Heterogeneous reactions with rotating disk electrode.

Hing Y. Lo
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HETEROGENEOUS REACTIONS WITH ROTATING DISK ELECTRODE

BY
HING Y. LO

A Thesis
Submitted to the Faculty of Graduate Studies through the
Department of Chemical Engineering in Partial
Fulfillment of the Requirements for the
Degree of Master of Applied Science
at the University of Windsor

Windsor, Ontario
1964
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ABSTRACT

The theory of convective diffusion to a rotating disk surface has been reviewed.

With the use of a rotating platinum plated cathode and platinum anode, the theory has been verified for rotational speeds up to 40,000 revolutions per minute.

The electrode process,

\[ \frac{1}{2} I^- + 2 e \rightarrow 3I^- \]

with potassium iodide as the supporting electrolyte, was chosen for this study.

Iodine concentrations ranged from \(1.01 \times 10^{-4}\) to \(32.4 \times 10^{-4}\) N in 0.1 N potassium iodide.

The reaction was also observed for several disk areas.

An average diffusion coefficient of the triiodide ions was calculated from the data to be \(1.01 \times 10^{-5}\) cm.\(^2\)/sec. at 24.6 ± 0.5°C.
ACKNOWLEDGEMENT

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CHAPTER I

INTRODUCTION

The nature of the rate processes of most chemical and physicochemical operations is largely determined by hydrodynamic factors. Among such operations, heterogeneous transformations in liquids and gases are of primary importance. The reaction rate of an electrode process, which can be considered of as a special type of heterogeneous chemical reaction, is governed by three steps: (1) transport of ions from the bulk of the solution to the surface of the electrode, (2) the electrochemical reaction itself, and (3) the removal of the final products.

In some cases, the heterogeneous reaction process is accompanied by secondary effects, such as the release of large amounts of heat or the appearance of bubbles due to formation of gaseous reaction products which complicate the course of the reactions. The net rate of the heterogeneous process is determined by the combined effect of its separate stages. However, the rate of the entire process is governed by the slowest step if this step is significantly slower than the others. This is common for reactions occurring in successive stages. In those cases where the slow step involves the introduction or removal of reactants, the reaction is said to be diffusion controlled and is governed by the laws of diffusion kinetics. If on the other hand, the chemical or physical transformations constitute the slowest step, the rate of the reactions is determined by the kinetics of these processes.
Of greatest interest in current research, are those reactions whose rates are determined by chemical reaction kinetics. However, the majority of heterogeneous reactions and especially those of industrial importance are diffusion controlled. Most electrochemical reactions are of this type, i.e. controlled by the transfer of ions to the surface of the electrode.

The passage of current through the solution leads to a change in concentration at one of the electrodes. This is called concentration overpotential, which is also known as concentration polarization in electrochemistry. In order to maintain a finite rate for the overall electrochemical process, an external electromotive force must be applied.

In electrolytic processes, ions are transported by three mechanisms under steady state and laminar flow conditions.

(1) Migration in the electric field applied to the cell.
(2) Diffusion from region of higher concentration to lower concentration.
(3) Convection due to motion of fluid.

In the absence of noticeable overvoltage, if the solution contains an excess amount of indifferent electrolyte, the magnitude of the current flowing to the electrode will depend on the hydrodynamic factors which determine the effective thickness of the boundary layer at the electrode surface.
CHAPTER II

A. Theoretical

Nernst (19) who was first to attempt to develop the theory of the diffusion layer suggested that

$$j_{\text{diff}} = D \cdot n \cdot F \cdot \frac{c_o - c^b}{\delta'}$$

where

- $j_{\text{diff}}$ = diffusion flux
- $c_o$ = concentration of ions at the electrode
- $c^b$ = the bulk concentration
- $D$ = diffusion coefficient
- $n$ = ion valency
- $F$ = Faraday number
- $\delta'$ = Nernst's diffusion layer

Nernst postulated that the thickness of the diffusion layer is independent of the nature of the electrochemical process on the electrode surface and independent of the character of the potential distribution. The absolute value of $\delta'$ depends on the regime of stirring and must be found experimentally.

This theory was found later to be inadequate, because it contains the erroneous assumption that the liquid is stationary within the diffusion layer, and it also does not allow quantitative prediction of the dependence of $\delta'$ on the regime of stirring.

This led to Eucken's (6) attempt to develop a strictly
hydrodynamic theory of the transport of matter in a moving fluid. However, he did not give a general theory of the transport of matter in a liquid.

In the theory of concentration polarization proposed by V. Levich (15), (16) a quantitative theory of the diffusion boundary layer for electrodes of several shapes has been treated in terms of modern hydrodynamic concepts following the lines of analogous heat transfer problems. For the case of a rotating disk, Levich found that the diffusion layer thickness is given by

\[
\delta = 1.61 \left( \frac{D}{\nu} \right)^{\frac{1}{3}} \left( \frac{\nu}{\omega} \right)^{\frac{1}{2}}
\]

(2)

where

\( \delta = \) diffusion boundary layer
\( D = \) diffusion coefficient
\( \nu = \) kinematic viscosity
\( \omega = \) angular speed

The hydrodynamic equations for a rotating disk were first solved by an approximate method given by Karman (13). Later Cochran (3) calculated more accurate values by a method of numerical integrations.

A more thorough discussion of a rotating disk electrode was given by Levich (17) in his theoretical studies of diffusion and kinetics.

B. Experimental

Experimental work has been done on the verification of the theory proposed by Levich and the development of the rotating
Kabanov and Siever (12) first verified the equation of ion transfer in their studies of the diffusional flow of dissolved oxygen to a rotating disk and the limiting current for hydrogen ion reduction. The results of their observations confirmed the correctness of the theory. Hogge and Kraichman (9) have applied the theory of concentration polarization for a rotating disk electrode to the KI-KI\textsubscript{3} system with a platinum electrode. Their speed of rotation extended to about 5000 revolutions per minute. A diffusion coefficient for triiodide ions was obtained from their results.

Excellent agreement of experimental results with the theory was also found by Aykazyan and Fedorova (1) in the study of anodic ionization of hydrogen atoms in different electrolytes.

