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MASS TRANSFER IN ROTATING ELECTRODE SYSTEMS

Charles Milton Mohr, Jr.
(Ph. D. thesis)

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# MASS TRANSFER IN ROTATING ELECTRODE SYSTEMS

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MASS TRANSFER IN ROTATING ELECTRODE SYSTEMS

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ABSTRACT

Four studies of rotating electrode systems are reported. An improved method of solution for the hydrodynamics of a rotating disk employing a series-matching technique is presented. The results represent the most accurate evaluation of certain flow-field parameters derived to date. The limiting-current mass-transfer characteristics of a rotating disk electrode with an offset center of rotation are treated via identification of certain behavior analogous to ring-disk and ring electrode systems. The existence of a critical eccentricity below which the offset does not affect the transfer rate is demonstrated. Mass-transfer rates are calculated as a function of the amount of offset employing a numerical technique, and an analytic asymptotic model for large offsets is developed. These predictions are tested by deposition experiments with a series of electrodes of varying eccentricities.

An experimental study of the diffusion-limited rate of mass transfer to a rotating disk electrode in the transition region between the laminar and turbulent flow regimes is reported. An empirical correlation of the local and average current densities is derived. An experimental study of the mass transfer in turbulent flow between concentric cylinders, the inner of which is rotated, is presented. The gap size, which was not found to be an important
parameter for large gaps, is discovered to influence significantly the mass-transfer rates for these small-gap experiments. A numerical model based upon the concept of a universal eddy diffusivity profile for turbulent flows is derived and is shown to be inappropriate for this turbulent flow.
I. MASS TRANSFER TO AN ECCENTRIC ROTATING DISK

I.1 Introduction

The widespread use of rotating-disk electrodes as analytical tools in electrochemical research is due predominantly to their ease of construction and operation and their well described mass-transfer characteristics. While other systems, such as the rotating spherical electrode\(^{(1,2)}\) or rotating concentric cylinder electrodes,\(^{(3)}\) have certain advantages for particular studies, the rotating disk, operated under conditions of laminar flow, has proven to be a versatile tool for a wide range of electrochemical research. An exhaustive review article by Riddiford\(^{(4)}\) outlines the uses of this device, including kinetic studies, determination of ionic diffusion coefficients, and polarography. In the latter two types of experiments, importance is placed upon the limiting-current behavior of the electrode. That is, the current of interest is the maximum (in the absence of ionic migration and parallel reactions) that can be achieved under the prevailing mass-transfer conditions.\(^{(5)}\) The data are then analyzed assuming that when mass-transfer limitation occurs, the concentration of the reactive species at the electrode surface is effectively zero. Thus prediction of limiting-current behavior for an electrode reduces to solution of the convective diffusion equation\(^{(6)}\) for the system of interest with a boundary condition of zero concentration of the active species on the electrode surface.

The description of the limiting current on a rotating disk was accomplished first by Levich,\(^{(7)}\) who showed that the disk is uniformly
accessible to mass transfer -- that is, the local current density is constant, independent of location on the disk. Subsequent investigations have considered the effect of radial diffusion near the edge of a finite-sized electrode,\(^{(8)}\) concentration-dependent transport properties,\(^{(9)}\) and various mechanical factors, as summarized by Riddiford\(^{(4)}\). Another effect which would be expected to influence the limiting current mass-transfer rate is the location of the circular electrode on the rotating plane. The studies mentioned above considered the electrode to be centered exactly on the axis of rotation of the disk, an idealization which may be difficult to realize -- particularly in the case of very small electrodes.

This effect of the centering of the electrode upon the mass-transfer behavior has received little attention to date. Riddiford\(^{(4)}\) briefly mentions that exact centering is very important, based upon the argument that any offset will cause an increase in the area swept out by the electrode, thus implying a direct relationship between mass-transfer rate and area swept by the electrode. Indeed, there seems to be a practice of correcting for small offsets by multiplying the observed current by a factor assumed to take this effect into account\(^{(10)}\)

\[
I_{\text{centered}} = I_{\text{offset}} \times \left(1 - \frac{\Delta r}{r_0}\right)
\]  

(1)

where \(r_0\) is the radius of the electrode and \(\Delta r\) is the offset (distance between the center of the electrode and the axis of rotation of the disk). This formula has been suggested for \(\Delta r / r_0 \ll 1.0\) \(^{(10)}\).
On the other hand, a short publication by Bardin and Dikusar\textsuperscript{(11)} reports an experimental and theoretical study performed for moderate offsets \((1.0 \leq \Delta r/r_o \leq 5)\). An immediate result of the underlying assumptions upon which their analysis is based is that the mass-transfer rate is unaffected until \(\Delta r/r_o > 1.0\), a somewhat surprising result, but reasonably well supported by their limited experimental data. Doubt is cast upon their analysis (and measurements) however by the exhaustive experimental study performed by Chin and Litt\textsuperscript{(12)} which showed that the predictions of Bardin and Dikusar were significantly in error for large eccentricities \((\Delta r/r_o > 9)\). Chin and Litt also developed an analytical model which was in close agreement with their data, but which is applicable only for large eccentricities, \(\Delta r/r_o >> 1\).

It then seems that a more rigorous study of the small-eccentricity behavior of offset rotating disk electrodes would be useful in assessing the tolerances to which these devices must be manufactured and operated in order to achieve predetermined levels of accuracy in the parameters determined by limiting-current measurements performed with such electrodes. This is the purpose with which this portion of the dissertation is concerned. Specifically, we wish to model the behavior of such electrodes for both large and small eccentricities and, via a suitable experiment, to test the predictions of such a model.
I.2 Theory

A. Background

The laminar flow pattern near a rotating disk has been described by von Kármán,\(^{(13)}\) who was able to solve the complete Navier-Stokes equations for an infinite disk rotating in an unbounded fluid by employing a transformation of variables which reduced these equations to four coupled ordinary differential equations which readily lend themselves to numerical solution. Cochran\(^{(14)}\) later corrected some errors in von Kármán's solution and provided the numerical data upon which this analysis is based. Features of interest of this solution are: 1) the \(z\)-component of velocity (the velocity toward the rotating plane) is independent of radial distance from the center of rotation, and 2) the radial and \(\theta\)-velocities relative to the plane are proportional to \(r\), the distance from the center of rotation. In the discussion which follows, cylindrical coordinates centered upon either the axis of rotation or the center of the (offset) electrode will be used, as shown on Figure 1.

A brief description of the fluid motion near the disk is as follows. Basically, a fluid particle drawn toward the center of the disk spirals outward while approaching the disk and eventually leaves the region of interest. For Schmidt numbers typical of electrolytic solutions, the diffusion layer resides very near the disk surface, and thus we suppose that the radial and tangential velocities of the fluid relative to the disk may be adequately expressed as linear functions of the distance from the disk, \(z\). Cochran\(^{(14)}\) found that these expressions for the velocities are
Figure 1. Coordinate Systems for use in Eccentric Rotating Disk Analysis.
where $v$ is the kinematic viscosity of the solution and $\omega$ is the rotation speed (sec$^{-1}$) of the disk. The validity of the assumption that these linear velocity profiles are adequate for our purposes can be seen from the fact that the Schmidt-number correction to the Levich formula$^{(35)}$ for a centered rotating disk, which is based upon these linear approximations, is only three percent for $Sc = 1000$, a value typical of electrolyte solutions. An alternative demonstration proceeds as follows: the Levich formula$^{(7)}$ for mass transfer to a rotating disk is

$$j = 0.62048 \, D (c_b - c_0) \, \sqrt{\omega/v} \, Sc^{1/3} \quad (3)$$

where $j$ is the mass flux rate to the disk, $D$ is the diffusion coefficient of the active species, $(c_b - c_0)$ the difference between the bulk and surface concentrations of the active species, and $Sc$ the Schmidt number ($v/D$) of the solution. Postulating a Nernst (stagnant) diffusion layer of thickness $\delta_I$, we find that

$$j = D \frac{(c_b - c_0)}{\delta_I} \quad \text{or}$$

$$\delta_I = Sc^{-1/3} \, \sqrt{v/\omega} \left(1/0.62048\right). \quad (4)$$
Examin ing a graph of \( v_r \) and \( v_0 \) versus \( z \) (e.g. ref. 4 or 14), we find that the linear assumption is good to a value of

\[
z \sim 0.2 \sqrt{v/\omega} = \delta_{II}.
\]

(5)

The ratio \( \delta_I/\delta_{II} \) is then equal to approximately \( 8\text{Sc}^{-1/3} \). Since electrolyte solutions have Schmidt numbers on the order of 1000, the assumption seems valid for most such solutions of interest, \( \delta_I/\delta_{II} < 1.0 \). For example, the solution used in the experimental portion of this study (dilute \( \text{CuSO}_4 \) in 1.5 molar \( \text{H}_2\text{SO}_4 \)) had a Schmidt number (at 25°C) of approximately 2000, so that \( \delta_I/\delta_{II} \sim 0.3 \), thus satisfying the requirement for the validity of the above mentioned assumption.

