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MASS TRANSFER AND POLARIZATION AT A ROTATING DISK ELECTRODE

Limin Hsueh

(M.S. Thesis)

January 1966
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MASS TRANSFER AND POLARIZATION AT A ROTATING DISK ELECTRODE

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ABSTRACT

The rotating disk electrode method is used to study mass transfer and polarization during metal deposition from a binary electrolytic solution at high concentrations. The effects of variation of physical properties in the diffusion layer and of a non-zero interfacial velocity due to the high mass-transfer rate have been taken into consideration in determining the velocity and concentration profiles. The results are used to evaluate the limiting current density and the concentration polarization.

A rigorous way to separate the total overpotential as the sum of concentration overpotential, activation overpotential and resistance overpotential in a concentrated solution is given. The proper choice of the location of the reference electrode and the surface treatment of electrodes for a metal deposition reaction are discussed.

For the limiting current density measurement in a low conductivity electrolyte, the method of "limiting speed" is introduced so that the resistance overpotential can be held constant. The experimental results of limiting current divided by the square root of the rotating speed, \( i_{\text{lim}}/\sqrt{\Omega} \), are found to agree well with the theoretically predicted values at high concentrations.
I. INTRODUCTION

The rotating disk electrode has been widely used as a tool for studying electrode processes and mass transfer because the velocity and concentration profiles can be predicted theoretically and the strong forced convection eliminates the effects of natural convection. Two branches of work have been done on this field:

i. to study mass transfer processes by means of the limiting current density or to obtain the diffusion coefficient as a function of concentration.

ii. to study electrode kinetics by means of the polarization curve, so as to obtain the kinetic parameters of the reaction as functions of concentrations, or as they are modified by additional agents.

For the first part, the theory of concentration polarization was developed in 1942 by Levich. The original theory of Levich involved the assumptions of constant physical properties throughout the diffusion layer and a zero interfacial velocity at the surface of the disk. In order to meet these assumptions, most experimental work has been done at relatively low concentrations (e.g., $10^{-5}$ to $10^{-3}$ M).

For the second branch, the main interest centered on activation polarization. In order to keep the uncertain value of ohmic resistance as low as possible, most experimental work involved high concentrations (e.g., 0.1 to 1 M), with excess supporting electrolyte. Generally the current density was low, far from the limiting current density.

For the case of constant physical properties of the electrolytic solution the (hydrodynamic) theory of the rotating disk electrode and its applications are given in the book of Levich and a review paper.
by Riddiford. The transient effect of hydrodynamics and mass transfer at a rotating disk were studied by Olander, Hale, and Filinovskii and Kiryanov.

Recently, the variation of physical properties and non-zero interfacial mass transfer velocity have been taken into consideration for a binary, concentrated electrolyte. Both the velocity profile and the concentration profile for the rotating disk electrode have been solved by Newman and Hsueh. Therefore, the primary aim of this work is to study the mass transfer rate by a limiting current technique for comparison with the theoretical results where the variation of physical properties in the diffusion layer was taken into consideration. The experiments were carried out with concentrated solutions without any supporting electrolyte.

Since the theoretical analysis involves solutions of a single salt, a metal deposition reaction in the system of copper-copper sulfate was chosen for this investigation, in spite of the fact that the metal deposition reaction has the following experimental difficulties compared with a redox reaction:

1. the electrode surface cannot remain unaltered;
2. it takes a longer time to reach the steady state electrode potential, as was pointed out by Brown and Thirsk.

II. THEORY OF THE ROTATING DISK ELECTRODE

§2-1 Fluid Flow

The general analytic approach to the influence of physical property variation on the velocity and concentration profiles was first solved by Olander in 1962 for steady, laminar flow at high Schmidt numbers.
In his paper, two parameters $\epsilon_D$ and $\epsilon_\rho$ were defined as follows:

$$\epsilon_D = - (\omega_\text{zero} - \omega_\infty) \frac{1}{D} \frac{dD}{d\omega_s} = \ln \left( \frac{D_\infty}{D_\text{zero}} \right)$$

$$\epsilon_\rho = - (\omega_\text{zero} - \omega_\infty) \frac{1}{\rho} \frac{d\rho}{d\omega_s} = \ln \left( \frac{\rho_\infty}{\rho_\text{zero}} \right)$$

where $\omega_s$ mass fraction of salt
$D$ diffusion coefficient
$\rho$ density of solution

subscript $\infty$ in the bulk of solution
subscript $0$ at interface of electrode.

With the assumption that the density and diffusivity vary exponentially with mass fraction over the concentration range of interest, i.e., both $\epsilon_D$ and $\epsilon_\rho$ are independent of composition, the rate of mass transfer in terms of the Nusselt number was solved by a perturbation method.

Without involving any limitation on how the physical properties vary with concentration, Newman and Hsueh\textsuperscript{7} have obtained numerical solutions of the velocity and concentration profiles for a binary, concentration electrolyte. We summarize here their method and results.

The analysis applies to a disk which provides a uniformly accessible surface and rotates horizontally about an axis through its center perpendicular to the plane of the disk at a constant angular speed $\Omega$ in a Newtonian fluid.

From an experimental viewpoint we must make the further assumptions that:

1. in order to maintain steady, laminar flow, the Reynolds number should not exceed $2 \times 10^5$. The Reynolds number for a rotating disk is defined as $\frac{r^2 \Omega}{v}$ where $r$ is the radius of disk, $\Omega$ is the angular velocity
of disk (radians per second) and \( \nu \) is the kinematic viscosity of the fluid.

ii. the effect of natural convection may be ignored, since the solution is strongly stirred by the disk.

iii. there are no bounding surfaces which may affect the velocity
and concentration profile. By bounding surface, we mean the wall of the
vessel, an air-solution interface, or any other experimental equipment,
such as a thermometer, or a reference electrode.

iv. the edge effects can be neglected both in the mass transfer
and in the hydrodynamic analysis.

For the velocity profile, the equation of motion has to be solved;
for steady state it reads

\[
\rho \gamma \cdot \nabla \gamma = - \nabla p - \nabla \cdot \tau + \rho g
\]  \hspace{1cm} (2-1)

where \( \tau \) is the stress tensor which for a Newtonian fluid reads in
rectangular coordinates

\[
\tau_{ij} = -\mu \left( \frac{\partial \gamma_i}{\partial x_j} + \frac{\partial \gamma_j}{\partial x_i} \right) + \frac{2}{3} \mu (\nabla \cdot \gamma) \delta_{ij}
\]  \hspace{1cm} (2-2)

where \( \delta_{ij} \) is the Kronecker delta

\[
\delta_{ij} = 1 \quad \text{if} \quad i = j
\]
\[
\delta_{ij} = 0 \quad \text{if} \quad i \neq j
\]

The equation of motion must be solved together with the equation
of continuity

\[
\nabla \cdot (\rho \gamma) = 0.
\]  \hspace{1cm} (2-3)

Because of the nature of the rotating disk, it is convenient to
choose cylindrical coordinates \( r, \theta \) and \( z \), where \( r \) is the radial distance
from the axis of rotation, \( \theta \) is the circumferential angle of rotation,
and \( z \) is the normal distance from the disk. The corresponding velocity
components are \(v_r\), \(v_\theta\) and \(v_z\), respectively.

By axial symmetry, all three velocity components are independent of \(\theta\). Furthermore, in solving for the velocity profile of the system, the most important feature which provides the major simplification from a set of partial differential equations to ordinary differential equations is that the \(z\)-component of velocity can be assumed to be a function of the perpendicular distance from the disk surface only. It is independent of the radial distance. Physically, this means that \(v_z\) brings fresh reacting ions to the electrode surface at a uniform rate over the whole disk.

It should be emphasized that the vector sum of \(v_r\), \(v_\theta\) and \(v_z\) does not have to be identical for the same distance from the disk, because of the dependence of \(v_r\) and \(v_\theta\) on \(r\).

The above assumptions are summarized as follows

\[
\begin{align*}
    v_r &= v_r(r, z) \\
    v_\theta &= v_\theta(r, z) \\
    v_z &= v_z(z) \\
    p &= p(z).
\end{align*}
\]

Since under these conditions \(v_z\) is the only velocity component which can affect the concentration in the boundary layer, one may conclude that the concentration near the disk is a function of \(z\) only. Furthermore, all the physical properties, such as density, viscosity, diffusivity, electric conductivity, and transference number of an electrolyte depend on concentration only at a constant temperature. Therefore all of the physical properties are assumed to vary in the \(z\)-direction only.

The components of the equation of motion, Equation (2-1), are given
in cylindrical coordinates in Bird, Steward and Lightfoot.  

\[
\begin{align*}
\rho \left( v_r \frac{\partial v_r}{\partial r} - \frac{v_r^2}{r} + v_z \frac{\partial v_r}{\partial z} \right) &= - \frac{1}{r} \frac{\partial}{\partial r} \left( r \tau_{rr} \right) - \frac{\tau_{\theta z}}{r} + \frac{\partial \tau_{rz}}{\partial z}, \\
\rho \left( v_r \frac{\partial v_\theta}{\partial r} + \frac{v_r}{r} v_\theta + v_z \frac{\partial v_\theta}{\partial z} \right) &= - \frac{1}{2} \frac{\partial}{\partial r} \left( r^2 \tau_{r\theta} \right) + \frac{\partial \tau_{\theta z}}{\partial z}, \\
\rho v_z \frac{\partial v_z}{\partial z} &= - \frac{\partial p_z}{\partial r} - \frac{1}{r} \frac{\partial}{\partial r} \left( r \tau_{rz} \right) + \frac{\partial \tau_{rz}}{\partial z} + \rho g_z,
\end{align*}
\]

(2.4)

where the nine components of the stress tensor in cylindrical coordinates are

\[
\begin{align*}
\tau_{rr} &= -\mu \left[ 2 \frac{\partial v_r}{\partial r} - \frac{2}{3} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r v_r \right) + \frac{\partial v_z}{\partial z} \right) \right], \\
\tau_{\theta \theta} &= -\mu \left[ 2 \frac{v_r}{r} - \frac{2}{3} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r v_r \right) + \frac{\partial v_z}{\partial z} \right) \right], \\
\tau_{zz} &= -\mu \left[ 2 \frac{\partial v_z}{\partial z} - \frac{2}{3} \left( \frac{1}{r} \frac{\partial}{\partial r} \left( r v_r \right) + \frac{\partial v_z}{\partial z} \right) \right], \\
\tau_{r \theta} &= \tau_{\theta r} = -\mu \left[ \frac{\partial v_\theta}{\partial r} \right], \\
\tau_{\theta z} &= \tau_{z \theta} = -\mu \left[ \frac{\partial v_z}{\partial z} \right], \\
\tau_{z r} &= \tau_{r z} = -\mu \left[ \frac{\partial v_r}{\partial z} \right].
\end{align*}
\]

(2.5)

The equation of continuity becomes

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \nu_r \right) + \frac{\partial v_z}{\partial z} = -\frac{v_z \partial p}{\partial z}.
\]

(2.6)

Since we are interested in a concentrated, binary electrolyte, the mass transfer rate at the surface is very high, and the interfacial velocity will no longer be zero. If a metal deposition reaction is being considered, the cation is the only substance which carries current to the electrode surface. In other words, the flux of anions \( N_{-z} \) and
the flux of the solvent \( \dot{\omega}_o \) are both zero at the surface.

\[
\dot{\omega}_o = \dot{\omega}_{-z} = 0 \quad \text{at } z = 0
\]

\[
\dot{\omega}_{+z} = \frac{i_z}{Fz_+} \quad \text{at } z = 0
\]  

where \( i_z \) is the current density normal to the electrode, 

\( F \) is Faraday's constant.