Other experimental studies using the rotating disk have been done by Beacom and Hollyer Jr. (2); and also Johnson and Turner (11) on the studies of addition agents; Jahn and Vielstick (10) and Galus and Adams (8) on the measurement of kinetics of several reactions; and Lewis and Ruetschi (18) on oxidation of hydrogen and deuterium.
CHAPTER III

THEORY

In an electrolytic solution, the equation for the transfer of ions due to diffusion and migration takes the form

$$i_r = D_r \frac{\partial c_r}{\partial y} + \frac{D_r F^2}{RT} \frac{\partial \phi}{c_r \partial y}$$  \hspace{1cm} (3)

where

- $i_r$ = limiting current density by ion type $r$
- $D_r$ = diffusion coefficient
- $F$ = Faraday number
- $\phi$ = potential
- $c_r$ = concentration of ions of type $r$
- $c^o$ = initial concentration
- $T$ = absolute temperature
- $R$ = gas constant
- $y$ = normal distance from reacting surface

with the conditions for electroneutrality in solution

$$\sum c_r n_r = 0$$  \hspace{1cm} (4)

In the case of the system KI-KI$_3^-$, with KI as the supporting electrolyte, the concentration of the reacting ion species, I$_3^-$, is small in comparison with the other types of ions. Equations (3) and (4) then become

$$i = D_r F \frac{\partial c_r}{\partial y} + \frac{D_r F^2}{RT} \frac{\partial \phi}{c_r \partial y}$$  \hspace{1cm} (5)

6

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\[ 0 = D_2 F \frac{\partial C_2}{\partial y} + \frac{D_2 F^2}{RT} C_2 \frac{\partial \phi}{\partial y} \quad (6) \]
\[ 0 = D_3 F \frac{\partial C_3}{\partial y} + \frac{D_3 F^2}{RT} C_3 \frac{\partial \phi}{\partial y} \quad (7) \]
\[ n_1 C_1 + n_2 C_2 + n_3 C_3 = 0 \quad (8) \]

where subscripts 1, 2 and 3 refer to ions of type \( I^- \), \( K^+ \) and \( I^- \) respectively. Equations (6) and (7) give
\[ C_2 = C_2^0 e^{-\varphi} \quad (9) \]
\[ C_3 = C_3^0 e^{\varphi} \quad (10) \]

where
\[ \varphi = \frac{F \phi}{RT} \]

From \( i = i_{\text{diff}} + i_{\text{migr}} \), equations (5), (8), (9) and (10), results were obtained for the currents due to diffusion and migration.

\[ i_{\text{diff}} = \frac{i}{2} \left[ 1 + \frac{C_2^0}{\left(1 + \frac{i y}{2 D_1 C_2^0 F}\right)^2 \frac{1}{C_3^0}} \right] \approx i \quad (11) \]
\[ i_{\text{migr}} = \frac{i}{2} \cdot \frac{C_3^0}{C_2^0} \ll i \quad (12) \]
\[ \varphi = \ln \left(1 + \frac{i y}{2 D_1 C_3^0 F} \right) \quad (13) \]
Therefore, the migration current can be neglected when compared to the diffusion current and it can be assumed that the flow of current-carrying ions in the solution, in the presence of foreign electrolyte, is equal to the diffusion flux of uncharged particles.

\[ i = D_f \left( \frac{\partial C}{\partial y} \right) \]  \hspace{1cm} (14)

To determine \( \frac{\partial C}{\partial y} \), the convective diffusion equation has to be solved.

The equations for convective diffusion acquire their simplest form when the surface of a rotating disk serves as the reaction site. The rotating disk is employed in electrochemistry and is convenient for studying chemical kinetics under laboratory conditions. The velocity distribution for a rotating disk is of special interest in hydrodynamics because it is one of the few examples where an exact solution of the hydrodynamic equations can be obtained. This exact solution gives the velocity distribution throughout the body of the viscous fluid. Far from the rotating disk, the fluid moves toward the disk, and in a thin layer immediately adjacent to its surface, the liquid acquires a rotating motion. The angular velocity of the fluid increases as the rotating disk is finally attained. Furthermore, the fluid also acquires a radial velocity under the influence of the centrifugal force.

The significant characteristic of the boundary layer at a rotating disk is that its thickness is not a function of the distance from the axis of rotation, but is constant over the entire disk surface.
It is possible to show by doing a material balance for the flux of ions in a control volume under steady state conditions that

$$\nabla \cdot \vec{j} = 0$$

(15)

where

$$\vec{j} = D \nabla c + \vec{v}c$$

(15a)

For one dimensional flow, equation (15) gives the convective diffusion equation:

$$v_y \frac{dc}{dy} = D \frac{d^2c}{dy^2}$$

(16)

with boundary conditions

$$c = c^b \quad \text{at} \quad y = \infty$$

$$c = 0 \quad \text{at} \quad y = 0$$

where

$$v_y = \text{velocity in normal direction to the disk}$$

$$c = \text{concentration}$$

$$c^b = \text{bulk concentration}$$

$$y = \text{normal distance to disk}$$

$$D = \text{diffusion coefficient}$$

$$j = \text{flux of ions}$$

The second term in equation (15a) expresses the convective
transport in the moving liquid, and the first term ordinary diffusion.

For the case of one dimensional flow, the ratio of these two terms in
order of magnitude equals to

\[ \frac{U_y C}{D \partial c/\partial y} = \frac{U_y C}{D} = Pe \] (17)

where \( Pe \) is the dimensionless Peklet number. It is analogous to the
Reynolds number for the flow of a liquid. In this sense, the regime
of transport of matter is determined by the value of the Peklet
number. The ratio of the Peklet to Reynolds numbers is the
dimensionless Schmidt number

\[ Sc = \frac{Pe}{Re} = \frac{y}{D} \] (18)

In liquids, the Schmidt number is always very much larger than unity.
Because of this fact, the Peklet number is large compared with unity,
even when the corresponding Reynolds number is small. Therefore, in
most cases molecular diffusion in the bulk of the liquid can be
neglected in comparison with the convective transport of matter. Thus
if the peklet number is large compared with unity, the term due to
molecular diffusion in equation (15a) may be dropped and the solution
of equation (15) will be \( \bar{c} = \text{constant} = \bar{c}_0 \). The concentration of matter
will thus be constant throughout the volume of the liquid. However,
this solution of the equation cannot be valid at the electrode surface
where the condition \( \bar{c} = 0 \) must be satisfied. There should, therefore,
be a thin layer of liquid near the surface of the electrode in which
the concentration varies rapidly. Thus, at large Peklet numbers, as well as at large Reynolds numbers, the entire liquid can be divided into two parts: a region of constant concentration far from the surface of the reaction and a region of rapid variation of concentration in the immediate vicinity of this surface. In the latter region, the derivatives of the concentration with respect to the co-ordinates are very large and as a result, the first term of equation (15a), expressing molecular diffusion, becomes comparable to the second term, despite the small value of the diffusion coefficient and thus it cannot be neglected. The layer is called the diffusion boundary layer which is analogous to the Prandtl boundary layer.