Equation 2 allows us to determine the path of a fluid particle, \( r(\theta) \), near the disk, which would be described by the differential equation

\[
\frac{1}{r} \frac{dr}{d\theta} = \frac{v_r}{v_0 - r\omega} = -0.828. 
\]

(6)

Note that the path is independent of \( z \) within the range of validity of the approximations employed in equations 2. Thus we conclude that the path followed by any fluid particle near the disk is such that its direction of travel is always at an angle \( \alpha \) to a ray drawn from the center of rotation (figure 1), and

\[
\alpha = \cot^{-1}(0.828) = 50.38^\circ .
\]

(7)
Equation 6 can be integrated to yield the equation for the trajectory passing through the point \((r_1, \theta_1)\)

\[
r = r_1 \exp \left[ (\theta_1 - \theta) \cot \alpha \right]. \tag{8}
\]

On the other hand, a point on the edge of the electrode (in this coordinate system) is given by

\[
r = r_0 \sqrt{\varepsilon^2 + 1 - 2\varepsilon \cos \theta'}. \tag{9}
\]

The condition of uniform accessibility, that is, a uniform rate of mass-transfer, will persist for non-zero eccentricities as long as fluid particles spiralling off of the electrode surface never return to or pass over the electrode again. Fluid begins to leave and then return to the electrode (as illustrated on figure 1) at an eccentricity at which a trajectory first becomes tangent to the edge of the electrode. Tangency corresponds to \(\beta = \alpha\) (figure 1), where \(\beta\) is the angle between the edge of the disk and a ray from the center of rotation. Geometrical considerations lead to the relationship

\[
\beta = \alpha = \theta + \theta' - \pi/2 \tag{10}
\]

for a tangent point on the edge of the electrode. Since the relationship between \(\theta\) and \(\theta'\) is

\[
\theta = \tan^{-1} \left( \frac{\sin \theta'}{\varepsilon - \cos \theta'} \right), \tag{11}
\]
the condition for a tangent point reduces to

\[ \theta' = \alpha + \cos^{-1}\left(\frac{\cos \alpha}{\epsilon}\right) \]  

(12)

after rearrangement using trigonometric identities. This equation shows that no point of tangency exists for \( \epsilon < \cos \alpha \). Thus the critical eccentricity we seek, at which the electrode departs from uniformly accessible behavior, is

\[ \epsilon = \cos \alpha = 0.6377 \]  

(13)

For \( \epsilon > \cos \alpha \), equation 12 gives two tangent points

\[ \theta'_{t1} = \alpha - \cos^{-1}\left(\frac{\cos \alpha}{\epsilon}\right) \]  

and

\[ \theta'_{t2} = \alpha + \cos^{-1}\left(\frac{\cos \alpha}{\epsilon}\right) \]  

(14)

where the principal branch of the inverse cosine function is now to be used.

As \( \epsilon \to 1.0 \), it eventually becomes possible for the same trajectory to spiral off of the electrode, return, spiral off again, and return once more. Since in this analysis we will not treat this case, we must determine at what eccentricity this behavior begins. At the onset of this behavior, the critical eccentricity is one such that a single spiral is tangent to the electrode at two points, \( (r_1, \theta'_{t1}) \) and \( (r_2, \theta'_{t2}) \), as shown on figure 2. In order to determine the eccentricity at which this occurs, we must start with five equations
Figure 2. Trajectory at Critical Eccentricity at which Ring-Disk Analogy becomes Inappropriate.
in the five unknowns, \( r_1, r_2, \theta'_{t1}, \theta'_{t2}, \) and \( \varepsilon : \)

1) the equation for the trajectory

\[
\begin{align*}
\theta'_{t2} = r_1 \exp \left\{ \tan^{-1} \left( \frac{\sin \theta'_{t1}}{\varepsilon - \cos \theta'_{t1}} \right) - \tan^{-1} \left( \frac{\sin \theta'_{t2}}{\varepsilon - \cos \theta'_{t2}} \right) + 2\pi \right\} \cot \alpha \right\}, (15)
\end{align*}
\]

2) the two equations for points on the edge of the disk

\[
\begin{align*}
r_1 &= \sqrt{\varepsilon^2 + 1 - 2\varepsilon \cos \theta'_{t1}} \\
r_2 &= \sqrt{\varepsilon^2 + 1 - 2\varepsilon \cos \theta'_{t2}} ,
\end{align*}
\]

(16)

3) and finally, two equations for points of tangency

\[
\begin{align*}
\theta'_{t1} &= \alpha - \cos^{-1}(\cos \alpha/\varepsilon) \\
\theta'_{t2} &= \alpha + \cos^{-1}(\cos \alpha/\varepsilon) .
\end{align*}
\]

(17)

These equations may be combined to yield one equation in \( \varepsilon \) only:

\[
\begin{align*}
\varepsilon^2 + 1 - 2\varepsilon \cos \left[ \alpha + \cos^{-1} \left( \frac{\cos \alpha}{\varepsilon} \right) \right] &= \exp \left\{ \left[ \pi + \cos^{-1} \left( \frac{\cos \alpha}{\varepsilon} \right) \right] 4 \cot \alpha \right\}, (18)
\end{align*}
\]

which has two solutions

\[
\begin{align*}
\varepsilon_1 &= 0.998476 \\
\varepsilon_2 &= 1.001523 .
\end{align*}
\]

(19)
These values were determined by a direct substitution numerical method, the computer program for which is given in Appendix A. The second solution is significant for calculations with $\varepsilon > 1$, since it gives the eccentricity at which fluid begins to pass over the disk only once. Eccentricities between these two values will not be treated in this dissertation. As will be shown later, detailed consideration of this very limited region about $\varepsilon = 1.0$ is not necessary.

B. Calculations for Small Eccentricities

If we follow a trajectory similar to that shown dashed on figure 1, which leaves and then returns to the electrode, we notice that the particles following this path experience a situation similar to what would occur while passing over a ring-disk electrode system, of appropriate dimensions, if the ring and disk both were operated at the limiting current for the same reaction. The particles leave the electrode at a radius $r_1$, return at a radius $r_2$, and finally leave at a radius $r_3$ ($r_3 > r_2 > r_1$). The transfer of mass from these particles should be identical to that to a centered ring-disk electrode with disk radius $r_1$ and inner and outer ring radii $r_2$ and $r_3$, respectively if the ring-disk system is operated under equivalent conditions (concentration, viscosity, rotation speed, etc.). Since each such trajectory on the eccentric disk would be analogous to a trajectory on a different ring-disk electrode, it is necessary to divide the disk into thin strips, bounded by trajectories (figure 3) and calculate the transfer rate to each by identifying the ring-disk
Figure 3. Sectioning Scheme for Numerical Calculation of Mass Transfer to an Eccentric Rotating Disk Electrode.
electrode analogous to each strip and using the known expressions for transfer to such electrodes.\(^{(15,16)}\) Smyrl and Newman\(^{(16)}\) give the total rate of mass transfer for a ring-disk electrode operated at the limiting current (for the same reaction) on both ring and disk as

\[
j = \pi j_{\text{disk}} \left\{ r_1^2 + \left( r_3^2 - r_2^2 \right) \left[ \frac{(r_3^2 - r_2^2)^{2/3}}{r_1^2} - N \right] \right\}
\]

where \(j_{\text{disk}}\) is the local rate of mass transfer to a centered disk electrode of radius \(r_1\), as predicted by the Levich formula\(^{(7)}\) and

\[
N = (A^3 - B^3)^{2/3} \left[ \frac{\sqrt{3}}{4\pi} \ln \frac{1 + \theta^3}{(1 + \theta)^3} - \frac{3}{2\pi} \tan^{-1} \left( \frac{2\theta - 1}{\sqrt{3}} \right) + \frac{3}{4} \right] \\
+ \frac{\sqrt{3}}{4\pi} \ln \frac{1 + A^3 \psi^3}{(1 + A\psi)^3} + \frac{3}{2\pi} \tan^{-1} \left( \frac{2A\psi - 1}{\sqrt{3}} \right) + \frac{1}{4} \\
- A^2 \left[ \frac{\sqrt{3}}{4\pi} \ln \frac{1 + \psi^3}{(1 + \psi)^3} + \frac{3}{2\pi} \tan^{-1} \left( \frac{2\psi - 1}{\sqrt{3}} \right) + \frac{1}{4} \right]
\]

where \(A = r_3/r_1\), \(B = r_2/r_1\), \(\theta = (B^3 - 1)^{1/3}\), and

\[
\psi = \frac{1}{A} \left( \frac{A^3 - B^3}{B^3 - 1} \right)^{1/3}.
\]

An expression equivalent to equation 20 was first derived by Bruckenstein.\(^{(58)}\)

The procedure for determining the mass-transfer rate to an electrode of given eccentricity is as follows:

1) The two trajectories which are tangent to the edge of the electrode are determined via equations 14, locating the
tangent points as shown on figure 3.