From here on, the subscript "+" refers to cations or cathodic, "-" refers to anions or anodic, and "o" refers to the solvent.

The mass average velocity is defined as

\[
v = \frac{\sum \rho_i v_i}{\sum \rho_i}
\]  

(2-8)

If the relation between mass flux and molar flux is used

\[
n_i = \rho_i v_i = \dot{\omega}_i M_i
\]

together with Equations (2-7) and (2-8), one obtains

\[
v_z = \frac{i_z M_+}{\rho Fz_+}
\]  

(2-9)

where \( M \) is molecular weight.

This is a major difference in the boundary condition compared with von Karman's solution\textsuperscript{11} where the Navier-Stokes equation was solved with the boundary condition \( v_z = 0 \) at \( z = 0 \).

In order to give an idea of the order of magnitude of \( v_z \) at \( z=0 \) when a rotating disk electrode is operated at limiting current density, i.e., the maximum rate of mass transfer, we present an example. If a disk electrode is rotated at a speed of 300 r.p.m. in 0.1 M copper sulfate solution at 25°C, the limiting current density is 79mA/cm², and
v_z equals $2.60 \times 10^{-5}$ cm/sec at the disk, compared with $v_z = 4.7 \times 10^{-1}$ cm/sec far from disk.

At the interface, the other two velocity components are

$$\begin{align*} v_r &= 0, \quad v_\theta = \rho \Omega \quad \text{at } z = 0. \end{align*}$$

As z increases, $v_r$ and $v_\theta$ must tend to die away, i.e.,

$$\begin{align*} v_r &= 0, \quad v_\theta = 0 \quad \text{at } z = \infty. \end{align*}$$

A dimensionless distance $\xi$, and dimensionless velocities $F$, $G$, and $H$ are defined as follows:

$$\begin{align*} \xi &= z \sqrt{\frac{\Omega}{v_\infty}} \quad (2-10) \\
v_r &= r \Omega F(\xi) \\
v_\theta &= r \Omega G(\xi) \\
v_z &= \sqrt{\Omega v_\infty} H(\xi) \\
p &= \mu_\infty \Omega F(\xi) + \rho z \int_0^z \rho dz. \quad (2-12) \end{align*}$$

These definitions assume the same dependence for $v_r$ and $v_\theta$ as assumed by von Karman\textsuperscript{11}. Now the nine components of the stress tensor become

$$\begin{align*} \tau_{rr} &= \tau_{\theta\theta} = - \frac{2}{3} \mu \Omega (F-H') \\
\tau_{zz} &= \frac{4}{3} \mu (F-H') \\
\tau_{r\theta} &= \tau_{\theta r} = 0 \\
\tau_{\theta z} &= \tau_{z\theta} = - \mu \Omega G \sqrt{\frac{\Omega}{v_\infty}} \\
\tau_{zr} &= \tau_{rz} = - \mu \Omega H \sqrt{\frac{\Omega}{v_\infty}} \end{align*} \quad (2-13)$$

and the equation of motion becomes:
\[
\begin{aligned}
F^2 - G^2 + H'H' &= \frac{\rho}{\rho_\infty} \frac{d}{d\xi} \left( \frac{\mu}{\mu_\infty} \frac{F'}{F} \right) \\
2FG + HG' &= \frac{\rho}{\rho_\infty} \frac{d}{d\xi} \left( \frac{\mu}{\mu_\infty} G' \right) \\
\frac{\rho}{\rho_\infty} HH' + P' &= \frac{4}{3} \frac{d}{d\xi} \left[ \frac{\mu}{\mu_\infty} (H' - F') \right] + \frac{2\mu}{\mu_\infty} P'
\end{aligned}
\]

and the equation of continuity becomes

\[
2F + H' = -H \frac{1}{\rho} \frac{d\rho}{d\xi}
\]

where primes denote differentiation with respect to \( \xi \). The boundary conditions become

\[
\begin{aligned}
\xi &= 0 \quad F(0) = 0 \quad G(0) = 1 \\
\xi &= \infty \quad F(\infty) = 0 \quad G(\infty) = 0.
\end{aligned}
\]

Since the variation of pressure due to the hydraulic head is very small and the variation of the fluid properties due to pressure is negligible, it is not necessary to solve \( z \)-component of the equation of motion (2-14), the only equation where the variation of pressure has been involved.

§2-2 Mass Transfer

The mechanism of transfer of cations from the bulk of the solution to the surface of the cathode consists, essentially, of three processes: molecular diffusion, migration, and convection. At steady state, the sum of the rate of these three processes is balanced by the rate of discharging at the electrode surface.

The flux of cations can be expressed as

\[
N_+ = -v_+ \frac{D_+}{M_+} \nabla u_+ + \frac{I_+}{F_+} + C_+ n_+ \quad (2-16)
\]

where \( t_+ \) cation transference number with respect to mass average velocity
M sub s, molecular weight of salt

v sub +, number of cations produced by dissociation of one molecule of electrolyte.

For consistency with the velocity profile of the previous section, the mass average velocity was chosen as the basis of the flux equation. This is the reason that the mass fraction gradient is used instead of a concentration gradient as the driving force for molecular diffusion.

If a material balance is applied to the cation over a volume element, the equation of continuity reads

\[
\frac{\partial c_+}{\partial t} = - \nabla \cdot N_+ .
\]  (2-17)

Inserting Equation (2-16) into Equation (2-17), with use of the basic relations of Equations (A-2), (A-4) and (A-5) for a binary electrolyte (see Appendix A) yields

\[
\rho \frac{\partial s}{\partial t} + \rho v \cdot \nabla \omega_s = \nabla \cdot (\rho D \nabla \omega_s) - \frac{M_s v}{z_+ v_+} .
\]  (2-18)

As it was assumed in section 2-1 that all physical properties vary in the z direction only, Equation (2-16) can be written

\[
N_{+z} = - v + \frac{Dp}{M_s} \frac{\partial \omega_s}{\partial z} + \frac{i t_+}{z_+} + C_+ v_z .
\]  (2-19)

At steady state, Equation (2-18) becomes

\[
\rho v \frac{\partial \omega_s}{\partial z} + \frac{M_s i z}{z_+ v_+} \frac{\partial \omega_s}{\partial t_+} + \rho D \frac{\partial^2 \omega_s}{\partial z^2} + \frac{\partial \omega_s}{\partial z} \frac{\partial}{\partial z} (\rho D) .
\]  (2-20)

The boundary conditions are

\[
z = 0 \quad \omega_s = \omega_{zero}
\]

\[
z = \infty \quad \omega_s = \omega_{\infty} .
\]  (2-21)
When the dimensionless variables $\xi$ and $H$ which have been defined in Equation (2-10) and (2-11) are introduced into Equation (2-20), it becomes

$$\left(\frac{\rho}{\rho_\infty} H + I \frac{dt_+}{d\omega_s}\right) \frac{d\omega_s}{d\xi} = \frac{d}{d\xi} \left(\frac{\rho}{\rho_\infty} \frac{d\omega_s}{d\xi}\right)$$

where $I$ is a dimensionless current density defined as

$$I = \frac{M_z}{\rho_\infty \nu E \sqrt{\Omega \nu}}.$$ 

It is clear that the current density is proportional to the square root of speed even in a concentrated solution.

Formal integration of Equation (2-22) gives

$$w_s = k_1 \int_0^\xi \mu_\infty \exp \int_0^\xi \mu_\infty \left(\frac{\rho}{\rho_\infty} H + I \frac{dt_+}{d\omega_s}\right) d\xi$$

where $k_1$ and $k_2$ are constants of integration to be determined by the boundary conditions (2-21). Finally, the concentration profile is

$$\frac{w_s - w_{zero}}{w_\infty - w_{zero}} = \frac{\int_0^\xi \mu_\infty \exp \int_0^\xi \mu_\infty \left(\frac{\rho}{\rho_\infty} H + I \frac{dt_+}{d\omega_s}\right) d\xi}{\int_0^\xi \mu_\infty \exp \int_0^\xi \mu_\infty \left(\frac{\rho}{\rho_\infty} H + I \frac{dt_+}{d\omega_s}\right) d\xi}.$$ 

(2-23)

Because of the non-zero interfacial velocity, the dimensionless current $I$ is further related to the dimensionless axial velocity $H$ by Equation (2-9) in the form

$$H(0) = \frac{\rho_\infty \nu M_z I}{\rho} \text{ at } \xi = 0.$$ 

(2-24)

§2-3 Limiting Current Density

The rate of charge transfer at the electrode surface in a metal deposition reaction by passing a current $i_z$ at the cathode is $i_z F z^+$. 

At steady state, it should be balanced by the rate of mass transfer to the surface by diffusion, migration and convection which has been defined in Equation (2-19):

\[
\frac{1}{F_z} \frac{dz}{dz} = -v \frac{D_0}{M_s} \frac{dw_s}{dz} + \frac{1}{F_z} \frac{dz}{dz} t_+ + \frac{\partial}{\partial z} \omega_+ v_+ \quad \text{at } z = 0. \tag{2-25}
\]

Notice that the convection term is not zero at the surface.