Integration of equation (16) yields

\[ C = K_1 \int_0^y \exp \left( \frac{1}{D} \int_0^t v_y(y) \, dy \right) \, dt + c(t) \quad (19) \]

where \( K_1 \) and \( c(t) \) are integration constants. Application of boundary conditions shows that \( c(t) = 0 \). Substitution of \( c(t) \) in equation (19) gives

\[ C = K_1 \int_0^\infty \exp \left( \frac{1}{D} \int_0^t v_y(y) \, dy \right) \, dt \quad (20) \]

where \( v_y \), the normal velocity distribution, was obtained by solving the Navier Stokes equations of motion. The values are

\[ v_y = -0.88 \left( \frac{\nu D}{
\right)^{\frac{1}{2}} \text{ at } y = \infty \]

\[ v_y = -0.51 \frac{y^2}{D} \left( \frac{\nu D}{
\right)^{\frac{1}{2}} \text{ at } y \ll \left( \frac{\nu D}{
\right)^{\frac{1}{2}} \quad (21) \]
and
\[ \delta_0 = 3.6 \left( \frac{U}{\omega} \right)^{1/2} \]

where \( \delta_0 \) is the hydrodynamic boundary layer thickness. Thus equation (19) can be integrated to give the limiting diffusion current density.

\[ i_{\text{lim}} = 0.62 D^{\frac{2}{3}} \nu^{-\frac{1}{6}} CF \pi \omega^{1/2} \quad (22) \]

and the diffusion boundary layer thickness

\[ \delta = 1.61 \left( \frac{D}{\nu} \right)^{\frac{1}{3}} \left( \frac{\nu}{\omega} \right)^{1/2} \quad (2) \]

Limiting diffusion current for a rotating disk with area A is obtained by rearranging equation (22)

\[ i_{\text{lim}} = \frac{\eta FD^{3/2}(\omega)^{1/2}CA}{1.61 \pi \omega} \quad (23) \]
CHAPTER VI
EXPERIMENTAL

A. Apparatus

(a) Turbine:

Because of the particular requirements of this experiment, a high speed vertical turbine, purchased from Barbour Stockwell Company, was used. The turbine was of the air driven type having a maximum safe operating speed of 150,000 revolutions per minute. The rotor of this turbine was one and one half inches in diameter and designed for a 3/16 inch spindle. The spindle was suspended by means of a special self locking hexagonal nut on top of the rotor as shown in Fig. 1. Ball bearings in the housing were lubricated with a continuous stream of oil mist generated by an Alamite oil mist lubricator. The purpose of the oil seal was to stop excess oil from leaking into the test fluid below. Excess oil collected in the turbine would flow out through an opening called the Breather which also maintained pressure equilibrium between the lower part of the turbine housing and the atmosphere.

The bottom part of the turbine was made of plexiglass to prevent unnecessary electrical contact between the metal of the turbine and the test fluid.

The vessel containing the test fluid was made air tight and concentric with the turbine by means of an O-ring inserted into a groove at the bottom face of the plexiglass.

The turbine was also equipped with an air brake in case
of emergency.

(b) Vessel:

The vessel consisted of two parts as shown in Fig. 2. The lower part was cut from five inches diameter plexiglass tubing to a length of four inches. This tube was glued to a plexiglass plate which acted as the bottom of the vessel. Near this plate, two openings were drilled in the wall of the plexiglass tube for filling and draining purposes. The upper part of the vessel machined from plexiglass block was six inches in diameter and one inch thick with a groove and an O-ring to accept the bottom half of the vessel. This part was so designed to keep the spindle from dragging air into the test fluid and forming a vortex. The opening at the side of the top part was for exhausting gases or liquid and the opening at the center was for the entrance of the spindle.

(c) Electrodes

Cathode - The spindles which were to serve as the cathodes were machined to give the desired surface area and shape. They were made of oil hardened, non-deforming type drill rod which was free from Decarb and annealed to give a fully spheriodized structure. No heat treatment was involved. Bright platinum was plated uniformly on the spindle only at the reaction surface by Johnson Matthey and Company Limited, Toronto. The rest of the spindle, extending outside the turbine was insulated with an electrical insulator, Dow Corning Varnish 980. The spindle was dipped in the insulating varnish and dried for four hours and then oven-dried at 150°C for six hours. The spindle was preheated to 150°C to drive out moisture before being dipped in the varnish.
Anode - The anode was a thin pure platinum plate 3.12 inches in diameter and 0.015 inches thick, located at the center of the vessel approximately 3.5 inches below the cathode surface.

(d) Speed control:

The speed of the turbine was controlled by regulating the air supply to the turbine by means of a pressure regulator and valves placed in series. The high pressure air from the main compressor first passed through a valve, then through an air filter. A fixed value of pressure was established by a pressure regulator. The desired pressure was determined by another valve just ahead of the turbine as shown in Fig. 4.

(e) Measuring apparatus:

The rotation of the turbine rotor was picked up by means of a magnetic device located inside the top part of the turbine which produced an alternating current with the frequency corresponding to the speed of rotation. This alternating current was amplified and fed into a digital electronic counter. For recording purposes, these digital numbers were converted in an analogue direct current signal which could be recorded by an x-y plot recorder reading in millivolts. The diffusion current was measured with a milliammeter. For recording purposes, this current was also converted into millivolts and recorded by the x-y plot recorder. The voltage was measured with a precision voltmeter.

(f) Electrical contacts:

A small hole was drilled at the top end of the spindle. Electrical contact was made by means of a small needle pressed into the small hole by a coiled spring. This assembly was located next to
the magnetic pick up.

The platinum plate anode was screwed into the bottom of the vessel with a metal screw which had been platinum plated. The other end of the screw extended out of the vessel so that electrical contact could be made. A small O-ring was placed between the platinum plate and the inside bottom face of the vessel to prevent leakage of fluid.

B. Solutions

Reagent grade potassium iodide solutions were used. A 0.1 N stock solution was prepared and deoxygenated by flushing with nitrogen which was first equilibrated with 0.1 N potassium iodide prior to introduction into the stock solution. The KI₃ complex was obtained by dissolving reagent grade iodine in a concentrated KI solution and diluting to produce the resulting solution which was 0.1N KI and 0.101 NI₂. The distilled water used in preparing the complex was also flushed with tank nitrogen.

The solutions for testing the effect of the supporting electrolyte on limiting current were prepared in a similar manner.

The concentration of prepared iodine solution was determined by titration with arsenious oxide according to Kolthoff and Sandell (14).