2) Trajectories are drawn at equal $\theta$-increments between these two paths dividing the region in which trajectories return over the electrode into a number of strips (following streamlines). A typical such strip is shown shaded on figure 3.

3) The mass-transfer rate to each strip is calculated from equation 21, and the contributions from all the strips are summed, to which is added the transfer rate to the rest of the disk, which is uniformly accessible and thus follows Levich's formula (7) (equation 3).

The computer program used to implement this procedure is given in Appendix A. The results will be reported later.

C. Calculations for Large Eccentricities

For eccentricities greater than 1.001523, considerable simplification is possible, since the fluid spirals outward over an insulating surface (at the beginning) then passes over the electrode only once before leaving the region of interest. We thus anticipate that the strips resulting from sectioning the electrode along streamlines will be analogous to strips on properly dimensioned ring electrodes, which have much simpler expressions for their mass-transfer rates than that given in equation 21 for a ring-disk electrode.

For a ring electrode with the active portion lying between $r = r_1$ and $r = r_2$ ($r_2 > r_1$), the mass-transfer rate has been
determined by Levich \(^{(17)}\) to be (for a strip of width \(d\theta\))

\[
d j = \left( r_2^3 - r_1^3 \right)^{2/3} \frac{D(c_b - c_o)}{2\Gamma(4/3)} \left( \frac{0.510 \nu}{3D} \right)^{1/3} V(b - c_o) (0.510 \nu) \frac{1}{3} d\theta.
\]

(23)

Upon changing the independent variable in this equation from \(\theta\) to \(\theta'\) (figure 1), dividing by the total rate of mass transfer to a centered disk of equal area, and integrating this expression between \(\theta_{t1}\) and \(\theta_{t2}\), we find that

\[
j/j_{disk} = \frac{1}{2\pi} \int_{\theta_{t1}}^{\theta_{t2}} \left( \frac{r_2}{r_1} \right)^{2/3} \left[ \varepsilon \frac{\cos(\theta' - \alpha)}{\cos \alpha} - 1 \right] d\theta'.
\]

(24)

Given \(\varepsilon\) and \(\theta'\), \(r_2/r_1\) can be determined by simultaneous solution of equations 8, 9, and 11. This must be done numerically due to the complexity of these equations. As a test of this numerical procedure, one may verify the identity

\[
2\pi = \int_{\theta_{t1}}^{\theta_{t2}} \left( \frac{r_2}{r_1} \right)^{2/3} \left[ \varepsilon \frac{\cos(\theta' - \alpha)}{\cos \alpha} - 1 \right] d\theta'.
\]

(25)

which results from calculating the area of the electrode in the \(r, \theta'\) coordinate system. The program used to calculate \(r_2/r_1\) and the resulting transfer rate to the disk is given in Appendix A.

D. Asymptotic Behavior for Large Eccentricity

The asymptotic behavior for \(\varepsilon \to \infty\) is of interest since it demonstrates clearly the difference between this analysis and those
of Chin and Litt \(^{(12)}\) and Bardin and Dikusar. \(^{(11)}\) As \(\varepsilon \to \infty\), the following asymptotic behavior is observed

\[
\begin{align*}
\frac{r_1}{r_o} &\to \varepsilon - \cos \theta' \\
\frac{r_2}{r_o} &\to \varepsilon + \cos (\theta' - 2\alpha)
\end{align*}
\]

\[\theta'_{t1} \to \alpha - \pi/2\]

\[\theta'_{t2} \to \alpha + \pi/2\].

When the variable transformation \(x = \sin (\theta' - \alpha)\) is employed in equation 24, the integral becomes, correct to the largest order in \(\varepsilon\),

\[
j/j_{\text{disk}} + \frac{1}{\pi} \left(\frac{36 \varepsilon}{\cos \alpha}\right)^{1/3} \int_0^1 \left(1 - x^2\right)^{1/3} dx
\]

\[= \frac{1}{\sqrt{\pi}} \left(\frac{9 \varepsilon}{2 \cos \alpha}\right)^{1/3} \frac{\Gamma(4/3)}{\Gamma(11/6)} = 1.0277 \varepsilon^{1/3} .
\]

The partitioning scheme of Bardin and Dikusar \(^{(11)}\) leads to

\[
j/j_{\text{disk}} \to \frac{1}{\sqrt{\pi}} \left(\frac{9 \varepsilon}{2}\right)^{1/3} \frac{\Gamma(4/3)}{\Gamma(11/6)} = 0.884 \varepsilon^{1/3} ,
\]

while that of Chin and Litt \(^{(12)}\) results in

\[
j/j_{\text{disk}} \to \frac{3}{2\pi^{1/6}} \left(\frac{\varepsilon}{3 \cos \alpha}\right)^{1/3} = 0.990 \varepsilon^{1/3} .
\]

The manner in which Chin and Litt and Bardin and Dikusar partitioned the electrodes, prior to using Levich's formula (equation 23)
for calculating the mass-transfer rate to each strip, is shown on figure 4, along with the partitioning scheme employed in this analysis. Chin and Litt approximate the circular electrode by a square of equal area, but with proper angle given to the spiral streamlines. Equations 27 and 29 show that this shape simplification introduces an error of less than 3 percent, but the neglect of the fluid trajectory by Bardin and Dikusar results in a 14 percent error even though the circular electrode geometry is retained.

A more exact treatment of the integral in equation 25 is also useful, since it will provide some justification for the form of the simple expression developed later for the transfer-rate ratio as a function of eccentricity. Equation 25 involves three quantities, \( \theta'_{t1} , \theta'_{t2} , \) and \( r_2 / r_1 \), which are functions of \( \varepsilon \). It will be necessary to express these variables as convergent power series in \( \varepsilon^{-1} \) (for large \( \varepsilon \)) and insert these expressions into equation 25 to yield the required result; \( j/j_{disk} \) as a convergent series in \( \varepsilon \).

We now proceed with this development.

The required expansions for \( \theta'_{t1} \) and \( \theta'_{t2} \) are quite straightforward. From equations 14, the terms involving \( \cos^{-1} \left( \frac{\cos \alpha}{\varepsilon} \right) \) may be expanded considering \( \frac{\cos \alpha}{\varepsilon} \ll 1 \) yielding (18)

\[
\theta'_{t1} = \alpha - \pi/2 + \frac{\cos \alpha}{\varepsilon} + \frac{\cos^3 \alpha}{6 \varepsilon^3} + 0(\varepsilon^{-5})
\]

(30)

and
Figure 4. Alternative Partitioning Schemes for Asymptotic Treatment of the Mass Transfer to an Eccentric Rotating Disk.
\[ \theta_{t2} = \alpha + \pi/2 - \frac{\cos \alpha}{\varepsilon} - \frac{\cos^3 \alpha}{6 \varepsilon^3} + 0(\varepsilon^{-5}). \]  

(31)

The expansion for \( r_2/r_1 \) is not so direct since it involves the simultaneous solution of two equations:

\[ (r_2/r_1)^2 = e^{2(\theta_2 - \theta_1) \cot \alpha}, \]  

(32)

derived from equation 8, and

\[ (r_2/r_1)^2 = \frac{\varepsilon^2 + 1 - 2\varepsilon \cos \theta_2^i}{\varepsilon^2 + 1 - 2\varepsilon \cos \theta_1^i}, \]  

(33)
a result of equation 9. For convenience we let

\[ \theta_2^i = -\theta_1^i + \pi + 2\alpha + \psi_1/\varepsilon + \psi_2/\varepsilon^2 + 0(\varepsilon^{-3}), \]  

(34)

and equation 33 becomes, upon expansion for asymptotically large \( \varepsilon \),

\[ (r_2/r_1)^2 = 1 + \frac{1}{\varepsilon} [2 \cos (2\alpha - \theta_1^i) + 2 \cos \theta_1^i] \]  

+ \[ \frac{1}{\varepsilon^2} \left[ 4 \cos^2 \theta_1^i - 2\psi_1 \sin (2\alpha - \theta_1^i) + 4 \cos \theta_1^i \cos (2\alpha - \theta_1^i) \right] + 0(\varepsilon^{-3}). \]  