Substitution of Equation (2-9) into Equation (2-25) and solving for the current density yields:

\[
i_z = \frac{\rho D F_z v_+}{M_s (1-t_+ - \omega_+)} \frac{dw_s}{dz} \bigg|_{z=0} \tag{2-26}
\]

or in dimensionless form

\[
I = -\frac{\rho D}{M_\infty (1-t_+ - \omega_+)} \frac{dw_s}{d\xi} \bigg|_{\xi=0}. \tag{2-27}
\]

This relates the current I to the concentration profile at the metal-solution interface, and it also serves as a boundary condition for solving the concentration profile in section 2-2. The limiting current density is obtained from Equation (2-26) by letting the interfacial mass fraction of salt \( \omega \) be zero

\[
\lim_{z \to \infty} i_z = -\frac{\rho D F_z v_+}{\sqrt{\nu} \sqrt{\nu} M_s (1-t_+)} \frac{dw_s}{d\xi} \bigg|_{\xi=0}. \tag{2-28}
\]

### §2-4 Numerical Solution Method

In the previous sections, a set of nonlinear equations were derived that would give the velocity profile at the disk and the concentration profile in the diffusion region. The equations to be solved numerically and their boundary conditions are summarized below.
\[
\begin{align*}
F^2 - G^2 + HF' &= VF'' + U'F' \\ 2FG + HF &= VG'' + U'G' \\ 2F + H' &= -HR' \\
\frac{d}{d\xi} \left( \frac{\rho D}{\mu_\infty} \omega_b' \right) + \frac{\rho}{\mu_\infty} H' + \frac{d}{d\omega_b} \omega_b' &= 0 
\end{align*}
\]  
(2-14) \]

where

\[
V = \frac{\mu}{\mu_\infty} \frac{\rho_\infty}{\rho} \\
U' = \frac{\rho_\infty}{\rho} \frac{d}{d\xi} \left( \frac{\mu}{\mu_\infty} \right) \\
R' = \frac{d}{d\xi} \ln \frac{\rho}{\rho_\infty} 
\]

We have four unknowns, \( F, G, H, \) and \( \omega_b \) to be determined as functions of \( \xi \) by these four equations. Since \( V, U', \) and \( R' \) are related to the concentration, they are not independent variables but are known once the concentration profile has been obtained. The boundary conditions are

at \( \xi = \infty \)
\[
\begin{align*}
F &= 0 & G &= 0 & \omega &= \omega_\infty \\
\xi &= 0 & F &= 0 & G &= 1 & \omega \approx \omega_{\text{zero}} 
\end{align*}
\]  
(2-21) 

\[
H = \frac{\rho_\infty}{\rho} \frac{\nu + M}{M_b} 
\]  
(2-24) 

\[
I = \frac{M_b z}{\rho_\omega \nu z + F \sqrt{\rho D}} = - \frac{\rho D}{\mu_\infty (1-t-M_\infty)} \frac{d\omega}{d\xi} \bigg|_{\xi=0} 
\]  
(2-28) 

In order to solve equations (2-14) and (2-15), we have to linearize them by assuming each variable, \( F, G, \) and \( H, \) to be the sum of a main term and a first order correction, i.e.,

\[
F = F_0 + F_1 \\
G = G_0 + G_1 \\
H = H_0 + H_1 
\]
By substituting $F$, $G$, and $H$ into Equation (2-14) and (2-15), neglecting the products of correction terms, and replacing all remaining $F_1$, $G_1$, and $H_1$ by the original functions $F$, $G$, and $H$ and $F_0$, $G_0$, and $H_0$, those differential equations become

\begin{align}
VF'' + \left(U' - H_0\right) F' - \left(2F_0 F - 2G_0 G + F_0^2 H\right) &= - \left(H_0 F' + F_0^2 - G_0^2\right) \tag{2-29}
\end{align}

\begin{align}
VG'' + \left(U' - H_0\right) G' - \left(2G_0 F + 2F_0 G + G_0^2 H\right) &= - \left(H_0 G' + 2F_0 G_0\right) \tag{2-30}
\end{align}

\begin{align}
H' + (2F + R'H) &= 0 \tag{2-31}
\end{align}

It is clear that Equations (2-29) and (2-30) are linear in $F$ and $G$, respectively, now. The next step is to convert them into difference equations so that they can be solved with a computer. With a mesh size of $h$ the first and second central difference quotients for $F$ and $G$ are

\begin{align}
F' &= \frac{F_{j+1} - F_{j-1}}{2h} \quad F'' = \frac{F_{j+1} - 2F_j + F_{j-1}}{h^2} \\
G' &= \frac{G_{j+1} - G_{j-1}}{2h} \quad G'' = \frac{G_{j+1} - 2G_j + G_{j-1}}{h^2}
\end{align}

Substitution into Equations (2-29), (2-30) and rearrangement gives

\begin{align}
\left(V + \frac{U' - H_0}{2h} \right) F_{j+1} - 2\left(V + \frac{U' - H_0}{2h}\right) F_j + \left(V + \frac{U' - H_0}{2h}\right) F_{j-1}
- F' H_j + 2G_j F_j &= - H_0 F' + F_0^2 + G_0^2 \tag{2-32}
\end{align}

\begin{align}
\left(V + \frac{U' - H_0}{2h} \right) G_{j+1} - 2\left(V + \frac{U' - H_0}{2h}\right) G_j + \left(V + \frac{U' - H_0}{2h}\right) G_{j-1}
- G' H_j + 2F_j G_j &= - H_0 G' - 2F_0 G_0 \tag{2-33}
\end{align}

Since only the first derivative is involved in Equation (2-31), the central difference quotient would cause the coefficient of $H$ at the mesh point $j$ to be zero if $R' = 0$, i.e., if density is constant. In view of this, the backward difference quotient was chosen and all numerical values were evaluated half-way between the mesh point $j$ and $j-1$:

\begin{align}
H' &= \frac{1}{h} \left(H_j - H_{j-1}\right) \quad F = \frac{1}{2} \left(F_j + F_{j-1}\right) \\
R'H = \frac{1}{2} \left(R'H_j + R'_{j-1}H_{j-1}\right).
\end{align}
The difference equation for Equation (2-31) is
\[
\left(\frac{2}{3}R_j h + 1\right) H_j + \frac{1}{2}(R_{j-1}^h h - 1) H_{j-1} + F_j h + F_{j-1} h = 0 \quad (2-34)
\]

The finite difference equations were solved on a high speed computer by solving the coupled tri-diagonal matrices, with a mean size of 0.01. Based on the asymptotic solution of the fluid mechanics for large \( \xi^{13} \), the boundary conditions at infinity were replaced by those at a finite distance, say \( \xi = 10 \), which is far beyond the hydrodynamic and diffusion boundary layers.

As for the concentration profile, Equation (2-22) has been solved analytically to yield the form of Equation (2-23). The trapezoidal rule was used for numerical integration of the latter equation. The upper limit of integration was replaced by the last mesh point.

Data for the physical properties of copper sulfate solutions at 25°C were collected from the literature \(^{32-47}\). Most of these were fitted by linear regression to finite power series in the mass fraction of copper sulfate. The graphs of the data and their equations are shown in Figures 2-1 to 2-5.

The calculated velocity profile for 0.02M and 0.5M copper sulfate solution are shown in Figure 2-6 and Figure 2-7. The velocity profile for 0.02M is very close to von Kármán's solution \(^{11}\), which may serve as a reference for the purpose of comparison.

### III. POLARIZATION AT A ROTATING DISK ELECTRODE

A great many studies have been made on the subject of the kinetics of electrode processes. The main purpose is to study the mechanisms of an electrode reaction and to relate the current density to the total overpotential measured. Vetter \(^{14}\) presented an extensive survey of this
The transference number of CuSO₄ solutions at 25°C is given by the equation:

\[ t_+ = 0.402937 - 3.5889 \omega + 8.21995 \omega^{1.5} \]

Figure 2-1. Transference number of CuSO₄ solutions at 25°C. O Fritz and Fuget³²
Figure 2-2. Diffusion coefficient of CuSO₄ solutions at 25°C.

- Eversole, Kindsvater and Peterson
- Emanuel and Olander

\[ D = (0.207 e^{-29.0 \sqrt{\omega}} + 0.638 - 0.580 \sqrt{\omega}) \times 10^{-5} \text{ cm}^2/\text{sec} \]
\[ \rho = 0.9967 + 0.0269 \omega^{1/2} + 0.7477 \omega + 0.8072 \omega^{1.5} \]

Figure 2-3. Density of CuSO₄ solutions at 25°C.
- Pearce and Pumplin
- Asmus
- Holler and Peffer
Figure 2-4. Specific conductivity of CuSO₄ solutions at 25°C. 
- Owen and Gurry
- Richardson and Taylor
- Fedoroff
Figure 2-5. Mean activity coefficient of CuSO₄ solutions at 25°C.

\[ -\log_{10} \gamma = 0.17459 + 6.87927 \omega^{0.5} - 15.0346 \omega + 13.8321 \omega^{1.5} \]

- Nielsen and Brown 61 Adjusted
- Wetmore and Gordon 63 Adjusted
- Wetmore and Gordon Smoothed
- Robinson and Stokes 64
Figure 2-6. Velocity profile in copper sulfate solutions at 25°C.
Figure 2-7. Velocity profile in copper sulfate solutions at 25°C.
field in his monograph. Several review papers on the basic ideas of electrode kinetics are due to Parsons\textsuperscript{15} and Petrocelli\textsuperscript{16}.

A fairly general equation which has been used frequently to relate the current density and overpotential for a first order electrode reaction is

\[ i = i_0 \left[ \frac{C_{ox}}{(C_{ox})_\infty} \exp \left( \frac{\alpha nF \varphi}{RT} \right) - \frac{C_{Red}}{(C_{Red})_\infty} \exp \left( - \frac{(1-\alpha) nF \varphi}{RT} \right) \right] \]  

(3-1)

where \( i_0 \) exchange current density
\( \alpha \) transfer coefficient
\( C_{ox} \) concentration of oxidized species at the interface
\( (C_{ox})_\infty \) concentration of oxidized species at the bulk solution.

The model and theory for this equation are by no means rigorous. However, it has been widely accepted for fitting experimental results. The main reason it fits the curve so well is that two parameters \( \alpha \) and \( i_0 \) may be adjusted to match the data. They are so flexible that for the same electrode system the values of \( i_0 \) frequently differ from author to author. Tanaka and Tamamushi\textsuperscript{17} have collected most available kinetic parameter data and tabulated them. They also complained that it was hard to compare the data on the same system obtained by different investigators by different methods.

The total overpotential is usually regarded as the sum of activation overpotential \( \varphi_a \), the concentration overpotential \( \varphi_c \), and the ohmic resistance of the solution \( \varphi_{ohm} \),

\[ \varphi_{tot} = \varphi_a + \varphi_c + \varphi_{ohm}. \]  

(3-2)

In Equation (3-1), \( \varphi \) presumably is the sum of \( \varphi_a \) and \( \varphi_c \). There is essentially no clear-cut line between \( \varphi_a \) and \( \varphi_c \). It depends on how they were defined.
Petrocelli\textsuperscript{16} separated the concentration overpotential from $\varphi_a$ by assuming that $\varphi = \varphi_c$ when the applied current $i$ is much less than $i_0$. Physically, this means that the electrode reaction is proceeding very close to equilibrium and the overpotential is due almost entirely to the concentration change and was designated by $\varphi_c$. Whereas, $\varphi_a$ was claimed by him to be the remaining part, i.e.,

$$\varphi_a = \varphi - \varphi_c$$

We will not follow his method. It is mentioned here simply for the purpose of comparison. The distinction we draw between $\varphi_a$ and $\varphi_c$ is clarified in sections 3-1 and 3-2.

In the absence of concentration polarization, the electrical resistivity of the solution may be taken as constant throughout the solution. The rigorous way to find the total resistance of solution lies in the theory of the potential and involves solving Laplace's equation $\nabla^2 \varphi = 0$ for the potential with consideration of the geometry of the electrode and insulator as boundary conditions. Kasper\textsuperscript{18} gives an excellent review of this field.

An additional contribution to the ohmic resistance arises when there is concentration polarization because the concentration variations in the diffusion layer change the conductivity of the solution. See Figure 3-1 for a schematic representation of the electrical resistivity in the solution. This additional resistance has been considered as a part of the concentration polarization in this paper.

§3-1 Concentration Overpotential

It has long been realized that when two identical single electrodes are in contact with different concentrations of solution, there exists
Figure 3-1. Resistivity in solution near the electrode surface. Dash line: shows the resistivity in the absence of concentration changes.
an e.m.f. between the two terminals. When an electrochemical process takes place at the surface of an electrode, the slowness of supply of ions by diffusion and migration produces a concentration gradient, or chemical potential gradient in the thermodynamic sense between the bulk solution and the interface near the surface of the electrode. This means that the applied potential must be large enough to balance the e.m.f. produced by the concentration difference in addition to the other voltage drops in the circuit.