C. Procedure

Solutions were prepared by adding known amounts of iodine complex into measured amounts of 0.1 N stock potassium iodide solutions. The solutions were further deoxygenated by flushing with nitrogen.
before introduction into the reaction vessel through one of the lower
openings. Leveling was done on the turbine surface by turning three
screws underneath the legs of the table as shown in Fig. 3. The oil
mist lubricator was turned on a few minutes before starting the turbine.
The setting of the needle valve and pressure of the lubricator was so
adjusted that there was always a small amount of oil leaking through
the Breather. The air pressure was set at 40 psig by adjusting the
regulator while the air pressure up stream was 70 psig. The speed of
the turbine then was increased slowly by turning the valve downstream
of the regulator.

Direct current was supplied from a dry cell battery. The
voltage across the electrodes was maintained at 0.4 volts during the
experiments by adjusting the rheostat to compensate for the ohmic drop
in the solution. Limiting current values were then read for correspond-
ing cathode speeds.

For the determination of potential-current curves at
constant speeds, current were recorded for corresponding potentials
which were varied by resetting the rheostat.

Temperatures were taken before and after each experiment.
FIG. 3 LAYOUT OF EQUIPMENT

- SILENCER
- TURBINE
- PLATFORM
- PLEXIGLASS WINDOW
- LEVELING SCREW
FIG. 4 SCHEMATIC DIAGRAM
CHAPTER V

RESULTS

The formal (plateau) potential, that is the voltage corresponding to the limiting current, was determined from the current potential curves obtained at constant rotational speeds. The data are shown in Fig. 5. The plateau potential for the system under study ranged from 0.3 to 0.55 volts. The value of 0.4 volts was chosen for all experiments. The same general shape of curves and the same potential were obtained regardless of the rotational speed of the disk.

Fig. 6. shows the effect of the concentration of the supporting electrolyte on limiting current. Above 0.05 N KI concentration, the change in limiting current with increasing KI concentration is negligible. To assure that the value of migration current would be negligible, the concentration of the supporting electrolyte, potassium iodide solution, was chosen to be 0.1 N.

Under the experimental conditions employed, the limiting diffusion currents were plotted against the square root of rotating speed for various concentrations of iodine, as shown in Fig. 7 and 8. Straight lines were drawn through the experimental points and extropolation of these lines back to zero rotating speed passed through the origin within the experimental errors.

Plots of the experimentally determined limiting diffusion currents against concentrations of iodine and disk area indicated the linear relationships shown in Fig 9 and 10. These lines passed through the origin at zero concentration and zero disk area.
by similar extrapolation.

Temperatures were measured before and after each experiment. An average temperature of 24.6 ± 0.5°C was obtained.

The areas of the disks were measured as 0.728 ± 0.01 cm$^2$, 0.479 ± 0.01 cm$^2$ and 0.570 ± 0.01 cm$^2$ for the three disks.

Values of the kinematic viscosity of the test fluids were taken from Hogge and Kraichman (9). $\nu = 0.8679$ centistoke at 25°C.
CONCENTRATION OF $I_2 = 12.6 \times 10^{-4}$ N
CONCENTRATION OF $KI = 0.1$ N
DISK AREA = $0.728 \text{ cm}^2$

FIG. 5 CURRENT VS. POTENTIAL

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CONCENTRATIONS OF $I_2 = 5.05 \times 10^{-4}$

DISK AREA = 0.728 CM$^2$

$E = 0.4$ VOLTS

- $0.0005$ N KI
- $0.010$ N KI
- $0.050$ N KI
- $0.075$ N KI
- $0.100$ N KI

FIG-6 EFFECTS OF THE CONCENTRATION OF KI ON LIMITING CURRENT
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FIG. 8 DIFFUSION CURRENT AS A FUNCTION OF $S^2$ (FOR HIGH CONCENTRATION OF $I_2$)

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CONCENTRATION OF KI = 0.1 N
S = 36,500 RPM
E = 0.4 VOLTS

C = 24.6 x 10^-4 N I₂

C = 1.01 x 10^-4 N I₂

FIG. 9 DIFFUSION CURRENT AS A FUNCTION OF DISK AREA
**CONCENTRATION OF KI = 0·1 N**
**DISK AREA = 0·728 CM²**
**E = 0·4 VOLTS**

**FIG.10 DIFFUSION CURRENT AS A FUNCTION OF CONCENTRATION OF I₂**
Values of Reynolds numbers from $3 \times 10^3$ to $1 \times 10^5$ were calculated from the equation

$$Re = \frac{\omega r^2}{v}$$

where

- $Re =$ Reynolds number
- $\omega =$ angular speed
- $r =$ radius of disk
- $v =$ kinematic viscosity

for maximum and minimum rotating speeds. This indicates that the flow of fluid was within the laminar region. The radii of the disks were large compared to the boundary layer thickness so that the edge effect could be neglected.

The experimental results showed that for the system KI - KI$_3$, under the above mentioned conditions, the mathematical prediction proposed by Levich, equation (23), is valid.

The values of diffusion coefficient of triiodide ion have been determined by electrolytic and non-electrolytic methods. Some values were given in Table 1.
Table 1

Data of Diffusion Coefficient

<table>
<thead>
<tr>
<th>AUTHOR</th>
<th>( D_{L} ) cm²/sec</th>
<th>°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hogge and Kraichman (9)</td>
<td>( 1.08 \times 10^{-5} )</td>
<td>26.2</td>
</tr>
<tr>
<td>Hogge and Kraichman (9)</td>
<td>( 1.02 \times 10^{-5} )</td>
<td>25.7</td>
</tr>
<tr>
<td>Edgar and Digge (5)</td>
<td>( 1.08 \times 10^{-5} )</td>
<td>25.0</td>
</tr>
<tr>
<td>Fedorov (7)</td>
<td>( 1.04 \times 10^{-5} )</td>
<td>25.0</td>
</tr>
</tbody>
</table>

These values compare favourably with the value, \( 1.01 \times 10^{-5} \) cm²/sec at 24.6°C found by this study.

Standard deviation of the term \( \frac{I_{mn}}{C(S)^{1/2}} \) was calculated from experimental data to be 2.83%.