(35)

Since

\[ \theta_1 - \theta_2 = \tan^{-1} \left( \frac{\sin \theta_1^i}{\varepsilon - \cos \theta_1^i} \right) - \tan^{-1} \left( \frac{\sin \theta_2^i}{\varepsilon - \cos \theta_2^i} \right), \]  

(36)
equations 32 and 34 can be combined and expanded to yield
\[
\left(\frac{r_2}{r_1}\right)^2 = 1 + \frac{2 \cot \alpha}{\epsilon} \left[ \sin \theta_1 + \sin (2\alpha - \theta_1') \right] + \frac{2 \cot \alpha}{\epsilon^2} \left\{ \sin \theta_1 \cos \theta_1 \\
+ \psi_1 \cos (2\alpha - \theta_1') - \sin (2\alpha - \theta_1') \cos (2\alpha - \theta_1') + \cot \alpha \left[ \sin^{-2} \theta_1 + \sin^2 (2\alpha - \theta_1') + 2 \sin \theta_1 \sin (2\alpha - \theta_1') \right] \right\} + O\left(\frac{1}{\epsilon^3}\right). \]  

(37)

Because these two expansions for \( \left(\frac{r_2}{r_1}\right)^2 \) must be equivalent, the corresponding terms of equal order in \( \epsilon \) must match. The terms of order \( 1/\epsilon \) do indeed match since rearrangement using trigonometric identities demonstrates that

\[ 2 \cot \alpha [\sin \theta_1 + \sin (2\alpha - \theta_1')] = 2[\cos \theta_1' + \cos (2\alpha - \theta_1')] . \]  

(38)

Matching the terms of order \( 1/\epsilon^2 \) is accomplished by requiring that

\[ \psi_1 = -2 \cos^2 \alpha (\sin \theta_1' - \tan \alpha \cos \theta_1') . \]  

(39)

This in turn, when substituted into either equation 35 or 37, results in

\[
\left(\frac{r_2}{r_1}\right)^2 = 1 + \frac{2}{\epsilon} \left[ \cos \theta_1' + \cos (2\alpha - \theta_1') \right] \\
+ \frac{4 \cos \alpha}{\epsilon^2} \left[ \sin (2\alpha - \theta_1') \sin (\alpha + \theta_1') + 2 \cos (2\alpha - \theta_1') \cos \theta_1' \cos \alpha \right] \\
+ O\left(\frac{1}{\epsilon^3}\right). \]  

(40)

When one substitutes these power series in \( \epsilon \) into the integral in equation 25, the expected result is a series of the form
\[ j/j_{\text{disk}} = c_1 \varepsilon^{1/3} + c_2 \varepsilon^{-2/3} + c_3 \varepsilon^{-5/3} + \ldots \] (41)

Somewhat surprisingly, the influence of the value of \( \psi \) is to make the constant \( c_2 \) equal to zero. Since vast complications arise when one attempts to evaluate \( \psi \) and \( c_3 \), this calculation was not carried out. The numerical results presented later demonstrate that the term of order \( \varepsilon^{-5/3} \) does indeed contribute to the series, and its value will be estimated in the section in which the numerical results are given.

1.3 Experimental Procedure

The mass-transfer rates for centered and eccentric disk electrodes were determined for electrodeposition of copper onto copper electrodes. The solution used was 0.008 M \( \text{CuSO}_4 \) with 1.5 M \( \text{H}_2\text{SO}_4 \) as the supporting electrolyte. Electrodes were machined from plexiglass, drilled and fitted with short lengths of 0.250 inch diameter copper rod, as shown on figure 5. The electrodes were attached to a steel spindle (insulated with Shell epoxy casting resin) which was tapered and tapped to fit the rotating bearing in a Pine Instruments Company commercial rotating ring-disk device (Model P.I.R.). The cell used was made of plexiglass, equipped with baffles to prevent excessive bulk fluid rotation. The counter electrode was a 4" copper disk, 1/8 inch thick, fastened to the bottom of the cell. The reference electrode was a copper wire fitted in a hole drilled in the side of the cell and
Fig. 5. Centered and eccentric disk electrodes and shaft assembly.
polished flush with the inside surface of the plexiglass. Details of the cell and counter and reference electrodes are given on figure 6. The rotating disk device and cell in operating position are shown on figure 7.

Prior to use, the electrodes were prepared by polishing with successively finer mesh emery paper (Armour Alliance Industries, Alliance, Ohio, Silicon Carbide paper 320A, 400A and 600A grit) and, lastly, with wet "crocus" cloth (Armour Alliance Ind. #710). After final polishing, the electrodes were washed with Amway "L.O.C." (liquid organic concentrate), rinsed with distilled water and acetone, and air dried.

Peripheral electronic equipment included a Wenking Potentiostat, model 66TS1, employed to control the potential between the working and reference electrodes and also to measure the cell current. A Magna voltage ramp generator was used to provide a voltage ramp signal to the potentiostat to cause an automatic potential versus current scan of cell behavior. A constant input voltage to the ramp generator was provided by a Hewlett-Packard model 6101A D.C. voltage power supply. Finally, a Hewlett-Packard model #7035B x - y plotter was employed to record the voltage scan polarogram. The rotation speeds of the disks were determined using a "Strobotac" stroboscopic tachometer. The wiring diagram for this equipment, and the cell, is shown on figure 8.

Due to the belt and pulley drive mechanism on the Pine Instruments device, the rotation speeds used were very reproducible
Figure 6. Cell and Electrode Assembly for Eccentric Disk Mass-transfer Study.
Part Nomenclature for Figure 6

1  Plexiglass cell.
2  Copper counter electrode.
3  $1/4 \times 20$ machine screw, silver soldered to 2.
4  Counter electrode lead to potentiostat.
5  $1/4''$ washers and $1/4 \times 20$ nut.
6  Buna "O"-ring seal.
7  Copper reference electrode, sealed with Dow-Corning "Silastic" putty.
8  Steel electrode shaft.
9  Shell epoxy casting resin insulation
10 $3/8''$ threaded stud.
11 Neoprene gasket.
12 Plexiglass rotating disk.
13 Copper electrode soldered to wire contact to 10.
Fig. 7. Cell and drive mechanism.
Figure 8. Peripheral Electronic Equipment for Eccentric Disk Measurements.
(± ~3%) for all disks used. Three rotation speeds, 405, 910, and 1590 RPM, were used for all electrodes.

Cell potential between the reference and working electrodes was measured directly by the x-y recorder. Current measurements were made using the potentiostat, which includes output jacks between which the potential varies from zero to 200 millivolts proportional to the meter reading (meter and jack locations are shown on figure 8). A signal proportional to the cell current could be transmitted to the x-y recorder by selecting the current mode for the meter. Using the ramp generator to force a scan of cell potential and recording the current as a function of potential produced a series of polarograms as shown on figure 9, which also illustrates the construction method used to determine the limiting current value from the slightly inclined current plateau. Three curves appear on figure 9 since three rotation speeds were used for each electrode. In order to minimize the effect of variations in temperature and copper ion concentration, which arise from viscous dissipation and hydrogen evolution respectively, every third run was made with the centered electrode, and these results were used to calculate the required ratios for the eccentric electrodes used in the immediately preceding and following runs.

The eccentricity of each electrode was determined while the electrode was being operated in the rotating disk device. A finely sharpened pencil was carefully raised onto the spinning disk at various distances from the center of rotation, thus drawing a series
Figure 9. Typical Polarograms for Eccentric Disk Experimental Study.
of concentric circles centered on the axis of rotation of the disk. The minimum distance from the edge of the copper electrode to the apparent center of rotation was measured to an accuracy of approximately 0.01 inch and the eccentricity then determined from this measurement and the known (0.250 inch) electrode diameter. For \( \varepsilon < 1 \), the eccentricity is

\[
\varepsilon = \frac{1}{0.125} (0.125 - x_{\text{min}}), \tag{42}
\]

where 0.125 (inch) equals the electrode radius and \( x_{\text{min}} \) (inches) is the minimum distance from the center of rotation to the edge of the electrode. For \( \varepsilon > 1 \), the eccentricity is

\[
\varepsilon = \frac{1}{0.125} (0.125 + x_{\text{min}}). \tag{43}
\]

For a measurement accuracy of 0.01 inch, the uncertainty in the calculated eccentricities ranged from ± 12% for the electrode with \( \varepsilon = 0.66 \) to ± 2% for the electrode with \( \varepsilon = 3.94 \).

The results of the experimental work are reported in the next section; the data upon which these results are based are given in table 1.