Also there is another effect which arises due to the concentration gradient in the diffusion layer. It is the change of electrical conductivity in the diffusion layer as was mentioned in the beginning of this chapter.

A general equation of concentration overpotential which includes both effects was presented by Newman\(^\text{12}\). In general an electrode reaction in a binary salt solution can involve the solvent and the ions

$$
S^z_Q^+ + S^{-z} Q^- + S^0 O^- \rightarrow ne^-
$$

(3-3)

where \(Q_i\) symbol for the formula of species \(i\),

\(S_i\) the stoichiometric coefficient of species \(i\).

In this case the potential gradient in the solution for such a reference electrode referred to a reference electrode at a fixed location is\(^\text{12}\)

$$
\nabla \phi = - \frac{1}{\kappa} - \frac{1}{Fz_+v_+} \left( \frac{z^+ S^+}{n} + t_+ - \frac{S^0 z^+ c^+}{n c_0} \right) \nabla \mu_e
$$

(3-4)

where \(\nabla \mu_e\) is the chemical potential gradient which equals

\((v_+ + v_-)RT \ln \gamma m, \gamma\) is the activity coefficient of the salt, \(m\) is the molality of the solution, and \(\kappa\) is specific conductivity of the solution.
As it has been assumed in section 2-1 that the physical properties of the solution in the diffusion layer are functions of \( z \) only, so are the electrical potential \( \phi \) and chemical potential \( \mu_e \):

\[
\frac{d\phi}{dz} = \frac{1}{\kappa} \left[ \frac{(v^+ + v^-)RT}{Fz^+} \left( \frac{z^+}{n} + t^+ - \frac{S_{o^+} + C_+}{n C_o} \right) \right] \frac{d\ln y_m}{dz}.
\] (3-5)

Introduction of the dimensionless distance \( \xi \) and dimensionless current density \( \bar{I} \), and integration with respect to \( \xi \) yields

\[
\phi(\xi) - \phi(0) = -\frac{\nu^+ I p_o v^+ Fz^+}{M_s} \int_0^\xi \frac{1}{\kappa} d\xi - \frac{(v^+ + \mu^-)RT}{Fz^+} \int_0^{(\gamma m)\xi} \frac{z^+}{n} + t^+ - \frac{S_{o^+} + C_+}{n C_o} \, d\gamma_m.
\] (3-6)

The concentration overpotential is then defined as the difference between this total potential difference and the ohmic drop in a uniform solution of conductivity \( \kappa_\infty \):

\[
\phi_c = \frac{\nu^+ I p_o v^+ Fz^+}{M_s} \int_0^\infty \left( \frac{1}{\kappa} - \frac{1}{\kappa_\infty} \right) d\xi + \frac{(v^+ + \mu^-)RT}{Fz^+} \int_0^{(\gamma m)\infty} \frac{z^+}{n} + t^+ - \frac{S_{o^+} + C_+}{n C_o} \, d\gamma_m.
\] (3-7)

§3-2 Activation Overpotential

According to the Arrhenius theory of chemical kinetics, a chemical reaction occurs when a sufficient driving force is provided to cause the reactants to overcome a certain energy barrier and reach an activated state, thus initiating the reaction. Similarly, for an electrode reaction, a potential must be applied in order to change the shape of the energy barrier such that it favors the electrode reaction in one direction rather than the other. This part of the overpotential which is used to overcome the activation energy barrier is called the activation overpotential. It is also said to be related to the slowness of the chemical step or the charge transfer at the electrode.
Jahn and Vielstich\textsuperscript{19} have used the rotating disk electrode to study the rates of electrode reactions. They claim that the activation overpotential can be measured by extrapolating the rotating speed to infinity. Physically, this means that the electrolyte is so well stirred that there is no concentration difference being set up at the interface when a current is passing through it. There would be no concentration overpotential if there is no concentration difference. This is to say that if $C_i = (C_i)_{\infty}$, the overpotential is all due to activation overpotential, and Equation (3-1) becomes

$$i = i_o \left[ \exp \left( \frac{\alpha nF}{RT} \phi_a \right) - \exp \left( - \frac{(1-\alpha)nF}{RT} \phi_a \right) \right]$$

(3-8)

where $\phi_a$ is activation overpotential.

\section*{§3-3 Resistance Overpotential}

For a disk electrode submerged into an electrolytic solution, the ohmic drop has been ignored by most workers\textsuperscript{8,19,20,21}. They all add a large amount of supporting electrolyte in order to increase the conductivity of solution and minimize the ohmic drop.

However, for a disk electrode, 5 mm in diameter, in a solution of specific conductivity as high as 0.1 ohm$^{-1}$cm$^{-1}$, the ohmic drop has almost the same order of magnitude as concentration and activation overpotential for many electrode reactions.

Levich\textsuperscript{2a} made an attempt to find the ohmic resistance by assuming that the potential is a function of normal distance from the disk only. Presumably, the disk has an infinite diameter. However, it turns out to be a very poor assumption for a disk of finite size.

Applying the theory of the potential, Newman\textsuperscript{22} solved Laplace's equation for the electric potential by using oblate spheroidal coordinates.
Surprisingly, for a small disk embedded in the surface of an insulator and a counter electrode which is located far from the disk, the ohmic resistance of a uniform solution is simply equal \( \frac{1}{4\pi r_0 \kappa} \) where \( r_0 \) is the radius of the disk electrode.

Furthermore, the resistance in the solution corrected to account for the placement of a reference electrode at a finite distance from the disk is given by

\[
R = \frac{\tan^{-1} \lambda_0}{2\pi r_0 \kappa}
\]

(3-9)

where \( \lambda_0 \) is dimensionless distance in spheroidal coordinates between the reference electrode and the rotating disk electrode. It is defined, in terms of cylindrical coordinates, as

\[
\lambda_0 = \frac{z}{r}
\]

at \( r = 0 \) (on the axis of the disk) (3-10)

\[
\lambda_0 = \sqrt{\left(\frac{r}{r_0}\right)^2 - 1}
\]

at \( z = 0 \), (in the plane of the disk) \( r > r_0 \) (3-11)

For any other arbitrary points, \( \lambda_0 \) can be solved from

\[
r_0^2 \lambda_0^4 + (r_0^2 - r^2 - z^2) \lambda_0^2 - z^2 = 0.
\]

(3-12)

Figure 3-2 shows the equipotential lines and current flow lines near to a disk electrode. In Figure 3-3 the dimensionless group \( r_0 \kappa R \) is plotted against \( \lambda_0 \), and it is seen that the resistance depends strongly on distance in the region near the disk electrode. The proper choice of the position of a reference electrode based on these results will be discussed in section 4-2.
Figure 3-2. Equipotential lines and current flow line near a disk electrode.
Figure 3-3. Correction to the resistance of the solution for the finite distance of the reference electrode.

\[ \lambda_0 = \frac{z}{r} \] on the axis of disk

\[ \lambda = \sqrt{\left(\frac{r}{r_0}\right)^2 - 1} \] in the plane of disk
VI. EXPERIMENTAL WORK

§4-1 Design and Description of Apparatus

Cathode (Rotating Disk Electrode)

The size and the shape of the rotating disk electrode is important, since it may affect the flow pattern. Riddiford\(^3\) summarized various shapes of disk which have been used in the past by different experimenters. In general, if there is no effect which may propagate backward from the edge of the disk and change the fundamental hydrodynamic model and concentration profile near the surface of disk, it may be considered to satisfy the original assumptions in the basic theory.

The shape recommended by Riddiford and also the one being used in this work is shown in Figure 4-1. Only the central portion of the upper surface is active.

Several criteria have been set up by Riddiford and by Theodorsen and Regier\(^23\) for the actual design of the size of the electrode. They are:

1. the outside diameter of disk \(d\) should be greater than the hydrodynamic boundary thickness;

2. the diameter of the working surface \(d_0\) should be greater than the mass transfer boundary layer thickness;

3. the size of the shaft should be less than 30% of the size of the disk, so that the shaft will not affect the main stream of flow;

4. the thickness of the disk should be less than \(1/30\) of the disk size, so that there will be no edge effect;

5. the Reynolds number at the edge should be less than \(2 \times 10^5\) in order to maintain laminar flow.

The disk has been carefully designed to meet the requirements
Figure 4-1. Disk electrode.
listed above. The disk is operated in CuSO₄ solution with the speed range from 60 r.p.m. to 500 r.p.m. Here are the specifications of the disk:

- Outside diameter of disk, \( d = 4 \text{ cm} \)
- Working electrode diameter, \( d_0 = 0.5 \text{ cm} \)
- Disk thickness, \( = 0.1 \text{ cm} \)
- Shaft diameter \( = 1 \text{ cm} \)

The central part of the electrode was machined from oxygen-free high purity copper to precise dimensions and then embedded in an epoxy resin cast. It was further machined to the desired shape.

The disk was attached to a spindle which was tightly fitted in two 7/8-inch o.d. New Departure 77 RC bearings. These bearings were mounted to a heavy brass bearing case in order to keep the eccentricity as small as possible. The eccentricity at the edge of disk was measured to be less than 0.002 inch.

**Anode**

The anode was designed to provide an area more than 100 times bigger than the cathode for the purpose of minimizing the anodic overpotential. The anode was embedded at the bottom of the vessel and could be taken apart to clean the surface before each experiment. It was made liquid tight with a rubber ring placed in a groove.

**Reference Electrode**

An oxygen-free high purity copper rod was used as the reference electrode. It was connected to the electrolyte cell through a capillary tube filled with electrolytic solution with the same concentration as in the cell. The capillary had a fine tip which faced downward and was located at the side of rotating disk. The use of a copper reference electrode was desirable since it would not contaminate this electrolyte and involved
no liquid junctions.

§ 4-2 The Position of Reference Electrode

As it was mentioned at the beginning, there was no supporting electrolyte in this work, and the electrical conductivity was very low compared to most other works in this field. A high ohmic drop may seriously interfere with the overpotential measurement. To minimize the resistance in overpotential measurements, Brown and Thirsk, Johnson and Turner, and Ibl and Schadegg placed their reference electrode directly underneath the disk. This arrangement may seriously disturb the hydrodynamic profile and current distribution under the rotating disk electrode. Belyaeva made some improvements on the design of a rotating disk by building the reference electrode inside the disk with a small hole (dia. 0.5 - 0.7 mm) at the center of the disk electrode which was 4 mm in diameter. This is still not a satisfactory way because of the small hole that still distorts the concentration profile and there is the uncertainty of the concentration inside the rotating disk.

Several preliminary experiments were conducted to measure the overpotential at a constant current density 40.7 mA/cm² in a 0.1M copper sulfate solution at 25°C with a rotating speed of 300 r.p.m. with the reference electrode at various distances from the disk. The results are tabulated in Table 1.

These data show that the cathodic overpotential depends strongly on the normal distance of the reference electrode from the disk electrode. For these cases where the reference electrode was placed underneath the disk or built into the rotating disk, a small misalignment in the position of the reference electrode from one experimental run to the next may cause
a serious difference in the ohmic drop contribution to the total over-potential measurement.