For the first order electrode reaction which is controlled by both diffusion and reaction kinetics, Levich (17) wrote:

\[
I = \frac{nFADc^b}{1.61D^{1/2}v^{1/2}w^{1/2} + \frac{D}{k}}
\]  

or

\[
I = \frac{nFADc^b}{\delta + \frac{D}{k}}
\]

where

\( c^b \) = the bulk solution concentration

\( n \) = ion valency
A = disk area
D = diffusion coefficient
k = kinetic rate constant
F = Faraday number
ω = angular speed
ν = kinematic viscosity
δ = diffusion boundary layer

For a diffusion controlled reaction \( \frac{D}{k} \) is small compared to the diffusion boundary layer thickness \( δ \), equation (2). Equation (25) becomes equation (23).

\[
I = 0.62 n F A D^{2/3} ν^{-1/6} c^b ω^{1/2}
\]  
(23)

On the other hand if \( δ \) can be decreased by increasing the speed of rotation without getting into hydrodynamic turbulence, equation (26) becomes

\[
I = n F A K c^b
\]  
(27)

It is clear that the observed limiting current becomes independent of the diffusion rate - the current is entirely controlled by the reaction rate. The linear relationship between the limiting current and the square root of the speed is no longer followed. The limiting current is a constant and depends only on the concentration of the reacting ions.

Calculation of the diffusion boundary layer thickness according to equation (2) yields a value of \( 2.5 \times 10^{-4} \) cm for a rotational speed of 40,000 revolutions per minute, at which point the limiting current showed no sign of changing slope or tending to
become constant for the electrode reaction under study.

This means that the rate constant for this process must have a value much larger than $4 \times 10^{-2} \text{cm/sec}$ if the thickness of the diffusion boundary layer is to be negligible at the rotational speed of 40,000 revolutions per minute.

Difficulties arose when rotational speed were increased beyond 40,000 revolutions per minute. Vortex problem became appreciable. Also, electrical contacts, speed control and insulation were difficult to maintain at high speeds.

It is recommended that a slower electrode reaction could be studied with the present equipment for elucidation of diffusion and reaction kinetics. Diffusion coefficients of ions can be determined fairly easily and accurately with the presently attainable speeds.
BIBLIOGRAPHY

13. Karman, T. Laminare and Tubulente Reibung ZAMM I., 233-252 (1921); NACA, T. M. 1092 (1946)
15. Lveich, V. Acta Physicochim 17, 257 (1942)
    N. J. (1962)
    New York (1960)
    99, 359C (1952)
NOMENCLATURE

A = disk area, cm$^2$

A = constant, eq. (A-13), (A-14) and (A-15)

a = constant, eq. (A-16), (A-17) and (A-18)

B = constant, eq. (A-13), (A-14) and (A-15)

b = constant, eq. (A-16), (A-17) and (A-18)

b = \frac{I_{lim}}{J^{\frac{1}{2}}C}

\bar{b} = mean value of b

b = intercept

C, C_1, C_2, C_3 and C_y

= concentrations, mol/ cm$^3$

C_0, C_1^0, C_2^0, C_3^0 and C_y

= initial concentrations, mol/ cm$^3$

C_b = bulk concentration, mol/ cm$^3$

C_0 = concentration at the electrode mol/ cm$^3$

C(t) = integration constant, eq. (19)

D, D_1, D_2, D_3 and D_y

= diffusivity coefficient, cm$^2$/sec

d = diameter, cm

e = electronic charge

E = voltage, volts

F = Faraday number

F', F'' and F''' = unknown functions, eq. (A-7)

G, G' and G'' = unknown functions, eq. (A-8)

H, H' and H'' = unknown functions, eq. (A-9)

I_{lim}, I_{lim} = limiting current, amperes

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\( i_{\text{diff}} \) = diffusion current, amperes
\( i_{\text{migr}} \) = migration current, amperes
\( j_{\text{lim}}, J_{\text{lim}} \) = limiting mass flux, mol / sec
\( J_1, J_2 \) = integrals
\( k \) = kinetic rate constant, cm / sec
\( K_l \) = integration constant, eq. (19)
\( N \) = normality
\( n \) = ion valency
\( p \) = pressure, gm / cm\(^2\)
\( P, P' \) = unknown functions
\( P_e \) = Peklet number, eq. (17), dimensionless
\( r \) = radius, cm
\( \text{Re} \) = Reynolds number, dimensionless
\( R \) = gas constant
\( S \) = rotating speed, rpm
\( s \) = rotating speed, rps
\( S_c \) = Schmidt number, dimensionless
\( S, D. \) = standard deviation
\( t \) = normal distance, cm
\( T \) = absolute temperature, °K
\( u \) = a function dependence
\( U \) = constant, eq. (A-12)
\( v_r \) = radial velocity, cm / sec
\( v_\theta \) = tangential velocity, cm / sec
\( v_y \) = normal velocity, cm / sec
\( y \)  = normal distance, cm

\( Y \)  = defined function

\( \alpha \)  = constant, eq. (A-11)

\( \theta \)  = angle

\( \omega \)  = angular speed, radian / sec

\( \phi \)  = potential, volts

\( \psi \)  = dimensionless function  = \( \frac{F \Phi}{RT} \)

\( \rho \)  = density, gm / cm\(^3\)

\( \delta_0 \)  = Prandtl boundary layer, cm

\( \delta \)  = diffusion boundary layer, cm

\( \delta' \)  = Nernst diffusion boundary layer, cm

\( \mu \)  = absolute viscosity

\( \nu \)  = kinematic viscosity, cm\(^2\) / sec

\( \delta \)  = parameter
APPENDIX A

THE SOLUTIONS OF THE NAVIER STOKES EQUATIONS OF MOTION

BY EXACT METHOD FOR ROTATING DISK

The disk is assumed to be sufficiently large, so that the edge effects can be neglected. Also taking into account rotational symmetry, Fig. 11, one can simplify the Navier Stokes equations and the continuity equation to

\[
\frac{\nu}{\rho} \frac{\partial u_r}{\partial r} - \frac{\nu}{\rho} \frac{u_r^2}{r} + \nu \frac{\partial u_r}{\partial y} = \gamma \left( \frac{\partial u_r}{\partial y} + \frac{\partial u_\theta}{\partial r} \right) \quad (A-1)
\]

\[
\frac{\nu}{\rho} \frac{\partial u_\theta}{\partial r} + \frac{\nu}{\rho} + \nu \frac{\partial u_\theta}{\partial y} = \gamma \left( \frac{\partial u_\theta}{\partial y} + \frac{\partial u_r}{\partial r} \right) \quad (A-2)
\]

\[
\frac{\nu}{\rho} \frac{\partial u_y}{\partial r} + \nu \frac{\partial u_y}{\partial y} = -\frac{1}{\rho} \frac{\partial P}{\partial y} + \gamma \left( \frac{\partial u_y}{\partial y} + \frac{\partial u_\theta}{\partial r} \right) \quad (A-3)
\]

\[
\frac{1}{\rho} \frac{\partial u_\theta}{\partial \theta} + \frac{\partial u_\theta}{\partial r} + \frac{u_r}{\rho} + \frac{\partial u_y}{\partial y} = 0 \quad (A-4)
\]

with boundary conditions

\[
v_r = 0 \quad v_\theta = r \quad v_y = 0 \quad \text{at } y = 0 \quad (A-5)
\]

\[
v_r = 0 \quad v_\theta = 0 \quad v_y = -V \quad y = \infty
\]

