg|_{x=0} \]

\[ \beta = \left( \frac{d \Phi}{dx} \right) \bigg|_{x=0} e^{-ql} - \left( \frac{d \Phi}{dx} \right) \bigg|_{x=l} \]

\[ \Delta \Phi = \left\{ \frac{1}{q} \left[ \left( \frac{d \Phi}{dx} \right) \bigg|_{x=0} \left( e^{-ql} - e^{ql} \right) \right] - \left( \frac{d \Phi}{dx} \right) \bigg|_{x=l} \left( e^{-ql} - e^{ql} \right) \right\} e^{-qx} + \left[ \left( \frac{d \Phi}{dx} \right) \bigg|_{x=0} \left( e^{-ql} - e^{ql} \right) \right] e^{ql} - \left( \frac{d \Phi}{dx} \right) \bigg|_{x=l} \left( e^{-ql} - e^{ql} \right) e^{ql} \]
\[ \Delta \bar{\Phi}_h = \frac{1}{q(e^{-q^2} - e^{-q^2})} \left\{ \left[ e^{-q(\lambda + x)} - e^{-q(\lambda + x)} + e^{-q(\lambda - x)} - e^{-q(\lambda - x)} \right] \left( \frac{d\bar{\Phi}}{dx} \right)_{x=0} \right\} - \\
\left[ e^{-q^2} + e^{q^2} \right] \left( \frac{d\bar{\Phi}}{dx} \right)_{x=1} \]

\[ \Delta \bar{\Phi}_h = \frac{1}{q} \left[ \frac{e^{-q(\lambda - x)} + e^{-q(\lambda - x)}}{e^{-q^2} - e^{-q^2}} \right] \left( \frac{d\bar{\Phi}}{dx} \right)_{x=0} - \\
\left[ \frac{e^{-q^2} + e^{q^2}}{q(e^{-q^2} - e^{-q^2})} \right] \left( \frac{d\bar{\Phi}}{dx} \right)_{x=1} \]

redefine \( q = \frac{(p + x^2 h)^{1/2}}{D^2} \)

\[ (\Delta \bar{\Phi}_h)_{x=0} = \frac{D^{1/2}}{(p + x^2 h)^{1/2}} \left[ \left( \frac{e^{-q^2} + e^{q^2}}{e^{-q^2} - e^{-q^2}} \right) \left( \frac{d\bar{\Phi}}{dx} \right)_{x=0} \right] - \\
\left( \frac{2}{e^{-q^2} - e^{-q^2}} \right) \left( \frac{d\bar{\Phi}}{dx} \right)_{x=1} \]

\[ (\Delta \bar{\Phi}_h)_{x=1} = \frac{D^{1/2}}{(p + x^2 h)^{1/2}} \left[ \left( \frac{e^{-q^2} + e^{q^2}}{e^{-q^2} - e^{-q^2}} \right) \left( \frac{d\bar{\Phi}}{dx} \right)_{x=0} \right] - \\
\left( \frac{e^{-q^2} + e^{q^2}}{e^{-q^2} - e^{-q^2}} \right) \left( \frac{d\bar{\Phi}}{dx} \right)_{x=1} \]

\[ \frac{(p + x^2 h)^{1/2}}{D^{1/2}} (\Delta \bar{\Phi}_h)_{x=0} = A \left( \frac{d\bar{\Phi}}{dx} \right)_{x=0} - B \left( \frac{d\bar{\Phi}}{dx} \right)_{x=1} \]
There is a complimentary form of this equation at \( x=0 \) but only one is needed.
Since
\[(\Delta \Phi^h)_{x=0} = \sum_g a_{gh} (\Delta \overline{c}_g)_{x=0}\]
and
\[(\Delta \Phi^h)_{x=0} = \sum_g a_{gh} (\Delta \overline{c}_g)_{x=0}\]
then
\[(\frac{\partial \Phi^h}{\partial X})_{x=0} = (p + \chi h)^{\frac{1}{2}} \sum_g a_{gh} (\Delta \overline{c}_g)_{x=0} - \frac{2}{e-qk - ek} \sum_g a_{gh} (\Delta \overline{c}_g)_{x=0}\]
Define
\[(\overline{J}_f)_{x=0} = -D \sum_h b_{hf} (\frac{\partial \Phi^h}{\partial X})_{x=0}\]
\[(\overline{J}_f)_{x=0} = D^{\frac{1}{2}} \sum_h (p + \chi h)^{\frac{1}{2}} \sum_g a_{gh} b_{hf} (\Delta \overline{c}_g)_{x=0} - \frac{2}{e-qk - ek} \sum_g a_{gh} b_{hf} (\Delta \overline{c}_g)_{x=0}\]
\[(\overline{J}_f)_{x=0} = -D^{\frac{1}{2}} \sum_h \frac{e-qk + ek}{e-qk - ek} \sum_g (\Delta \overline{c}_g)_{x=0} k_{fg} (p + \chi h)^{\frac{1}{2}} + \frac{1}{h} \sum_g (\Delta \overline{c}_g)_{x=0} k_{fg} (p + \chi h)^{\frac{1}{2}}\]
(J)_{x=0} = -D \sum_g (\Delta \overline{c}_g)_{x=0} \sum_h K fgh (p + \infty h)^{\frac{1}{2}} \left( \frac{e^{-aql} + e^{aql}}{e^{-aql} - e^{aql}} \right)