Table 1 also shows that the resistance overpotential is almost as large as the total cathodic overpotential. The difference between the experimental value of total overpotential and the calculated value of resistance overpotential is about 70-80 mV and is the sum of activation and concentration overpotential under these experimental conditions.

From both the theoretical analysis in section 3-3 and the experimental results in Table 1, we concluded that the reference electrode should be placed sufficiently far from the disk, e.g., \( \lambda_0 > 10 \). The distance parameter \( \lambda_0 \) was defined in Equation (3-10) to (3-12).

§4-3 Surface Treatment of Electrode

Because of the inevitability of surface change during a metal deposition reaction, we need to know how smooth the electrode surface should be or what is the maximum tolerable roughness in order to maintain the theoretically expected velocity profile.

Schlichting gave a systematic presentation and study of the effect of surface roughness. Generally speaking, a surface may be considered hydraulically smooth if the roughness is smaller than the hydrodynamic boundary layer for the case where there is no mass transfer occurring at the surface.

Brown and Thirsk, and Beacom and Hollyer worked on rotating disk electrodes with the same electrolytic system as the author. The former used electron micrographs and found a deposited copper film with a surface roughness negligible when compared with the diffusion layer. On the other hand, Beacom and Hollyer measured the copper deposition by interference microscope and found a uniform deposit on the disk.
Table 1. The cathodic overpotential with respect to normal distance from the disk electrode

\[ c = 0.1 \text{ M CuSO}_4 \]
\[ \Omega = 300 \text{ r.p.m.} \]
\[ i = 40.7 \text{ mA/cm}^2 \]
\[ \kappa = 0.00872 \text{ cm}^{-1} \text{ohm}^{-1} \]
\[ A = 0.1962 \text{ cm}^2 \]
\[ r_0 = 0.25 \text{ cm} \]

<table>
<thead>
<tr>
<th>Normal distance</th>
<th>Resistance Overpot. calculated from Fig. 3-3</th>
<th>Experimental result</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 cm</td>
<td>224 mV</td>
<td>290-300 mV</td>
</tr>
<tr>
<td>0.2 cm</td>
<td>392 mV</td>
<td>461-465 mV</td>
</tr>
<tr>
<td>0.3 cm</td>
<td>546 mV</td>
<td>620 mV</td>
</tr>
<tr>
<td>0.5 cm</td>
<td>646 mV</td>
<td>721 mV</td>
</tr>
<tr>
<td>2.0 cm</td>
<td>845 mV</td>
<td>924 mV</td>
</tr>
<tr>
<td>5.0 cm</td>
<td>892 mV</td>
<td>965 mV</td>
</tr>
<tr>
<td>beside the disk (r = 2.5 cm)</td>
<td>866 mV</td>
<td>942 mV</td>
</tr>
</tbody>
</table>
Ibl and Schadegg\textsuperscript{24} characterized the roughness of copper deposition by impedance measurements. They found that there is essentially no formation of a roughness or powdery deposit if the copper is deposited below the limiting current. On the other hand, a very rough deposit was formed at limiting current or higher even with a strong stirring of the solution.

An extensive study on the effect of small protrusions on mass transfer to a rotating disk electrode was given by Rogers and Taylor\textsuperscript{28}. Their autoradiographic results, with carbon-1\textsuperscript{4} as a tracer showed that the mass transfer rate is lower in the traces of wakes behind burrs or gas bubbles. However, it is compensated by the slight increase of available area of the small protrusions. Hence there is no significant difference in the total rate of mass transfer between the one with burrs and the one without burrs.

Karasyk and Linford\textsuperscript{29} studied the effect of organic contaminants on the electrode surface to the polarization curve of copper plated from an acid copper sulfate bath. They found that trace contaminants cause a reduction in the double layer capacity, and consequently the polarization curves are much steeper than those for clean ones.

We concluded that in order to maintain hydrodynamic smoothness of the electrode surface, the polarization measurement should be conducted below the limiting current density. Once a surface reaches the limiting current density, it should be retreated before being used for further measurement.

The maximum roughness should be less than the diffusion layer thickness. From the theoretical analysis of the concentration profile, the diffusion layer thickness for a disk electrode at 300 r.p.m. in a
0.1M copper sulfate solution is 37.1 x 10^{-3} cm.

Summarized below are the steps in treating the surfaces of the cathode, the anode, and the reference electrode before conducting each experiment:

1. The electrodes were polished with 600-A silicon carbide paper until all previous traces of deposit or corrosion were gone. The maximum scratch on the surface is then on the order of 10 μ (10^{-3} cm).

2. The cathode was further polished on plate glass using fine lens powder (aluminum oxide powder mixture) of 0.3 μ grain size as grinding compound.

3. The electrode was washed with carbon tetrachloride followed by 5% sodium carbonate solution.

4. The surfaces were rinsed with tap water followed by distilled water.

§4-4 The Electrical Circuit

The schematic diagram of the circuit for measuring cathodic polarization is shown in Figure 4-2. The current source was a Lambda model 28 regulated power supply. The current flow in the cell was measured with a Keithley Model 610R Electrometer which has an accuracy of 2%. The potential was measured with a Houston Model HV-160 DC vacuum tube voltmeter which has an accuracy of 0.3%. The results were recorded on a t-y recorder.

The electrical connection to the rotating disk electrode was accomplished by means of a mercury well. The disk was rotated with a variable speed motor*, controlled by a precision DC voltage power

* Bodine Electric Company, Type MSE 11R, Two shafts AC-DC motor with a gear ration 10 to 1.
Figure 4-2. The block diagram of the rotating disk electrode system.
Figure 4-3. The rotating disk electrode set up.
supply*. The speed of rotation was determined by a General Radio Type 631-BL strobotac which has an accuracy of 1%.

Figure 4-3 shows the assembled rotating disk electrode apparatus.

§4-5 Experimental Procedure

Reagent grade CuSO₄ was used without further purification. Distilled water was used in the preparation of all solutions. Cylinder nitrogen was bubbled through the solution to expel all dissolved oxygen which may affect the surface of the electrode during the reaction.

Before each run, the surfaces of the electrodes were cleaned as described in section 4-3.

Because of the high ohmic drop in the solution compared with the concentration and activation overpotential, the plateau on the current voltage curve due to concentration polarization was essentially overshadowed, and it was difficult to locate the limiting current density by a current vs. voltage measurement. Therefore, instead of keeping the rotating speed constant and varying the current density, as most other experimenters have done, we held the current density constant and varied the rotation speed. Thus the resistance overpotential was kept constant throughout a run.

The disk electrode was initially set at a relatively high speed (5-10 times higher than the "limiting speed"). The speed was decreased by decreasing the voltage to the motor which drove the shaft of the disk. The total overpotential was not very sensitive to this decrease of speed at a given current density until it came close to the limiting speed where the potential sharply increased. At this point the rotation speed was measured by a strobotac.

The measurement of limiting speed has the same physical significance

* Power Design Inc., Model 5015A.
as a limiting current density measurement. The limiting current density gives the minimum current required to discharge all the reactive ions brought to the electrode surface at a given speed of rotation, whereas the limiting speed gives the minimum speed required to supply the reacting ions at a given current density. Both measurements correspond to a zero concentration of ions at the electrode surface.

V. RESULTS

1. The limiting speeds ranging from 60 r.p.m. to 500 r.p.m. were measured at constant current density according to the procedure given in the section 4-5. The square root of limiting speed was plotted against current density. Straight lines passing through the origin were obtained for all four concentrations, 0.02M, 0.05M, 0.1M and 0.3M. The slopes of these lines $\frac{i_{\text{lim}}}{\sqrt{\Omega}}$, have been compared with the values predicted from Equation (2-28).

This theory gives +1.57% correction to the Levich theory for a copper sulfate solution concentration of 0.02 M, and +13.1% correction at concentration of 0.3 M. The experimental results show a negative deviation at low concentration, but agree well with the value predicted from this theory at high concentration. It reveals the importance of the effects of the variation of physical properties in the diffusion layer and non-zero interfacial velocity at the electrode surface when the rotating disk electrode method is used to measure the diffusion coefficient in a highly concentrated solution.

We may also want to compare our results with the $\frac{i_{\text{lim}}}{\sqrt{\Omega}}$ values calculated from Levich's equation where constant physical properties, zero interfacial velocity, and infinite Schmidt number were assumed.

$$\frac{i_{\text{lim}}}{\sqrt{\Omega}} = 0.620 \, \text{Sc}^{-2/3} \frac{nF \, C_{\infty} \sqrt{\nu}}{(1 - t_+)}$$

(5-1)
and from the modified equation which was given by Gregory and Riddiford

\[ \lim_{\Delta \theta \rightarrow 0} = \frac{0.554 \text{Sc}^{-2/3}}{0.8934 + 0.316 \text{Sc}^{-0.36}} \frac{\eta F c_{\infty} \sqrt{\nu}}{(1 - t_+)} \]  

(5-2)

Further correction for finite Schmidt number (range from 100 to infinity) was made by Newman. He used the expansion of the velocity profile obtained by Cochran and integrated analytically to obtain

\[ \lim_{\Delta \theta \rightarrow 0} = \frac{0.62048 \text{Sc}^{-2/3}}{1 + 0.2980 \text{Sc}^{-1/3} + 0.14514 \text{Sc}^{-2/3}} \frac{\eta F c_{\infty} \sqrt{\nu}}{(1 - t_+)} \]  

(5-3)

The numerical comparison of Equations (2-28), (5-1), (5-2), (5-3) and experimental results for copper solutions at 25°C are given in Table 2. They are also shown in Figure 5-1.

2. For the cathodic reaction of copper sulfate at a copper electrode, the electrode reaction is

\[ \text{Cu}^{2+} + 2e^{-} \rightarrow \text{Cu} \]

Therefore \( S_+ = -1, S_0 = 0, n = 2, z_+ = 2 \) and \( \nu = 2 \) in Equation (3-3). The potential far away from the electrode was chosen as the reference point; \( \varphi(\infty) = 0 \). Equation (3-7) multiplied by \( \frac{F}{RT} \) on both sides of the equation, so that each term is dimensionless, becomes

\[ \frac{F \varphi(0)}{RT} = \frac{\nu_0 \varphi_0 + F^2 z_+}{RT M_g} \int_0^\infty \left( \frac{1}{\kappa} - \frac{1}{\kappa_\infty} \right) d\xi + \frac{\nu + \nu_0}{z_+ \mu_+} \int (\gamma_m) \eta (t_+ - 1) d \lambda \gamma_m \]

(5-4)

The first term on the right-hand side represents the additional ohmic resistance due to the conductivity change in the diffusion layer. The integration was performed numerically with the computer. The conductivity at each mesh point was evaluated according to the concentration profile from Equation (2-23).