Assume that the solutions to the equation of continuity which satisfy the boundary conditions take the form.

\[
v_r = r \omega P(\xi), \quad v_\theta = r \omega G(\xi), \quad v_y = (\gamma\omega)^{\frac{1}{2}} H(\xi) \quad (A-6)
\]

and the independent variable \( \xi \) is given by

\[
\xi = \left( \frac{\omega}{V} \right)^{\frac{1}{2}} y
\]
Substitute equation (A-6) into equations (A-1) (A-2) (A-3) and (A-4) to obtain the following equations

\[ F^2 - G^2 + F H = F'' \]  \hspace{1cm} (A-7)

\[ 2 F G + G' = G'' \]  \hspace{1cm} (A-8)

\[ H H' = P' + H'' \]  \hspace{1cm} (A-9)

\[ 2 F + H' = 0 \]  \hspace{1cm} (A-10)

where \( F, G, H \) and \( P \) are functions to be determined, the boundary conditions become

\[ F = 0 \quad G = 1 \quad H = 0 \quad \xi = 0 \]

\[ F \rightarrow 0 \quad G \rightarrow 0 \quad H = \alpha \text{ at } \xi = \infty \]  \hspace{1cm} (A-11)

where

\[ \alpha = \frac{U}{(y \omega)^{\frac{1}{2}}} \]  \hspace{1cm} (A-12)

Since the differential equations and the boundary conditions depend only on the variable \( \xi \), the assumption made is justified. The functions \( F, G, \) and \( H \) may be made to satisfy the above equations and boundary conditions by formal series expansions. For large values of \( \xi \):

\[ F = A e^{-\xi^2} - \frac{A^2 + B^2}{2 \xi^2} e^{-2\xi^2} + \frac{A(A^2 + B^2)}{4 \xi^4} e^{-3\xi^2} + \ldots \]  \hspace{1cm} (A-13)

\[ G = B e^{-\xi^2} - \frac{B(A^2 + B^2)}{12 \xi^4} e^{-3\xi^2} + \ldots \]  \hspace{1cm} (A-14)

\[ H = -\alpha + \frac{2A}{\alpha} e^{-\xi^2} - \frac{A^2 + B^2}{2 \xi^3} e^{-2\xi^2} + \frac{A(A^2 + B^2)}{6 \xi^5} e^{-3\xi^2} + \ldots \]  \hspace{1cm} (A-15)
and for small values of $\xi$,

\[
F = a\xi - \frac{\xi^2}{2} - \frac{1}{3} b\xi^3 + \cdots \tag{A-16}
\]

\[
G = 1 + b\xi + \frac{1}{3} a\xi^3 + \cdots \tag{A-17}
\]

\[
H = -a\xi + \frac{1}{3} \xi^3 + \cdots \tag{A-18}
\]

The constants $A$, $B$, $a$, $b$, and $\lambda$ can be determined by numerical integration. Their values are:

- $a = 0.51023$
- $b = -0.616$
- $\lambda = 0.88447$
- $A = 0.934$
- $B = 1.208$

The functions $F$, $G$ and $H$ are shown in Fig. 12 and the values of the velocity in the direction normal to the disk are

\[
U_y \propto -0.88(y\omega)^{\frac{1}{2}} \quad \text{as} \quad y \to \infty \tag{A-19}
\]

\[
U_y \propto -0.51 \left( \frac{\omega^3}{y} \right)^{\frac{1}{2}} y^2 \quad \text{as} \quad y \ll \left( \frac{y}{\omega} \right)^{\frac{1}{2}} \tag{A-20}
\]

and it follows that

\[
\xi_0 = 3.6 \left( \frac{y}{\omega} \right)^{\frac{1}{2}} \tag{A-21}
\]
FIG. 11 FLOW IN THE NEIGHBOURHOOD OF A ROTATING DISK IN A FLUID AT REST
APPENDIX B

CONCENTRATION DISTRIBUTION FOR A ROTATING DISK

From equation (19)

\[ C = k_1 \int_0^\infty \exp \left( \frac{t}{b} \int_0^y \psi(y') dy' \right) dt \]  

(19)

For purposes of evaluation, the range of the integral is subdivided into two regions: from zero to \( S_0 \) and from \( S_0 \) to infinity

\[ J = \int_0^{\infty} \exp \left( \frac{t}{b} \int_0^y \psi(y') dy' \right) dt \]

\[ = \int_0^{S_0} \exp \left( \frac{t}{b} \int_0^y \psi(y') dy' \right) dt + \int_{S_0}^{\infty} \exp \left( \frac{t}{b} \int_0^y \psi(y') dy' \right) dt \]

\[ = J_1 + J_2 \]  

(B-1)

Using the values from equations (A-19) and (A-20), one can evaluate the integrals \( J_1 \) and \( J_2 \)

\[ J_1 = \int_0^{S_0} \exp \left( - \frac{\omega^{3/2} t^3}{5.88 D y^{1/2}} \right) dt \]  

(B-2)

Letting

\[ u = \frac{\omega^{1/2} t}{\sqrt[3]{5.88} D^{1/3} y^{1/2}} \]  

(B-3)

\[ J_1 = \left( \frac{1.81 D^{1/2} y^{1/2}}{\omega^{1/2}} \right) \int_0^\infty e^{-u^3} du = 1.61166 \frac{D^{1/3} y^{1/2}}{\omega^{1/2}} \]  

(B-4)
\[ J_2 = \int_0^\infty \exp \left( \frac{1}{D} \int_0^t u_y(y) dy \right) dt \]

\[ = \frac{D}{0.89 (\omega y)^{1/2}} e^{-3(y/D)} \quad (8-5) \]

Thus

\[ J_1 >> J_2 = J \]

The integral can be rewritten as

\[ C = \frac{C_o}{1.61 (\frac{D}{\delta})^{3/2} (\frac{y}{D})^{1/2}} \int_0^Y \exp \left( \frac{1}{D} \int_0^t u_y(y) dy \right) dt \quad (8-6) \]

or

\[ \frac{C}{C_o} = \frac{\int_0^Y e^{-u} du}{\int_0^\infty e^{-u^3} du} \quad (8-7) \]

where

\[ Y = \frac{2y}{\delta_d} \left( \frac{y}{D} \right)^{1/3} \]
Equation (B-7) shows that for small values of $y$, the concentration increases very rapidly with distance $y$ and for

$$y > \frac{1}{2} \left( \frac{D}{v} \right)^{\frac{1}{3}} \delta$$

$Y$ can be replaced by infinity, and the value of concentration reduced to $C^*$. The ratio $\frac{c}{c^*}$ from equation (B-7) is plotted in Fig. 13.
FIG. 13 CONCENTRATION DISTRIBUTION