p^{\frac{1}{2}} \sum_g (\Delta \overline{c}_g)_{x=0} \sum_h K fgh (p + \infty h)^{\frac{1}{2}} \left( \frac{2}{e^{-aql} - e^{aql}} \right)

The expression for the current in the absence of kinetics is as follows:

\[(c)_{x=0} = 0\]

\[(\Delta c)_{x=0} = c^0/p\]

\[(J)_{x=0} = \frac{2D^2 c^0 (p + 0)^{\frac{1}{2}}}{p} \sum_{n=0}^{\infty} \exp - \frac{(2n+1) \sqrt{p}}{2} \frac{(p+0)^{\frac{1}{2}}}{D^{\frac{1}{2}}}\]

where

\[(\Delta \overline{c}_g)_{x=0} = 0\]

\[\infty \sum_{n=0}^{\infty} \exp - (2n+1) x \]

and in transposing out of the Laplace transform

\[(J)_{x=0} = \frac{2D^2 c^0}{\sqrt{\pi t}} \sum_{n=0}^{\infty} \exp - \frac{\left[(2n+1) \frac{\sqrt{p}}{4Dt} \right]^2}{4Dt}\]

Hint: \[\frac{1}{\sqrt{p}} \quad \frac{1}{\sqrt{\pi t}}\]

exp \(-ap^{\frac{1}{2}}\) \rightarrow exp \left(-\frac{s^2}{4t}\right)
therefore

\[
i = \frac{2nFAD^2C^0}{\sqrt{\pi t}} \sum_{n=0}^{\infty} \exp \left(-\frac{(2n+1)l}{4Dt}\right)^2
\]

Folding Technic applied to the derivation of the flux to an electrode in the absence of kinetic reactions.

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

\[
C(l,t=0) = C^0 ; \quad C(x,t) = 0
\]

\[
C(x,t) = C^0 \left[ \text{erfc} \left( \frac{l-x}{2D^\frac{3}{2}t^\frac{1}{2}} \right) - \text{erfc} \left( \frac{l+x}{2D^\frac{3}{2}t^\frac{1}{2}} \right) \right]
\]

\[
+ \text{erfc} \left( \frac{3-x}{2D^\frac{3}{2}t^\frac{1}{2}} \right) - \text{erfc} \left( \frac{3+x}{2D^\frac{3}{2}t^\frac{1}{2}} \right) + \ldots .
\]

\[
C(x,t) = C^0 \sum_{n=0}^{\infty} \text{erf} \left[ \frac{(2n+1)l+x}{2D^\frac{3}{2}t^\frac{1}{2}} \right] - \text{erf} \left[ \frac{(2n+1)l-x}{2D^\frac{3}{2}t^\frac{1}{2}} \right]
\]

Flux at \( x = 0 \)

\[
= D \left[ \frac{\partial^2 C(x,t)}{\partial x^2} \right]_{x=0}
\]

\[
\left[ \frac{\partial^2 C(x,t)}{\partial x^2} \right] = \frac{2C^0}{\pi^\frac{1}{2}} \sum_{n=0}^{\infty} \frac{1}{2D^\frac{3}{2}t^\frac{1}{2}} \left\{ \exp \left(-\frac{(2n+1)l+x}{4Dt}\right) \right\}
\]

\[
+ \exp \left(-\frac{(2n+1)l-x}{4Dt}\right)^2
\]
\[
\frac{\partial^2 c(x,t)}{\partial x^2} \bigg|_{x=0} = \frac{2c^0}{\sqrt{\pi Dt}} \sum_{n=0}^{\infty} \exp \left( - \left( \frac{(2n+1) \lambda}{4Dt} \right)^2 \right)
\]

Finally

\[
\frac{1}{n FAD} = \frac{2c^0}{\sqrt{\pi Dt}} \sum_{n=0}^{\infty} \exp \left( - \left( \frac{(2n+1) \lambda}{4Dt} \right)^2 \right)
\]