The second term on the right of Equation (5-4) represents the part
Table 2. Comparison of $\frac{\lim}{\sqrt{\Omega}} \left[ \frac{mA}{cm/\sqrt{rad/sec}} \right]$ predicted by different authors with experimental results

<table>
<thead>
<tr>
<th>c</th>
<th>Sc*</th>
<th>Levich Eq(5-1)</th>
<th>Gregory &amp; Riddiford Eq(5-2)</th>
<th>Newman Eq(5-3)</th>
<th>This theory Eq(2-28)</th>
<th>Exptl. Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02 M</td>
<td>1407</td>
<td>2.995</td>
<td>2.919</td>
<td>2.914</td>
<td>3.042</td>
<td>2.86</td>
</tr>
<tr>
<td>0.05 M</td>
<td>1530</td>
<td>6.986</td>
<td>6.814</td>
<td>6.803</td>
<td>7.173</td>
<td>7.04</td>
</tr>
<tr>
<td>0.1 M</td>
<td>1650</td>
<td>13.05</td>
<td>12.74</td>
<td>12.72</td>
<td>14.13</td>
<td>14.06</td>
</tr>
<tr>
<td>0.3 M</td>
<td>2012</td>
<td>33.71</td>
<td>32.96</td>
<td>32.91</td>
<td>38.12</td>
<td>38.1</td>
</tr>
</tbody>
</table>

* Schmidt number was calculated based on bulk properties of the solution.
Figure 5-1. Comparison of the exact value of $\frac{1}{\sqrt{\Omega}}$ with Levich's equation and experimental results for CuSO$_4$ solutions at 25°C.
of the potential necessary for overcoming the e.m.f. due to the concentration difference. The integration was performed by changing the variable of integration to \( \omega_s \). The cation transference number \( t_+ \) and \( \log_{10} r \) have been linearly regressed as a finite polynomial of \( \omega_s \) in 2-4, while the molality \( m \) is related to \( \omega \) by

\[
m = \frac{1000 \omega_s}{(1-\omega_s)M_s}
\]

\[
\frac{d \ln m}{d \omega_s} = \frac{1}{\omega_s} + \frac{1}{1-\omega_s} = \omega_s^{-1} + 1 + \omega_s + \omega_s^{-2}
\]

There was no difficulty in performing this integration analytically. The result \( \phi_c \) was plotted as a function of \( \frac{1}{z_+ FC_\infty \sqrt{\Omega_\infty}} \) and is shown in Figure 5-2.

3. According to the classical mass transfer theory for constant properties, the interfacial concentration is related to the current density by

\[
\frac{C_o}{C_\infty} = 1 - \frac{1}{i_{\text{lim}}}
\]

If the ratio \( \frac{C_o}{C_\infty} \) is plotted against \( \frac{1}{i_{\text{lim}}} \), a straight diagonal line should be obtained for each bulk concentration. This equation was tested at different concentrations taking into consideration the effect of variations of physical properties. Figure 5-3 shows that the higher the bulk concentration, the more the results deviate from the diagonal line.

4. For the purpose of comparison of the total overpotential predicted for the theory with the experimental values, several experiments were conducted separately to measure the total overpotential. Figure 5-4 shows one of the examples. The total overpotential was measured in a 0.1 M copper sulfate solution at a constant rotating speed of 300 r.p.m.
Figure 5-2. Concentration overpotential at different bulk concentration of CuSO$_4$ at 25°C.
Figure 5-3. Interfacial concentration vs. current density for CuSO₄ solutions at 25°C.
Figure 5-4. Comparison of measured total overpotential to the theoretical value for copper deposition from CuSO₄ solutions at 25°C. 

\[ \Omega = 300 \text{ r.p.m.} \quad c = 0.1 \text{ M} \]
The theoretical concentration overpotential $\varphi_c$ was calculated from the results shown in Figure 5-2. The theoretical activation overpotential $\varphi_a$ was calculated from Equation (3-8); an exchange current density of \( i_o = 1.0 \text{ mA} \text{ cm}^{-2} \) and a transfer coefficient of $\alpha = 0.5$ were assumed. The resistance overpotential $\varphi_{\text{ohm}}$ was calculated from Equation (3-9) taking account of the fact that the reference electrode probe was located in the plane of the disk 2.5 cm from the axis of rotation, that is, $r = 2.5 \text{ cm}$ and $r_o = 0.25 \text{ cm}$ in Equation (3-11) for calculating the parameter $\lambda_o$. The specific conductivity of the solution was 0.00872 ohm$^{-1}$ cm$^{-1}$. The theoretical total overpotential is the sum of $\varphi_a$, $\varphi_c$, and $\varphi_{\text{ohm}}$.

In view of Figure 5-4, we may see that the resistance overpotential predominates the overall polarization measurement. Therefore, if we wish to study the electrode kinetics in a low conductivity electrolyte, the two large numbers, the measured overpotential, and the resistance overpotential must be subtracted with a consequent loss of significant figures. Therefore, unless a highly accurate voltmeter is available, the rotating disk electrode method is not suitable for kinetic studies in a low conductivity electrolyte.

VI. SUMMARY AND CONCLUSIONS

1. Compared to Levich's early treatment$^1$ of the rotating disk electrode, two major differences arise in the study of mass transfer in a concentrated electrolyte: the physical properties of the solution vary across the diffusion layer, and the interfacial velocity can no longer be considered to equal zero.

2. In view of these differences, more general forms of the equation of motion, Equation (2-1), and the equation of continuity, Equation (2-3),
than those considered by von Kármán and Levich must be used to calculate the velocity profiles in the vicinity of the rotating disk. In solving these equations, the $z$-component velocity was assumed to be a function of the normal distance from the disk only. This assumption allowed the set of partial differential equations to be simplified to a set of ordinary differential equations, which were solved numerically by the computer.

3. For the solution of a single salt, the concentration profile is determined from Equation (2-18). The concentration and all the physical properties of solution have also been assumed to be functions of the normal distance only in solving the said equation.

4. It is found that the limiting current is still proportional to the square root of rotating speed even at high concentrations. The experimental results of $\frac{I_{lim}}{\sqrt{\Omega}}$ plotted against the bulk concentration were found to agree well with those predicted from this theory. The theory predicts a value 13% higher than the Levich equation for a 0.3 M copper sulfate solution.

5. Perhaps the most important assumption involved in the rotating disk electrode method is that $v_z$, $c$, $\phi$ and all physical properties of the solution are functions of the normal distance only. There is no doubt for very large disks. Practically, it is impossible to construct such a disk without creating turbulence at the edge of the disk.

If we are interested only in the region very close to the electrode, then this assumption holds quite well. One may visualize this fact from the equal potential lines plotted in Figure 3-2. Near the disk the equal potential lines are parallel to the disk, but the assumption becomes poorer farther from the disk.
A similar picture of equal concentration lines may be obtained if there is no convection, that is, if the concentration satisfies the equation \( \nabla^2 C = 0 \). If convection diffusion and migration are involved, the equation for a binary electrolyte with the assumption of constant physical properties becomes

\[ \nabla \cdot \nabla C = D \nabla^2 C. \]

It may be expected that the convection compresses the equal concentration lines in the diffusion layer. The thinner the diffusion layer, the less the error involved in the assumption that the concentration is a function of normal distance. A similar conclusion should hold for \( \nu_z \).

6. The concentration overpotential was defined as the overpotential due to the concentration gradient in the diffusion layer. It includes two contributions due to the difference of the chemical potential between the bulk and electrode surface, and the change of the electrical conductivity in the diffusion layer.

7. In the absence of supporting electrolyte, the ohmic resistance contribution to total overpotential is very high. The ohmic drop between a small disk embedded in the surface of an insulator and a counter-electrode far from the disk is \( \frac{1}{4 \kappa r_o} \). The ohmic resistance corrected to account for the placement of a reference electrode at a finite distance \( \tan^{-1} \frac{\lambda_o}{2\pi r_o \kappa} \). The distance parameter \( \lambda_o \) was defined in Equations (3-10) to (3-12). Because the ohmic drop is concentrated near the disk, the reference electrode should be placed sufficiently far from the disk that its location is not a highly critical factor.

8. The large ohmic drop essentially overshadowed the plateau on the current-voltage curve due to the concentration polarization. This led to the development of a "limiting speed" technique rather than...
limiting current measurements. The current was held constant and the rotating speed was decreased until the potential showed a large increase corresponding to a zero concentration of the reacting ion at the electrode surface. In this way the ohmic potential drop was held constant and did not obscure the concentration polarization effects.

In conclusion, the effects of the variation of physical properties in mass transfer to a rotating disk electrode are important in a concentrated solution. It is not recommended to use the rotating disk electrode for the electrode kinetic study in a low conductivity electrolyte where the ohmic resistance dominates the total overpotential.

ACKNOWLEDGMENTS

I wish to express my deep gratitude to Professor J. Newman for initiating my thinking and for the patient instruction in this work. Gratitude is also due to Professor C. W. Tobias and Mr. Thomas Chapman for their useful advice and to Mr. Larry Horvath for his help in setting up the experimental apparatus.

I wish to express my appreciation to the Lawrence Radiation Laboratory for the use of needed experimental equipment, and to Mrs. Jane Schroeder for typing the final manuscript.

This work was done under the auspices of the United States Army Signal Corps and of the United States Atomic Energy Commission.
APPENDIX A. SOME BASIC RELATIONS FOR BINARY ELECTROLYTES

An electrolytic solution containing only one kind of cation and one kind of anion in addition to the solvent is called a binary electrolyte. Some basic relations which have been used for deriving most of the fundamental equations in this paper may be summarized as follows:

Let the electrode reaction at a reference electrode be

\[ S^- Q^+ + S^- Q^- + S^0 Q^0 \rightarrow n e^- \]

and let

\[ C_+, C_-, C_0 \]

be concentration of cation, anion, and solvent

\[ n_+, n_- \]

be number of cations and anions produced by dissociation of one molecule of electrolyte.

The following relations hold for binary electrolytes. We present them without proof.

\[ n_+ z_+ + n_- z_- = 0 \] \hspace{1cm} (A-1)

\[ \frac{C_+}{n_+} = \frac{C_-}{n_-} = C \] \hspace{1cm} (A-2)

\[ S_+ z_+ + S_- z_- = -n \] \hspace{1cm} (A-3)

\[ C_{M_+} = \rho \omega_+ \] \hspace{1cm} (A-4)

\[ C_{M_-} = \rho \omega_- \] \hspace{1cm} (A-5)

\[ M_s \equiv n_+ M_+ + n_- M_- \]

\[ \mu_e \equiv n_+ M_+ + n_- M_- \] \hspace{1cm} (A-6)

\[ \omega_s = \omega_+ + \omega_- \]

\[ \frac{1}{\rho} \left( C_{M_+} + C_{M_-} \right) \] \hspace{1cm} (A-7)
Finally, at constant temperature and pressure, the Gibbs-Duhem relation for a binary electrolyte is

\[ C_+ \nabla \mu_+ + C_- \nabla \mu_- + C_0 \nabla \mu_0 = 0 \]

or

\[ C \nabla \mu_e = - C_0 \nabla \mu_0 \quad (A-8) \]

**APPENDIX B. COMPUTER PROGRAM**

The original computer program written for the numerical solution of velocity and concentration profiles has several slight differences in the definitions of the dimensionless quantities.