I.4 Results

The results of the computer calculations for eccentricities less than and greater than 1.0 are given in tables 2 and 3, respectively. The equation for the asymptotic behavior, equation 27 or 41, may be
Table 1. Experimental Data for Eccentric and Centered Electrodes

Solution: 0.008 M CuSO₄ in 1.5 M H₂SO₄
Temperature: 22.8°C

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<th>Run Number</th>
<th>Electrode</th>
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<th>( \frac{j}{j_{disk}} )</th>
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Table 2. Numerical Results, $\varepsilon < 1.0$

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Table 3. Numerical Results, $\varepsilon > 1.0$

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extended to include an estimate of the next most significant term by plotting \( \log \left( \frac{j}{j_{\text{disk}}} - 1.0277 \varepsilon^{1/3} \right) \) versus \( \log \varepsilon \) (where \( j/j_{\text{disk}} \) refers to the numerical results), as shown on figure 10, for large eccentricities. The slope of the resultant straight-line fit of the points is \(-5/3\), as predicted by the results of the extended asymptotic expansion which demonstrated that the term of order \( \varepsilon^{-2/3} \) would not contribute to the series. The equation for this straight line leads to the expression

\[
\frac{j}{j_{\text{disk}}} = 1.0277 \varepsilon^{1/3} + 0.044 \varepsilon^{-5/3} + ... \quad (44)
\]

as a close approximation to the asymptotic behavior of the integral in equation 25.

The experimental results, along with the numerical calculations and the large-eccentricity asymptote, equation 44, are given in figure 11, which also includes the data and large eccentricity asymptotic analysis of Bardin and Dikusar. (11) Our data disagree significantly with theirs due, perhaps, to their use of quite small electrodes (approximately 1 millimeter in diameter). This small size might make accurate determination of the eccentricity quite difficult, and would also tend to emphasize edge effects. (8) The data of Chin and Litt, (12) while outside the range of figure 11, support this work well, since it correlated well with their analytical predictions (equation 29) which differ from our analysis by only about 3 percent at the large eccentricities treated in their experimental work (\( \varepsilon > 9 \)).
Figure 10. Error in One-term Asymptotic Expression as a Function of Eccentricity.
Figure 11. Theoretical and Experimental Transfer Rates for an Eccentric Rotating Disk as a Function of Eccentricity.
Although, as previously noted, this analysis fails in a limited region about \( \varepsilon = 1.0 \), the curves representing the numerical results for \( \varepsilon < 1.0 \) and \( \varepsilon > 1.0 \) can be joined with no discernable discontinuity at \( \varepsilon = 1 \), as shown on figure 11.

The close agreement between the numerical and asymptotic results is somewhat surprising in view of the fact that the curvature of the streamlines becomes pronounced as \( \varepsilon \to 0 \), a feature that one would not expect the two-term asymptotic series to describe adequately. It appears that equation 44 is accurate to within one percent for \( \varepsilon > 0.8 \), thus removing the need for detailed calculation over a considerable range of interest.

In retrospect, it would appear that the full spectrum of transfer-rate behavior as a function of eccentricity is of very limited utility. The operation of disks with large eccentricities due to poor manufacture (or, perhaps, bad bearings in the rotating apparatus) could be downright dangerous due to the mechanical vibrations (and splashing electrolyte) that would undoubtedly result.

The most useful feature of this analysis would appear to be the rigorous determination of the value of the eccentricity at which deviation from uniformly accessible behavior at the limiting current begins. The fact that this turns out to be at a rather large eccentricity - roughly two thirds of the electrode radius - should serve to reassure those working with such electrodes that meaningful data can be gathered without placing extreme demands upon the machinists responsible for making the electrodes, or equipment manufacturers who make commercial rotating disk devices.
II. MASS TRANSFER TO A ROTATING DISK IN TRANSITION FLOW

II.1 Introduction

The mass-transfer behavior of the rotating disk electrode is of continuing interest. While the bulk of its uses are based upon the uniform-accessibility property described by Levich (7) for disks upon which simple laminar flow (13) prevails, for sufficiently high rotation speeds turbulence may be reached near the edge of the disk. The non-uniform (enhanced) mass-transfer rate resulting from this turbulence may be a desirable feature for some studies. In particular, this behavior has been found useful for studies of corrosion, when the effect of a varying local rate of oxygen transport to the surface of the corroding metal is of interest.(26-28,32)

An accurate description of the behavior of such an electrode requires knowledge of the local transfer rate for the full range of Reynolds numbers involved. The Reynolds number found appropriate for the disk is \( \text{Re} = \frac{r^2 \omega}{v} \), where \( r \) is the radial distance from the center of rotation, \( \omega \) the angular rotation speed, and \( v \) the kinematic viscosity of the fluid in which the disk rotates. This behavior for simple laminar flow, as described by von Kármán, (13) is well known, having been first described by Levich, (7) who gave the mass-transfer rate as

\[
\bar{N}_{ulam} = 0.6205 \text{Re}^{1/2} \text{Sc}^{1/3},
\]
where the Nusselt number $\overline{\text{Nu}} = \frac{\bar{i}r_0}{nFV\Delta c}$, and the Schmidt number $\text{Sc} = \nu/D$. $\bar{i}$ is the average current density on the electrode, $r_0$ the electrode radius, $n$ the number of electrons transferred per ion reacting, $F$ Faraday's constant, $D$ the diffusion coefficient of the active species, and $\Delta c$ is the concentration driving force for diffusion—bulk concentration minus concentration at the electrode surface.

The transfer rate for well developed turbulent flow has been the subject of several studies, (19-24) and accurate correlations have been proposed for its dependence upon the Reynolds number. The two most useful of these correlations are due to Ellison and Cornet (19) and Daguenet, (21) since both of these also include the Schmidt number influence upon the Nusselt number. Ellison and Cornet report that the mass transfer may be described as

$$\overline{\text{Nu}}_{\text{turb}} = 0.0117 \text{Re}^{0.896} \text{Sc}^{0.249},$$

while the result of Daguenet is

$$\overline{\text{Nu}}_{\text{turb}} = 0.00725 \text{Re}^{0.9} \text{Sc}^{0.33}.$$  

We have chosen to use Daguenet's equation for two reasons. First, the bulk of the data gathered by Ellison were for larger Reynolds numbers than are of interest here (Re $> 10^6$), while Daguenet thoroughly investigated the flow regime immediately adjacent to the transition region ($3 \times 10^5 < \text{Re} < 10^6$). Second, in light of the
many studies of turbulent transfer in different geometries, it seems that the exponent 1/3 is more realistic than 1/4 for the Schmidt number dependence. This conclusion is supported by the investigations of Donovan et al. for turbulent boundary layers, Hubbard and Lightfoot, and Vielstich et al. for turbulent channel and pipe flow. The influence of the structure of the turbulent flow upon this exponent is discussed by Levich. Also, Ellison and Cornet's data for Re < 10^6 are quite scattered and may possibly be better fit by a Sc^{1/3} dependence. As discussed in Appendix B, however, it is necessary to modify the results of Daguenet to achieve a better fit of his turbulent-regime data. This has led to the following correlation for the large Reynolds number asymptotic mass-transfer behavior:

\[ \frac{\text{Nu}}{\text{Nu}_{\text{turb}}} = 0.0078 \text{ Re}^{0.9} \text{ Sc}^{1/3} \]  

The problem remains to describe the mass-transfer behavior as a function of Reynolds number for the region in which the simple laminar flow becomes unstable and yields to turbulence. The range of Reynolds numbers over which this change takes place has been termed the "transition region," and the experimental determination of its mass-transfer behavior is the purpose of this portion of the dissertation.

The nature of this transition region was first described by Gregory, Stuart, and Walker, who demonstrated that the simple laminar flow found near the center of the disk becomes unstable at a
Reynolds number equal to approximately $1.8 \times 10^5$, and that fully developed turbulence was not reached until $Re \approx 3 \times 10^5$. Two experimental techniques were employed by these authors. In the first, wet clay disks were rotated in air; as the clay dried it turned a lighter color. The turbulent region dried first, and if the experiments were stopped at the proper time, different regions of color could be noticed. The turbulent region was a uniform light color, the laminar region a uniform dark, and the transition region was marked by a pinwheel light-and-dark stripe pattern which the investigators assumed was due to the presence of vortices which remained stationary relative to the disk. The experimental Reynolds number limits of this region were verified in another experiment in which a stethoscope probe was placed near the surface of the disk and moved radially to monitor the sound of the air moving near the disk: the laminar region gave a low hiss, the turbulent region a loud "noise," and the transition region a distinct note due to the uniform rate of movement of the vortices past the probe. The results of both experiments were in very good agreement. Stuart\textsuperscript{25} also developed a nonlinear stability analysis which showed that stable periodic solutions to the Navier-Stokes equations could be expected for this range of Reynolds numbers. Subsequent work by others has served to reinforce the conclusions of Gregory et al. In particular, the work of Chin and Litt\textsuperscript{33} has provided perhaps the most accurate determination of the critical Reynolds numbers bounding the transition region. These investigators embedded a small electrode in a disk at some
distance from the center of rotation. By varying the rotation speed, the electrode was subjected to a range of Reynolds numbers. A spectral analysis of the current signal to the electrode was used to determine if a regularly varying mass transfer mode was present, indicating vortices moving across the electrode. Their results agreed well with Gregory et al. (25) for the lower bound of the transition region, their value being \( \text{Re} = 1.7 \times 10^5 \), but they found evidence that the vortices persist to a Reynolds number of about \( 3.5 \times 10^5 \), well beyond the value reported by Gregory.