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APPENDIX C
CALCULATIONS OF DIFFUSION COEFFICIENT

The slope of the lines were calculated by the least square method as shown for the case of concentration of

\[ I_2 = 32.4 \times 10^{-4} \text{ N.} \]

Assume the equation

\[ I_{\text{lim}} = m (S)^{\frac{1}{2}} + b \]

and

\[ m = \frac{n \sum I_{\text{lim}} (S)^{\frac{1}{2}} - \sum I_{\text{lim}} \sum (S)^{\frac{1}{2}}}{n \sum (S) - (\sum (S)^{\frac{1}{2}})^2} \]

TABLE 2
Sample Calculation Of Slope

<table>
<thead>
<tr>
<th>( n )</th>
<th>( S^{\frac{1}{2}} )</th>
<th>( I_{\text{lim}} )</th>
<th>( S )</th>
<th>( S^{\frac{1}{2}} \cdot I_{\text{lim}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60.0</td>
<td>2.90</td>
<td>3600</td>
<td>174.00</td>
</tr>
<tr>
<td>2</td>
<td>70.6</td>
<td>3.20</td>
<td>4984</td>
<td>225.92</td>
</tr>
<tr>
<td>3</td>
<td>94.8</td>
<td>4.20</td>
<td>8987</td>
<td>398.16</td>
</tr>
<tr>
<td>4</td>
<td>100.0</td>
<td>4.35</td>
<td>10000</td>
<td>435.00</td>
</tr>
<tr>
<td>5</td>
<td>114.0</td>
<td>5.30</td>
<td>12996</td>
<td>604.20</td>
</tr>
<tr>
<td>6</td>
<td>120.0</td>
<td>5.50</td>
<td>14400</td>
<td>660.00</td>
</tr>
<tr>
<td>7</td>
<td>141.0</td>
<td>6.50</td>
<td>19881</td>
<td>916.50</td>
</tr>
<tr>
<td>8</td>
<td>173.0</td>
<td>8.00</td>
<td>29929</td>
<td>1384.00</td>
</tr>
<tr>
<td>9</td>
<td>182.0</td>
<td>8.48</td>
<td>33124</td>
<td>1543.36</td>
</tr>
</tbody>
</table>

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TABLE 2 (cont'd)

<table>
<thead>
<tr>
<th>n</th>
<th>$S^\frac{1}{2}$</th>
<th>$I_{lim}$</th>
<th>$S$</th>
<th>$S^\frac{1}{2} \cdot I_{lim}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>184.0</td>
<td>8.50</td>
<td>33856</td>
<td>1564.00</td>
</tr>
<tr>
<td>11</td>
<td>190.0</td>
<td>8.70</td>
<td>36100</td>
<td>1653.00</td>
</tr>
<tr>
<td>12</td>
<td>195.0</td>
<td>9.00</td>
<td>38025</td>
<td>1755.00</td>
</tr>
<tr>
<td>12</td>
<td>1624.4</td>
<td>74.63</td>
<td>245882</td>
<td>11313.14</td>
</tr>
</tbody>
</table>

\[
m = \frac{135751.68 - 121228.97}{2950584 - 2638675}
\]
\[
= 4.658 \times 10^{-2}
\]
\[
\frac{m}{c} = 14.38
\]

From equation (23)

\[
D = \left( \frac{0.647 \ v^\frac{1}{2} \ I_{lim}}{C \ (5)^\frac{1}{2} \ A \ n \ F \ x10^3} \right)^\frac{3}{2}
\]
\[
= 0.993 \times 10^{-5} \ cm^2/\text{sec}
\]
TABLE 3
Tabulated Results

<table>
<thead>
<tr>
<th>CONCENTRATION</th>
<th>$\frac{I_{lim}}{J^2}$</th>
<th>$b = \frac{I_{lim}}{J^2 c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.01 \times 10^{-4}$</td>
<td>1.524</td>
<td>15.08</td>
</tr>
<tr>
<td>$2.52 \times 10^{-4}$</td>
<td>3.532</td>
<td>14.02</td>
</tr>
<tr>
<td>$5.05 \times 10^{-4}$</td>
<td>7.149</td>
<td>14.16</td>
</tr>
<tr>
<td>$7.56 \times 10^{-4}$</td>
<td>10.925</td>
<td>14.45</td>
</tr>
<tr>
<td>$10.10 \times 10^{-4}$</td>
<td>14.106</td>
<td>14.08</td>
</tr>
<tr>
<td>$12.60 \times 10^{-4}$</td>
<td>17.942</td>
<td>14.24</td>
</tr>
<tr>
<td>$15.20 \times 10^{-4}$</td>
<td>21.931</td>
<td>14.43</td>
</tr>
<tr>
<td>$17.70 \times 10^{-4}$</td>
<td>25.295</td>
<td>14.29</td>
</tr>
<tr>
<td>$20.20 \times 10^{-4}$</td>
<td>30.773</td>
<td>15.23</td>
</tr>
<tr>
<td>$32.40 \times 10^{-4}$</td>
<td>46.580</td>
<td>14.38</td>
</tr>
</tbody>
</table>

Average = 14.44

$\left( \frac{D_{i3}}{I_3} \right)_{ave.} = 1.01 \times 10^{-5} \text{ cm}^2/\text{sec.}$
APPENDIX  D

CALCULATION OF STANDARD DEVIATION

The standard deviation of the experimental term \( \frac{I_{10m}}{S^{2}C} \), called \( b \) was calculated from the following equation.

\[
S. D. = \left( \frac{\sum (b_i - \bar{b})^2}{n-1} \right)^{\frac{1}{2}}
\]

where

- \( S. D. \) = standard deviation
- \( b_i \) = individual value of \( b \)
- \( \bar{b} \) = means value of \( b \)
- \( n \) = number of values of \( b \)

Values of \( b \) were taken from Table 3 and the calculations of \((b_i - \bar{b})^2\) were shown in Table 4.