The dimensionless distance was defined as (cf. Equation (2-10))

\[ \zeta = \sqrt{\frac{\Omega}{\mu_0 \rho_0}} \int_0^z \rho dz \quad (B-1) \]

and the velocity components were

\[ v_r = r \Omega F(\zeta) \]
\[ v_\theta = r \Omega G(\zeta) \]
\[ v_z = \frac{\sqrt{\Omega \mu_0 \rho_0}}{\rho} \#(\zeta) \quad (B-2) \]

where \( \zeta \) and \( \# \) are related to \( \xi \) and \( H \) by

\[ \xi = \sqrt{\frac{\Omega \rho_0}{\rho}} \int_0^\xi \frac{d\xi}{\rho} \quad (B-3) \]

and

\[ H = \sqrt{\frac{\Omega \rho_0 \#}{\rho}} \quad (B-4) \]

Based on the definition of Equations (B-1) and (B-2) the dimensionless equations of motion and continuity to be solved with the computer were (cf. Equations (2-14) and (2-15))

\[ F^2 - C^2 + \#F' = \frac{d}{d\xi} \left( \frac{\rho \mu}{\rho_0 \mu_0} F' \right) \quad (B-5) \]

\[ 2FG + \#C' = \frac{d}{d\xi} \left( \frac{\rho \mu}{\rho_0 \mu_0} C' \right) \]
\[ 2F + \#^1 = 0 \] \hspace{1cm} (B-6)

where primes refer to differentiation with respect to \( \zeta \). The dimensionless equation of convection diffusion becomes (cf. Equation (2-22))

\[
\left( \# + \mathcal{J} \frac{dt}{d\omega} \right) \frac{d\omega}{d\zeta} = \frac{q}{\mu_0 \rho_0} \left( \frac{d^2 \omega}{d\zeta^2} \right).
\] \hspace{1cm} (B-7)

The dimensionless current was defined as

\[
\mathcal{J} = \frac{M_s \zeta}{z_+ \nu_+ \sqrt{\mu_0 \rho_0}}.
\] \hspace{1cm} (B-8)

It is related to \( I \) by

\[
I = \sqrt{\frac{\mu_0 \rho_0}{\nu_\infty}} \mathcal{J}.
\] \hspace{1cm} (B-9)

The boundary conditions in terms of these dimensionless quantities are at \( \zeta = 0, \ F = 0, \ G = 1, \ \# = \frac{\nu_+ M_s \mathcal{J}}{M_s} \)

\[
\omega_\infty = \omega_{\text{zero}}
\]

\[
- \frac{d^2 \omega}{d\zeta^2} = \mathcal{J} \omega_\infty.
\]

at \( \zeta = \infty, \ F = 0, \ G = 0, \ \omega_\infty = \omega_\infty \).

For the concentration polarization, the equation corresponding to Equation (5-4) becomes

\[
\frac{\Phi_0 (0)}{RT} - \frac{z_+ \nu_+ \mu_0 \rho_0 \mathcal{J}}{RT M_s} \int_0^\infty \left( \frac{1}{\kappa} - \frac{1}{\kappa_\infty} \right) \frac{d\zeta}{\rho} + \frac{(\nu_+ + \nu_\infty)}{z_+ \nu_+} \int_r(\gamma_m)_0 (t - 1) \frac{d\gamma_m}{\gamma_m}.
\]

The program was written in FORTRAN II; it consisted of the main program DISK and three subroutines FLUID, CALC, and INFSC.

DISK is the overall control program. It read the input data and wrote the output. It calculated the concentration polarization and converted the old definitions of dimensionless quantities \( \zeta, \# \) and
LABEL
DECKS
FORTRAN
FUNCTION CAPP (W)
CAPP = 0.2179 × W**0.78957
RETURN
END

LABEL
DECKS
FORTRAN
FUNCTION RHO(W)
RHO = 0.99669 + 0.02691 × W**0.5 + 0.74771 × W + 0.80721 × W**1.5
RETURN
END

LABEL
DECKS
FORTRAN
FUNCTION TM (W)
TM = 0.597063 + 3.57889 × W - 8.21995 × W**1.5
RETURN
END

LABEL
DECKS
FORTRAN
FUNCTION TP (W)
TP = -3.57889 × W + 12.329925 × W**0.3
RETURN
END

FUNCTION S (W)
DM = 0.207 × EXPF (-29.0 × W**0.5) + 0.638 - 0.510 × W**0.5
RHO = 0.9967 + 0.02691 × W**0.5 + 0.74771 × W + 0.80721 × W**1.5
S = DM × RHO**2 / (0.8937 × 0.99708) / 10 * 2
RETURN
END

FUNCTION VIS (W)
RH = 0.9967 + 0.02691 × W**0.5 + 0.74771 × W + 0.80721 × W**1.5
U = 0.4865 + 0.33675 × W**0.5 + 11.3382 × W**1.5 + 4.99107 × W**2
VIS = RH × U / (0.99708 × U / 0.8937)
RETURN
END

FUNCTION VISP (W)
VISP = (1.17077/0.9967 + 0.02691 × W**0.5 + 0.74771 × W + 0.80721 × W**1.5
1.5 + 38.65205 × W**2 + 14.10788 × W**2.5) / (0.8937 × 0.99708)
RETURN
END

DECKS
FORTRAN
FUNCTION CONC (W)
CONC = -0.50706 × LOGF (W) + 9.4576 × W**0.5 - 24.8456 × W + 43.3031 × W**1.5
3 - 96.5876 × W**2 + 185.5056 × W**2.5 - 132.2938 × W**3.5 + 2.34855 × W**3.6
**SUBROUTINE CALC**

**SUBROUTINE FOR OBTAINING THE FIRST TERMS OF THE INNER EXPANSIONS OF THE VELOCITIES FOR HIGH SCHMIDT NUMBERS FOR A ROTATING DISK WITH ACCOUNT BEING TAKEN OF PROPERTY VARIATIONS AND A FINITE INTERFACIAL VELOCITY**

**SUBROUTINE INFSC**

```
$ -0.89472*W**4.0+1.82266*W**4.5
RETURN
END

* LABEL
* DECKS
FORTRAN

DIMENSION F(1001),G(1001),H(1001),W(1001),V(1001),VP(1001),B(1001),
DUM(5005)
COMMON WINF,N,NM1,DY,AMP,GNUP,TMO,VINF,HINF,W,F,G,H,V,VP,B,DUM,$
ZERO
TPINF= TP(WINF)
W(1)= 0.0
B(1)= 0.0
$\text{S1}= S(WZERO)$.
ADD1= (AMP*TP(WZERO) + H(1))/S1
$\text{DO 3 J}= 2, N$
S2= $S(W(J))$
ADD2= (AMP*TP(W(J)) + H(J))/S2
B(J)= B(J-1) + DY/2.0*(ADD1 + ADD2)
W(J)= .W(J-1) + DY/2.0*(EXP(B(J))/S2 + EXPF(B(J-1))/S1)
ADD1= ADD2
$\text{S1}= S2$
$\text{CONST}= (WINF-WZERO)/(W(N)-EXPF(N))/($\text{AMP*TPINF + HINF})$
$\text{DO 4 J}= 1, N$
$\text{W(J)}= \text{CONST*W(J) + WZERO}$
AMP= - CONST/TM0/1.0-WZERO
H(1)= GNUP*AMP
V(1)= VIS(W(1))
VP(1)= VISP(W(1))/CONST/S(W(1))
$\text{NP}= N$-1
$\text{DO 5 J}= 2, NP$
V(J)= VIS(W(J))
VP(J)= VISP(W(J))*(W(J+1)-W(J-1))/(2.0*DY)
V(N)= VIS(W(N))
$\text{VP(N)}= \text{VISP(W(N))*(W(N)-W(N-1))}/DY$
RETURN
END

* LABEL
* DECKS
FORTRAN

DIMENSION F(1001),G(1001),H(1001),W(1001),V(1001)
COMMON WINF,N,NM1,DY,AMP,GNUP,TMO,VINF,HINF,W,F,G,H,V,
CONST= 0.51023*DY/2.0*SORTF(WINF)
F(1)= 0.0
G(1)= 1.0
$\text{DO 1 J}= 2, N$
G(J)= 1.0
F(J)= F(J-1) + CONST/V(J) + CONST/V(J-1)
$\text{H(J)}= H(J-1) - DY*(F(J) + F(J-1))$
RETURN
END
```
*  
* SYMBOL TABLE
*  
* DECKS
*  
* FORTRAN

SUBROUTINE FLUID
DIMENSION F(1001), G(1001), H(1001), W(1001), V(1001), VP(1001), FF(1001)

COMMON WINF, N, NM1, DY, AMP, GNUP, TMO, VINF, HINF, W, F, G, H, V, VP,

1 FF, FG, GG, HF, HG

GPS = 0.5/DY*(G(3) - G(1))
FPS = 0.5/DY*(F(3) - F(1))

GG(1) = 0.0
GF(1) = 0.0
FF(1) = 0.0
HF(1) = 0.0
HG(1) = 0.0

DO 1 J = 2, NM1

GP = GPS
FP = FPS

GPS = 0.5/DY*(G(J+2) - G(J))
FPS = 0.5/DY*(F(J+2) - F(J))

H1 = DY + DY*FF(J-1) - HF(J-1)
H2 = DY*FG(J-1) - HG(J-1)

A = (V(J)/DY - 0.5*(VP(J) - HT(J))/DY
C1 = - 2.0*(V(J)/DY/DY + F(J)) + A*GG(J-1) + H2*GP
C2 = - 2.0*G(J) + A*GF(J-1) + H1*GP
R = -(V(J)/DY + 0.5*(VP(J) - H(J)))/DY
RG = GP*(H(J-1) - DY*F(J-1) - H(J)) - 2.0*F(J)*G(J) - A*G(J-1)

C3 = 2.0*G(J) + A*FG(J-1) + H2*FP

C4 = - 2.0*(V(J)/DY/DY + F(J)) + A*FF(J-1) + H1*FP

RF = FP*(H(J-1) - DY*F(J-1) - H(J)) - F(J)*F(J) + G(J)*G(J) - A*F(J-1)

DET = C1*C4 - C3*C2
FG(J) = - C3*R/DET
GG(J) = C4*R/DET

FF(J) = C1*R/DET

GF(J) = - C2*R/DET

F(J) = (C1*RF - C3*RG)/DET

G(J) = (C4*RG - C2*RF)/DET

HF(J) = - H1*FF(J) - H2*GF(J)

HG(J) = - H1*FG(J) - H2*GG(J)

1 H(J) = H(J-1) - H1*F(J) - H2*G(J) - DY*F(J-1)

DO 3 K = 1, 10

C3 = 2.0*VINF/HINF
C1 = (C3-DY)/(C3+DY) - GG(NM1)
C2 = (C3-DY)/(C3+DY) - FF(NM1)

DET = C1*C2 - GF(NM1)*FG(NM1)

F(N) = (FG(NM1)*G(NM1) + C1*F(NM1))/DET

G(N) = (GF(NM1)*F(NM1) + C2*G(NM1))/DET

3 HINF = H(NM1) + C3*F(NM1) + (HG(NM1) + C3*FG(NM1))*G(N) + (HF(N-1) + C3*

1 FF(NM1))*F(N)

H(N) = HINF - C3*F(N)