Various studies of mass transfer in the turbulent flow regime also include some data in the transition region. Kreith, Taylor, and Chong (23) report significant deviation from values predicted by the Levich analysis for laminar flow beginning at a Reynolds number of about \( 2 \times 10^5 \). The rather scattered data of Cobb and Saunders (24) tend to agree with this. Daguenet (21) reported a lower bound of the transition region of approximately \( 2.6 \times 10^5 \), but this value varied with the Schmidt number (\( \text{Sc} = \nu / D \), where \( D \) is the diffusion coefficient of the active species) of the solution. An experimental study performed by Tien and Campbell (22) agreed more closely with Chin and Litt in that they reported enhanced mass transfer beginning at \( \text{Re} = 1.8 \times 10^5 \). Ellison and Cornet (19) have also performed an experimental (and theoretical) investigation of mass transfer in the turbulent regime. While their data for low \( (<3 \times 10^5) \) Reynolds numbers is somewhat scattered, they state that significant deviation from the Levich theory does not begin until \( \text{Re} = 3 \times 10^5 \) is reached.
In view of the lack of agreement about the value of the Reynolds number at which the Levich theory becomes inappropriate and the lack of a correlation for mass transfer in the transition region, an experimental study of this problem is proposed. It is hoped that a more exact treatment of the dependence of the local transfer rate upon the Reynolds number, particularly in the transition region, will be found useful for such studies in which variation of the local mass-transfer rate (as a function of position) is desired.

II.2 Experimental Work

A. Electrochemical Systems of Interest

Two reactions were chosen for study: the electrodeposition of copper from a cupric sulfate - sulfuric acid solution onto a rotating copper disk, and cathodic reduction of ferricyanide ions to ferrocyanide ions, also on a copper disk, from a potassium ferricyanide - potassium ferrocyanide - potassium hydroxide solution. Concentrations of the active species were approximately 0.005 molar, while 1.5 molar sulfuric acid and 0.85 molar potassium hydroxide were used as supporting electrolytes. For the ferricyanide reduction, an excess of ferrocyanide was used (c ~ 0.007 molar) to help insure that the limiting current was achieved on the cathode (disk) before excessive oxygen evolution occurred at the anode. The reactions involved at each electrode were
for the cupric sulfate system, and

\[ \text{Cu}^{++} + 2e^- \rightarrow \text{Cu}(s) \quad \text{(cathode)} \]  \hspace{1cm} (49a)

\[ \text{Cu}(s) - 2e^- \rightarrow \text{Cu}^{++} \quad \text{(anode)} \]

for the ferricyanide-ferrocyanide system. Oxygen evolution at the anode of the ferricyanide system is not desirable since it reduces the amount of ferrocyanide oxidized, thus depleting the solution of ferricyanide. A counter electrode of copper was used for the cupric-acid system to provide the atomic copper for the anodic reaction. A nickel counter electrode was used for the ferricyanide system anode.

B. Experimental Apparatus

The electrode, drive mechanism, and cell are depicted in figures 12 and 13. Power for the drive mechanism was provided by a Minarik 1/2 horsepower variable speed motor, type DM. A series of three slinger rings, figure 13, each in its own compartment, was used to prevent loss of the solution at high rates of revolution and minimize aeration of the solution during the trials. The slinger rings and insulation on the brass shaft were machined out of a single piece of teflon. The electrode consisted of a copper disk approximately 2 1/4 inches in diameter soldered to a 1/4" - 20 machine screw which provided electrical continuity to the shaft. The back and edge of
Fig. 12. Drive mechanism and cell assembly for mass transfer to a rotating disk electrode in transition flow.
Figure 13. Cell and Electrode Schematic for Mass Transfer to a Rotating Disk.
Nomenclature for Figure 13

1 Threaded plexiglass cell top.
2 Threaded intermediate plexiglass piece.
3 Buna "0" ring seals.
4 Plexiglass cell (main compartment).
5 Baffles (6 total).
6 Copper (or nickel) counter electrode.
7 1/4 × 20 machine screw silver soldered to 6.
8 1/4" washers and nut.
9 Counter electrode lead to galvanostat.
10 Copper (or nickel) reference electrode, sealed with Dow-Corning "Silastic" putty.
11 Neoprene rubber gaskets.
12 Teflon insulation and slinger rings.
13 1/4 × 20 machine screw.
14 Shell epoxy casting resin insulation.
15 Copper electrode, silver soldered to 13.
16 Brass rotating shaft.
the electrode were insulated with Shell epoxy casting resin which was extended 1/4 inch beyond the edge of the electrode to reduce the effect of the hydrodynamic disturbance due to the edge of the disk upon the flow field over the conducting area. The cell, figure 13, consisted of an upper portion with the compartments for the slinger rings which screwed into the lower portion which contained the bulk of the solution, the copper or nickel reference and counter electrodes, and a series of six baffles around the perimeter to minimize bulk rotation of the fluid. The top was provided with a hole drilled to permit insertion of a thermometer which was left in place during each series of trials. The thermometer hole and joint between top and bottom portions of the cell were sealed with O-rings.

The peripheral electronic equipment consisted of a galvanostat (with a built-in current ramp generator) which was built to order for high current applications and is to be described elsewhere. Continuous polarograms were recorded on a Hewlett-Packard model 7044A x-y plotter. Current measurements were made by placing a precision resistor (0.1495 Ω, 25 watt maximum power dissipation) in the lead to the counter electrode, and the voltage drop across it measured directly using the x-y plotter. The rotation speed of the electrode was determined with a "Strobotac" stroboscopic tachometer.
C. **Electrode Preparation**

The electrode was polished prior to each series of runs with 4/0 grit emery paper followed by buffing on a canvas polishing wheel coated with six micron diamond paste to a mirror finish. Following both the polishing and buffing, the electrode was washed with Amway L.O.C. cleaning solution followed by rinsing with distilled water and ethanol and drying in a stream of hot air. Due to the low concentrations of Cu$^{++}$ in the cupric sulfate solutions (approximately 0.005 molar) and the short duration of the trials, the surface remained quite smooth and mirrorlike even after a series of fifteen to twenty trials. The trials involving the ferricyanide solutions were observed not to alter the surface detectably during the experiments, although the copper would apparently corrode if allowed to remain in contact with the KOH solution.

D. **Experimental Procedure**

For each series of trials, the cell was disassembled and cleaned, and the proper counter and reference electrodes were installed and polished with emery paper. Freshly prepared solution was introduced into the cell, with care being taken to exclude air bubbles. The solution level found to minimize apparent aeration at high rotation speeds was reached when the surface was approximately at the same level as the middle slinger ring, which required about 1.6 l of solution. The polarograms were recorded at various rotation speeds, noting the temperature of the solution at each trial. A series of fifteen trials was found to increase the temperature about 1°C.
Typical polarograms for a series of measurements are shown on figure 14. Viscosities of the solutions were determined for the range of temperatures encountered using a capillary viscometer. Diffusion coefficients were measured with the experimental electrode system operated at low revolution speeds using the Levich formula for laminar flow to a rotating disk. For slight temperature variations, the Stokes-Einstein equation, $D \mu = CT$, where $T$ is °K and $\mu$ = absolute viscosity, was used. During the run, measurements were made at low rotation speeds to monitor possible concentration variation, a problem which occurred in the ferricyanide system due to oxygen evolution at the anode. A summary of the data for the five runs reported herein follows on table 4.

II.3 Results

The experimental results are presented on figure 15 as a graph of $\bar{Nu}Sc^{-1/3}$ versus $Re$. The data gathered for $Re < 1.4 \times 10^5$, used to determine the diffusivity of the reacting species and monitor concentration changes, are not shown on this figure. The departure from the predictions of the Levich formula, equation 45, are observed to begin at approximately $Re = 2 \times 10^5$, in agreement with previous studies. The approach to the values predicted by the equation 48 is also shown.