<table>
<thead>
<tr>
<th>( n )</th>
<th>( b )</th>
<th>( b_i - \bar{b} )</th>
<th>((b_i - \bar{b})^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.08</td>
<td>-.64</td>
<td>.4100</td>
</tr>
<tr>
<td>2</td>
<td>14.02</td>
<td>+.42</td>
<td>.1770</td>
</tr>
<tr>
<td>3</td>
<td>14.16</td>
<td>+.28</td>
<td>.0780</td>
</tr>
<tr>
<td>4</td>
<td>14.45</td>
<td>-.01</td>
<td>.0001</td>
</tr>
<tr>
<td>5</td>
<td>18.08</td>
<td>+.38</td>
<td>.1300</td>
</tr>
<tr>
<td>6</td>
<td>14.25</td>
<td>+.19</td>
<td>.0360</td>
</tr>
</tbody>
</table>

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TABLE 4 (cont'd)

<table>
<thead>
<tr>
<th>n</th>
<th>b</th>
<th>$b_i - \bar{b}$</th>
<th>$(b_i - \bar{b})^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>14.43</td>
<td>+.01</td>
<td>.0001</td>
</tr>
<tr>
<td>8</td>
<td>14.29</td>
<td>-.15</td>
<td>.0225</td>
</tr>
<tr>
<td>9</td>
<td>15.23</td>
<td>-.79</td>
<td>.6250</td>
</tr>
<tr>
<td>10</td>
<td>14.38</td>
<td>+.16</td>
<td>.0256</td>
</tr>
<tr>
<td>Σ</td>
<td>10</td>
<td>144.40</td>
<td>1.5033</td>
</tr>
</tbody>
</table>

$$S.D. = \left( \frac{\Sigma (b_i - \bar{b})^2}{n-1} \right)^{\frac{1}{2}}$$

$$= 0.407$$

% deviation = \( \frac{0.407}{14.44} \times 100 = 2.83 \% \)
Table 5
Potential vs. Current
Concentration of \( I_2 = 12.6 \times 10^{-4} \text{N} \)
Concentration of KI = 0.1 N
Disk area = 0.728 cm²

<table>
<thead>
<tr>
<th>E volts</th>
<th>2500 rpm</th>
<th>12500 rpm</th>
<th>20500 rpm</th>
<th>25500 rpm</th>
<th>27500 rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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</table>

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Table 6
Effect of Concentration of KI on Limiting Current

Concentration of $I_2 = 5.05 \times 10^{-4}$ N

Disk Area = 0.728 cm$^2$

$E = 0.4$ volts

<table>
<thead>
<tr>
<th>$\frac{s}{r_{\text{rpm}}}^2$</th>
<th>0.0005 N</th>
<th>0.01 N</th>
<th>0.05 N</th>
<th>0.075 N</th>
<th>0.10 N</th>
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</thead>
<tbody>
<tr>
<td>63.2</td>
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<td>-</td>
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</tr>
<tr>
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<td>0.52</td>
<td>0.52</td>
<td>-</td>
</tr>
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<td>83.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.66</td>
</tr>
<tr>
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<td>0.09</td>
<td>0.59</td>
<td>0.74</td>
<td>0.72</td>
<td>0.78</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>0.95</td>
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<tr>
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</tr>
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<td>1.50</td>
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</table>
Table 7
Diffusion Current as a Function of $S^{1/2}$ [low concentration]

Concentration of KI=0.1 N

Disk area = 0.728 cm$^2$

E=0.4 volts

<table>
<thead>
<tr>
<th>$S^{1/2}$</th>
<th>I$_{ma}$ 1.0x10$^{-4}$ N</th>
<th>I$_{ma}$ 2.52x10$^{-4}$ N</th>
<th>I$_{ma}$ 5.05x10$^{-4}$ N</th>
<th>I$_{ma}$ 7.56x10$^{-4}$ N</th>
<th>I$_{ma}$ 10.1x10$^{-4}$ N</th>
</tr>
</thead>
<tbody>
<tr>
<td>rpm$^{1/2}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>54.7</td>
<td>-</td>
<td>-</td>
<td>0.45</td>
<td>0.56</td>
<td>0.75</td>
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<td>-</td>
<td>-</td>
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<tr>
<td>63.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<td>0.52</td>
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<td>0.95</td>
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<tr>
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<td>-</td>
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<td>-</td>
<td>0.80</td>
<td>-</td>
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<tr>
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<td>-</td>
<td>0.66</td>
<td>-</td>
<td>1.15</td>
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<td>0.78</td>
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<td>1.65</td>
</tr>
<tr>
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<td>0.85</td>
<td>1.31</td>
<td>1.71</td>
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<td>-</td>
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<td>1.45</td>
<td>1.90</td>
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Table 8

Diffusion Current as a Function of $S^{1/2}$ [high concentration]

Concentration of KI = 0.1 N

Disk area = 0.728 cm$^2$

$E = 0.4$ volts

<table>
<thead>
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<th>$S^{1/2}$ (rpm $^{1/2}$)</th>
<th>I (ma)</th>
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<td>12.6 x 10^{-4}N</td>
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<td>54.7</td>
<td>1.03</td>
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<td>1.12</td>
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<td>182.0</td>
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<tr>
<td>200.0</td>
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Table 9
Diffusion Current as Function of $S^{1/2}$ for two disk area

Concentration of $I_2 = 24.6 \times 10^{-4} \text{N}$

Concentration of KI = 0.1 N

$E = 0.4 \text{ volts}$

<table>
<thead>
<tr>
<th>$S^{1/2}$ $\text{rpm}^{1/2}$</th>
<th>I ma</th>
<th>$0.728 \text{cm}^2$</th>
<th>$0.479 \text{cm}^2$</th>
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</tr>
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<td></td>
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Table 10

Diffusion Current as Function of $S^{1/2}$

Concentration of $I_2 = 1.0 \times 10^{-4} \text{ N}$

Concentration of KI = 0.1 N

Disk area = 0.570 cm$^2$

$E = 0.4 \text{ volts}$

<table>
<thead>
<tr>
<th>$S^{1/2} \cdot \text{rpm}^{1/2}$</th>
<th>I (ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65.5</td>
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<td>67.0</td>
<td>0.09</td>
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<td>105.0</td>
<td>0.13</td>
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<tr>
<td>107.5</td>
<td>0.14</td>
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<tr>
<td>127.0</td>
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</tr>
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<td>0.22</td>
</tr>
<tr>
<td>190.0</td>
<td>0.23</td>
</tr>
</tbody>
</table>
VITA AUCTORIS

1936 Born in Canton, China, on October 7, 1936.

1956 Completed middle school education at Pui Ching Middle School, Hong Kong.

1961 Received the Degree of Bachelor of Applied Science in Chemical Engineering from Assumption University of Windsor, Windsor, Ontario.

1964 Currently a candidate for the Degree of Master of Applied Science in Chemical Engineering at the University of Windsor.