DO 2 K = 2, NM1

J = N - K + 1

3 G(J) = G(J) + GG(J)*G(J+1) + GF(J)*F(J+1)

F(J) = F(J) + FG(J)*G(J+1) + FF(J)*F(J+1)

H(J) = H(J) + HG(J)*G(J+1) + HF(J)*F(J+1)

2 RETURN

END
C2DISK

PROGRAM FOR MASS TRANSFER TO ROTATING DISK, BINARY SOLUTION

DIMENSION F(1001), G(1001), H(1001), W(1001), DUH(1007)
COMMON WINF,N,NM1,dy,AMP,GNUP,TMO,VINF,HINF,W,F,G,H,V,DUH,WZERO
101 FORMAT (/••• 12X, 35H INFINITE SCHMIDT NUMBER IS ASSUMED)
102 FORMAT (15,1PE14.4)
103 FORMAT (5E8.4,4X,5I4)
104 FORMAT (5SH1, AMP, WINF, DY, GNUP, TMO, WZERO)
105 FORMAT (32HO CONCENTRATION OVERPOTENTIAL IS, 1PE14.4, 6H PLUS+ 1
1 PE14.4/ 7H WZERO, 1 PE16.6)
106 FORMAT (1H //)
107 FORMAT (1H1,8X, 24H DIMENSIONLESS CURRENT = ,E12.4/
$ 8X, 17H HH AT INFINITY = ,E12.4/ 73H0 J XI
$ 3 F G HH )
108 FORMAT (15, 1PE14.4)
HINF= - 0.884
READ INPUT TAPE 2,103, DY
N= 201
NM1= 200
DO 6 J=1,N
V(J)= 1.0
6 G(J)= 0.005*FLOATF(N-J)
DO 7 J=1,5
7 CALL FLUID
1 READ INPUT TAPE 2,103,WINF,WZERO,ERR,GNUP,CONST,N,M,N,S,INF,NO
VINF= VIS(WINF)
TMO = TM(WZERO)
NM1= N - 1
DO 2 J=1,N
2 W(J)= 0.0
AMP= 0.0
3 AO= AMP
HNO= HINF
CALL CALC
GO TO (11,12)*INF
11 CALL FLUID
GO TO 13
12 CALL INFSC
13 IF (ARSF(HINF - HNO) - ERR) 4,4,3
4 IF (ARSF(AMP - AO) - ERR*ARSF(AMP)) 5,5,3
5 GPO= (G(2) - G(1))/DY/(1.0+0.5*DY*H(1))
RAB= - GNUP*(WINF-WZERO)/TMO/(1.0-WZERO)
AKW= - TMO*AMP/(WINF-WZERO)*(1.0-WZERO)
RV= 0.0
GO TO (14,15)*INF
14 RV= - H(1)/GPO
15 WRITE OUTPUT TAPE 3,104, AMP, WINF, DY, GNUP, TMO, HINF, RAB, AKW, RV,
1 GPO, (J,W(J),F(J),G(J),H(J),J=1,10)
GO TO (8,9)*NO
8 GO TO (17,16)*INF
16 WRITE OUTPUT TAPE 3,101
17 WRITE OUTPUT TAPE 3,106
WRITE OUTPUT TAPE 3,102, (J,W(J),F(J),G(J),H(J),J=1,NS,M)

9 IF (W(1)) 1,1,18
18 ETAC1=0.0
CAPINF=CAPPA(WINF)
DO 24 J=1,10
CAPPA1=CAPPA(W(J))*RHO(W(J))
CAPPA2=CAPPA(W(J+1))*RHO(W(J+1))

24 ETAC1=ETAC1+DY*(1.0/(CAPPA2-CAPPA1)*LOGF(CAPPA2/CAPPA1)-1.0/CAPINF
$*(0.5/RHO(W(J))+0.5/RHO(W(J+1))))
DO 19 J=12,NS
19 ETAC1=ETAC1+DY*(0.5/CAPPA(W(J-1))/RHO(W(J-1))+0.5/CAPPA(W(J))/RHO(5 W(J))-1.0/CAPINF*(0.5/RHO(W(J-1))+0.5/RHO(W(J))))

20 ETAC1= CONST*AMP*ETAC1
ETAC2= CONC(WINF)-CONC(W(1))
WRITE OUTPUT TAPE 3,105, ETAC1,ETAC2,WZERO
SUM=0.0
XI=0.0
RINF=RHO(WINF)
COEFF=RINF*1.0/SORTF(VINF)
CURREN=1.0/SORTF(VINF)*AMP
HHINF=1.0/SORTF(VINF)*HINF
WRITE OUTPUT TAPE 3,107, CURREN,HHINF
DO 22 J=1,NS
HH=COEFF/RHO(W(J))*H(J)

21 IF (J-1) 21,21,20
20 SUM=SUM+DY*(0.5/RHO(W(J-1))+0.5/RHO(W(J))])
XI=COEFF*SUM
IF (J-41) 21,21,23
23 MM=(J-1)/M
JJ=MM*M+1

21 IF (J-JJ) 22,22,22
22 WRITE OUTPUT TAPE 3,108, (J,XI,W(J),F(J),G(J),HJ)
22 CONTINUE
GO TO 1
END
to the definitions used in this paper, \( \xi, \eta \) and \( \zeta \) by Equations (B-3), (B-4) and (B-9), respectively.

**FLUID** is the subroutine which carries out the numerical solution of the three velocity components \( F, G \) and \( H \) at each mesh point. The detailed numerical method has been given in section 2-4.

**INFSC** is the subroutine for calculating the velocity components \( F, G, \) and \( H \) by a singular perturbation method when an infinite Schmidt number is assumed.

**CALC** handles the concentration profile by solving Equation (B-7).

Eight functional programs were designed for evaluating the physical properties and other necessary dimensionless groups of copper sulfate solution at 25°C, they are:

1. \( \text{CAPPA} = \kappa \)
2. \( \text{RHO} = \rho \)
3. \( \text{TM} = t^- \)
4. \( \text{TP} = \frac{dL^+}{dW} \)
5. \( S = \frac{D_0^2}{\mu_0 \rho_0} \)
6. \( \text{VIS} = \frac{1}{\rho_0 \mu_0} \)
7. \( \text{VISP} = \frac{d}{dx} \left( \frac{\rho_0 \mu_0}{\mu_0} \right) \)
8. \( \text{CONC} = \int_{(\gamma_m)^o}^{(\gamma_m)^\infty} (t_+^o - 1) \frac{dy_m}{\gamma_m} \)

Two data cards are required, they are:

**Card I**

\( DY \) is mesh size used in solving the linearized ordinary differential
equations. The total mesh number is 1001, the mesh size should not
be smaller than 0.01 in order to have an accurate calculation of
the fluid velocity. Otherwise the range of $\zeta$ covered will not include
enough of the hydrodynamic boundary layer.

Card II

1. WINF is bulk concentration of solution in terms of mass fraction.
2. WZERO is the concentration at interface in terms of mass fraction.
3. ERR is error tolerance in calculating normal component velocity
   $\bar{H}$. $10^{-5}$ is recommended for this program.
4. GNUP is $\frac{v + M_+}{M_8}$.
5. CONST is $\frac{z + \frac{F\mu_0\rho_0}{RT M_8}}{s}$.
6. N is total number of mesh points to be used. The maximum
   storage is 1001.
7. M is the interval of mesh points to be printed out.
8. NS is the number of mesh points to be printed out.
9. INF is a selector.
   INF = 1 subroutine FLUID being used for calculating
   velocity profile.
   INF = 2 subroutine INFSC being used.
10. NO is output selector.
    NO = 1 program printed out
        mesh number, $\omega_8$, $F$, $G$, $\bar{H}$.
    NO = 2 program printed out
        mesh number, $\xi$, $\omega_8$, $F$, $G$, $H$. 
NOMENCLATURE

C - concentration of binary electrolyte.

C_i - concentration of species i (moles/cm^3).

d - diameter of disk.

d_0 - diameter of disk electrode.

D - molecular diffusion coefficient of binary electrolyte.

e^- - symbol for electron.

F - radial dimensionless velocity component (2-11).

F - Faraday's constant (coulomb/equiv).

G - tangential dimensionless velocity component (2-11).

h - mesh size for numerical solution of differential equation.

H - normal dimensionless velocity component (2-11).

\n - normal dimensionless velocity component (B-2).

g - acceleration of gravity (cm/sec^2).

i - current density (amp/cm^2).

i_o - exchange current density (amp/cm^2).

I - dimensionless current density.

\iota - dimensionless current density.

m - molality.

M_i - molecular weight of species i.

M_g - molecular weight of salt.

n - number of electrons in equation for electrode reaction.

N_i - molar flux of species i (moles/cm^2-sec).

n_i - mass flux of species i (g/cm^2-sec).

p - pressure (dyne/cm^2).

P - dimensionless pressure.
$Q_i$ - symbol for the chemical formula of species $i$.

$r$ - radius of disk.

$r_0$ - radius of disk electrode.

$R$ - universal gas constant.

$R$ - total resistance of solution.

$R' = \frac{d \ln \rho}{d \xi}$.

$S_i$ - stoichiometric coefficient in equation for electrode reaction.

$Sc$ - Schmidt number $Sc = \frac{\nu}{D}$.

$t_i$ - transference number with respect to mass average velocity at species $i$.

$\nu' = \frac{\rho \omega \frac{d}{d \xi} \left( \frac{\mu}{\mu_\infty} \right)}{\rho}$.

$v$ - (mass average) fluid velocity (cm/sec)

$V = \frac{\mu}{\mu_\infty \rho}$.

$z_i$ - valence or charge number of species $i$.

$\alpha$ - transfer coefficient in polarization equation.

$\gamma$ - mean molal activity coefficient.

$\delta_{ij}$ - the Kronecker delta

$\delta_{ij} = 1$ if $i = j$

$\delta_{ij} = 0$ if $i \neq j$.

$\epsilon_D$ - diffusivity perturbation parameter.

$\epsilon_\rho$ - density perturbation parameter.

$\zeta$ - dimensionless distance (3-1).

$\kappa$ - specific conductivity ohm$^{-1}$cm$^{-1}$. 
\( \lambda_0 \) - dimensionless distance between reference electrode and rotating disk electrode.

\( \mu_c \) - chemical potential of salt in binary electrolyte.

\( \nu \) - kinematic viscosity \(( \text{cm}^2/\text{sec})\).

\( \nu^+, \nu^- \) - number of cations and anions produced by dissociation of one molecule of electrolyte.

\( \xi \) - dimensionless distance from the rotating disk (2-10).

\( \rho \) - density of solution.

\( \tau \) - stress tensor (2-2).

\( \phi_a \) - activation (chemical) overpotential.

\( \phi_c \) - concentration (diffusion) overpotential.

\( \phi_{\text{ohm}} \) - ohmic resistance overpotential.

\( \omega_s \) - mass fraction of salt in binary electrolyte.

\( \Omega \) - rotating speed of disk electrode (radians/sec).

**Subscripts**

+,-,o - cation, anion, and solvent in binary electrolyte.

\( \infty \) - in the bulk of solution.

\( s \) - salt.

lim - denotes limiting current.

zero - at the interface of electrode and solution.
LITERATURE CITED


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