To determine the local mass-transfer rate as a function of Reynolds number from the experimental data and equations 45 and 48, one may use the expression.
Solution 5
$3.427 \times 10^{-3}$ M Cu SO$_4$
1.50 M H$_2$SO$_4$
Run 4
Trials 12-15

Figure 14. Typical Polarograms for Mass Transfer to a Rotating Disk.
Table 4. Experimental Results for Mass Transfer to a Rotating Disk Electrode in the Transition Range of Reynolds Numbers.
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Table 4. (continued)
Table 4. (continued)

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Table 4. (continued)
Figure 15. Overall Mass-transfer Rate ($\frac{\text{NuSc}^{-1/3}}{}$) Versus Reynolds Number for Laminar, Transition, and Turbulent Regimes.
\[
\frac{\bar{\text{Nu}}}{\text{Sc}^{-1/3} \text{Re}^{1/2}} = \frac{i_{\text{loc}}^r}{nF \Lambda C} = \frac{1}{2} \frac{d}{d(\text{Re}^{1/2})} [\text{Nu} \text{Re}^{1/2}] . \quad (50)
\]

\(\frac{\bar{\text{Nu}}}{\text{Sc}^{-1/3} \text{Re}^{1/2}}\) is shown on figure 16 as a function of the square root of the Reynolds number. While the scatter in the data detracts from the accuracy of the derivatives determined from the curve fit, the results should still be useful in providing an estimate of the local and transfer rates which lie within the data scatter. It should provide an improvement over previous work\(^{(27,28)}\) in which the local transfer rate for the laminar region was spliced (with considerable discontinuity) directly to the local transfer rate predicted from the work of Ellison and Cornet, equation 46.

The local Nusselt number derived from equation 45 (using equation 50) is

\[
\text{Nu}_{\text{lam}} = 0.6205 \text{Re}^{1/2} \text{Sc}^{1/3} . \quad (51)
\]

In a similar manner, equation 48 yields

\[
\text{Nu}_{\text{turb}} = 0.01092 \text{Re}^{0.9} \text{Sc}^{1/3} . \quad (52)
\]

These equations, along with the local Nusselt numbers for the transition region determined by differentiation of the curve fit given in figure 16, are given in figure 17. A straight-line fit of the data for the transition region seems reasonable; the one shown dotted in figure 17 leads to a correlation for the local Nusselt number.
Figure 16. Overall Mass-transfer Rate Versus Square Root of the Reynolds Number.
Figure 17. Local Mass Transfer Rate Versus Reynolds Number for Transition, Laminar, and Turbulent Regimes.
for Reynolds numbers between $2.0 \times 10^5$ and $3.0 \times 10^5$ and is continuous with the laminar and turbulent equations 51 and 52 at these values of $Re$.

Given these results for the local transfer rate in the three regions, we may reconstruct the overall transfer-rate behavior by integrating equation 50. For the laminar region, equation 45 is unchanged. In the transition region, $2 \times 10^5 < Re < 3 \times 10^5$, integration of equation 53 leads to

$$
\bar{Nu}_{trans} \frac{Re^{1/2}}{\sqrt{2 \times 10^5}} = 2 \int_0^{\sqrt{2 \times 10^5}} Nu_{lam} d(Re^{1/2}) + 2 \int_{\sqrt{2 \times 10^5}}^{\sqrt{Re}} Nu_{trans} d(Re^{1/2}) + 2 \int_{\sqrt{Re}}^{\sqrt{3 \times 10^5}} Nu_{trans} d(Re^{1/2})
$$

$$
= (0.89 \times 10^5 + 9.7 \times 10^{-15} Re^{3.5}) Sc^{1/3}
$$

For the turbulent region, $Re < 3 \times 10^5$,

$$
\bar{Nu}_{turb} \frac{Re^{1/2}}{\sqrt{3 \times 10^5}} = 2 \int_0^{\sqrt{2 \times 10^5}} Nu_{lam} d(Re^{1/2}) + 2 \int_{\sqrt{2 \times 10^5}}^{\sqrt{Re}} Nu_{trans} d(Re^{1/2}) + 2 \int_{\sqrt{Re}}^{\sqrt{3 \times 10^5}} Nu_{turb} d(Re^{1/2})
$$

$$
= (0.0078 Re^{1.4} - 1.3 \times 10^5) Sc^{1/3}
$$

when the appropriate expressions are substituted for $Nu_{lam}$, $Nu_{trans}$, and $Nu_{turb}$.

The overall Nusselt numbers given by equations 45, 54, and 55 are shown on figure 18 as a function of Reynolds number. The curve
Figure 18. Overall Mass-transfer Rate as Predicted by Correlations for the Transition and Turbulent Flow Regimes.
representing the fitted experimental data is also shown, along with the modified correlation of Daguenet for the turbulent region. The graph supports the statement by Ellison and Cornet\textsuperscript{(19)} that for Re > 10^6 only the contribution to the overall mass transfer due to the turbulent region is of consequence. At Re = 10^6, the difference between the correlation of Daguenet, equation 48, and the results which include the contribution of the laminar and transition regions, equation 55, is less than seven percent. This is within the range of the maximum deviation of the data from the fitting curve. The estimated local Nusselt numbers in the transition region differ from the experimentally determined values, shown on figure 17 by at most ten percent near Re = 3.5 \times 10^5; the fit is improved for larger Reynolds numbers.

II.4 Recommendations

The scatter of the data is an unpleasant facet of this investigation – particularly in reference to the evaluation of the local transfer rate which requires a differentiation of a fit of this data. The elimination of the need for this differentiation could be accomplished by direct measurement of the deposit thickness for a deposition reaction such as performed by Marathe\textsuperscript{(41)} for measurement of current densities below the limiting current on a rotating disk electrode. This type of study was attempted during this investigation but was abandoned due to the problem of temperature control. While heating due to viscous dissipation was not significant
at the rotation speeds used by Marathe, with the larger electrode, the presence of the slinger rings, and the high rotation speeds needed to reach turbulence at the outer edge of the electrode, viscous heating resulted in a rate of temperature rise of about 1°C/min; and existing equipment could not be easily modified to correct this tendency. The development of a controlled temperature cell suitable for this study would undoubtedly decrease the data scatter and would yield an immediately measurable local transfer rate, the result of primary interest.
III. MASS TRANSFER IN TURBULENT FLOW BETWEEN ROTATING CYLINDERS WITH SMALL SEPARATION GAPS

III.1 Introduction

The electrode system employing concentric rotating cylinders offers considerable promise for electrochemical investigations. While its advantages are many: uniform potential, current, and concentration distributions at the working electrode surface and the capability of building a system with relatively high surface area per unit volume of solution (for a non-porous electrode), it suffers from a serious handicap that has prevented its widespread adoption as an experimental tool. That is, the mass-transfer behavior of this system is not described sufficiently well to allow accurate determination of the interfacial concentration from current and bulk concentration measurements. The suppression of natural convection in this system dictates the use of high rotation speeds (usually for the inner cylinder while the outer one remains stationary) so that turbulent flow conditions prevail. While the behavior of rotating turbulent flows has received some attention, the empirical treatment of this situation does not appear to be sufficiently advanced to allow its immediate usage to predict friction-factor and mass-transfer behavior in such flows.

Gabe(4) has recently reviewed the several studies that have been directed toward resolving the experimental correlation for mass transfer in this system. The pioneering work in this field was performed by Eisenberg, (43,44) and his correlation for the mass-transfer dependence upon the system and solution parameters has been substantiated
by subsequent investigations. For all systems that appear to have been studied to date, the gap between the inner and outer cylinders has comprised a significant portion of the outer cylinder radius:

\[ 0 < \kappa \leq 0.85 \quad (56) \]

where \( \kappa = \frac{R_i}{R_o} \) and \( R_i \) and \( R_o \) are the inner and outer cylinder radii respectively. These studies concluded that mass transfer and friction factor could be correlated best with a Reynolds number based on the inner cylinder radius

\[ Re_i = \frac{R_i^2 \Omega}{\nu} \quad (57) \]

where \( \Omega \) is the rotation speed of the inner cylinder and \( \nu \) is the kinematic viscosity of the solution. This result is not anticipated by traditional views of shear-induced turbulence, which would lead one to expect that the proper Reynolds number for a best fit would be based upon the gap dimension,

\[ Re = \frac{R_i (R_o - R_i) \Omega}{\nu}, \quad (58) \]

rather than the form given in equation 57. The classic stability study of Taylor has demonstrated that the proper dimensionless group for correlating the point of instability of the simple cylindrical couette flow is
as given by Schlichting;\(^{(48)}\) \(Ta\) is the "Taylor" number. The similarity between this group and the gap-distance based Reynolds number, equation 58, is apparent.

This study has been proposed to investigate the small-gap mass-transfer behavior for such rotating cylinder systems and to test whether or not current empirical models for the structure of shear-induced turbulence are appropriate for such small gaps. While Gabe and Robinson\(^{(45)}\) have suggested that for small gaps the gap size must eventually become significant, the form that this influence may take has not yet been elucidated by previously published studies.

III.2 Experimental Measurements of Mass Transfer in Turbulent Cylindrical Couette Flow

A. Electrode Reactions

The oxidation-reduction reactions involving ferricyanide and ferrocyanide ions, as discussed in II.2, were chosen for this investigation. Eisenberg\(^{(44)}\) has discussed these reactions and has shown that their use with nickel electrodes provides excellent limiting-current behavior when hydrogen evolution is suppressed through the use of an alkaline supporting electrolyte. Accordingly, NaOH and KOH were used in this study as supporting electrolytes.
B. Equipment

Eisenberg's original equipment was modified to meet the needs of this study. The cell and drive mechanism are shown on figure 19. The reference electrode, shown to the right of the cell, consisted of a nickel wire in a reservoir connected to the cell through a capillary through the water jacket. A schematic drawing of the cell is given in figure 20. The drive mechanism and peripheral electronic equipment described in II.2 for the mass transfer to a rotating disk in transition flow were employed in these experiments also. The nickel electrode sizes were chosen to emphasize the influence of small gaps upon the transfer rate. The outer electrode was 5.380 inches in internal diameter. The four inner cylinders ranged from 4.9 to 5.29 inches in diameter, resulting in gap ratios, \( R_1/R_0 \), of from 0.916 to 0.983. Due to the decreased gap sizes, viscous dissipation was more pronounced in this study than in Eisenberg's, so a more efficient method of cooling the solution was required. While Eisenberg reported that adequate temperature control could be achieved by blowing hot or cold air on the cell, it was found necessary to install a water jacket on the outer electrode in order to control the temperature to within the 0.2°C claimed by Eisenberg. Another modification found useful was the installation of a circulating pump and thermometer chamber, shown on figure 19, to monitor the cell temperature, since the thin gaps did not allow direct insertion of a thermometer. The pump was a Teel model 1P579 general purpose positive displacement pump which circulated solution drawn from the bottom.
Fig. 19. Drive mechanism and cell assembly for rotating concentric cylinder electrodes.
Figure 20. Schematic of Equipment.
Cell and Electrode Nomenclature for Figure 20

1  Plexiglass top of cell.
2  Plexiglass bottom of cell.
3  Teflon bearing.
4  Outlet from cell (to pump and thermometer container).
5  Brass water jacket.
6  Cooling water inlet to 5.
7  Glass capillary to reference electrode.
8  Nickel inner rotating cylinder.
9  Nickel outer cylinder welded to 5.
10 Threaded stud for contact to counter electrode lead, soldered to water jacket.
11 1/8" threaded stainless steel rod, securing top and bottom of cell to outer electrode, fastened with wing nuts.
12 Stainless steel edge on nickel outer electrode.
13 Buna "0" ring seals.
14 Cooling water jacket outlet.
15 Stainless steel shaft, threaded to fit inner electrode.
16 Spring loaded rotating seal.
17 Entrance for solution from thermometer chamber.
of the cell past the thermometer and returned it to the top of the
cell. Pumping rates were high enough to affect noticeably the values
of the limiting currents, so the pump was turned off before measurements
were made.

The exact centering of the inner electrode can present a problem
in this geometry. Any offset from the concentric alignment of the
electrodes could be quite significant in this investigation since very
small gaps (0.05 to 0.25 inches) were employed. Caliper and micrometer
measurements indicated that the inner cylinders were of uniform radius
(to within less than 0.001 inches) and that the internal diameter
of the outer cylinder was 5.380 ± 0.001 inches. The cell could be
centered relative to the rotating shaft to within approximately 0.003
inches and "run-out" in the rotating shaft with the cell and electrode
in place was less than 0.001 inches, as measured by a dial indicator
with its point inserted in the access port for the capillary lead to
the counter electrode. This results in a possible deviation of less
than 0.005 inches, a maximum percent deviation of less than ten percent
for the smallest gap tested.

Surface roughness is another potential difficulty. A Gould
"Surfanalyzer" was used to determine a typical roughness profile for
the electrodes. A scan of a typical segment of inner cylinder radius
is shown on figure 21. Surface deviation appears to be approximately
20 microinches, which should cause no appreciable effect upon the
mass transfer according to the results of Kappesser, Cornet, and
Greif, (46) who determined that for
Figure 21. Typical Surface Profile of Inner Cylindrical Electrode.
where \( \varepsilon \) is the magnitude of the surface irregularities, the surface behaved in a "smooth" manner and the results for mass transfer followed the prediction of Eisenberg et al.

C. Procedure

Prior to each run a fresh solution was prepared, and the electrodes were polished and washed. The electrode preparation scheme used by Eisenberg\(^{44}\) was followed, except that cathodic treatment of the electrodes in a five percent NaOH solution was not performed. Eisenberg indicates that this is required for accurate determination of the kinetic parameters for the reaction but does not affect the limiting-current measurements.

The solution was introduced into the cell through the reference electrode reservoir; the air being forced out through a bleed line at the top of the thermometer chamber. The circulating pump was started, and the cylinder rotated at approximately 1000 RPM to allow viscous dissipation to heat the solution to 25°C. Manual control of the cooling water (industrial cold tap water) was found adequate to maintain the temperature of the solution at 25.0 ± 0.2°C. When temperature control was achieved at the rotation speed of interest, the circulating pump was turned off. A short delay allowed bubbles introduced by the pumping to leave the solution in the gap, after which a current scan using the ramp galvanostat was made. Scan rates were between 2 and 5 amperes/minute. A set of the resulting
polarograms is shown on figure 22. The scan was halted when the limiting current plateau was reached since hydrogen evolution tended to alter the concentrations of the solution. Some change in the ferricyanide concentration seems unavoidable due to oxygen evolution at the anode. Eisenberg's measurements of the limiting currents for the oxidation of ferrocyanide indicated a very poor plateau, demonstrating the presence of oxygen evolution. Thus the solutions were gradually depleted of ferricyanide, which made necessary periodic determination of the ferricyanide concentration. The iodometric titration for ferricyanide described by Kolthoff(51) was employed. Preparation of the solutions required for the titrations is discussed by Swift(52).

D. Physical Properties of the Electrolyte Solutions

Two different solutions were used so that the Schmidt number of the solutions could be varied. The less viscous solution, which was used for most of the experiments, consisted of

\[
0.0047 \text{ mole/l } \text{K}_3\text{Fe(CN)}_6 \\
0.0050 \text{ mole/l } \text{K}_4\text{Fe(CN)}_6 \\
\text{and } 0.850 \text{ mole/l KOH}.
\]

The kinematic viscosity of these solutions was determined using a Ubbelohde capillary viscometer and was found to be \(0.00952 \text{ cm}^2/\text{sec}\). The diffusion coefficient was determined using a nickel rotating disk electrode and was found to be \(5.73 \times 10^{-6} \text{ cm}^2/\text{sec}\). Both these
Electrode 1; $\kappa = 0.9829$

Solution properties:

$\nu = 0.0189 \text{ cm}^2/\text{sec}$

$D = 3.27 \times 10^{-6} \text{ cm}^2/\text{sec}$

$c = 4.55 \times 10^{-6} \text{ mole/cm}^3$

Figure 22. Typical Polarograms for Turbulent Mass Transfer Between Rotating Cylinders.
values were measured at a temperature of 25.0°C.  
The second solution consisted of  

\[ 0.0047 \text{ mole/ℓ } \text{K}_3\text{Fe(CN)}_6 \]
\[ 0.0050 \text{ mole/ℓ } \text{K}_4\text{Fe(CN)}_6 \]
\[ 1.500 \text{ mole/ℓ } \text{Na}_2\text{SO}_4 \]

and  

\[ 0.500 \text{ mole/ℓ } \text{NaOH} \]

The kinematic viscosity and diffusivity were found to be  

0.0189 cm\(^2\)/sec and 3.27 \(10^{-6}\) cm\(^2\)/sec, respectively, at 25°C.

The Schmidt number of this solution was 5780, compared to a value of 1660 for the first solution. This second solution appeared to have a rather short useful lifetime. While it remained clear for approximately twenty-four hours following its use in the cylinder device, small crystals of precipitate were noticed after this time and could not be redissolved. More concentrated Na\(_2\)SO\(_4\) solutions were prepared (2.0 M), but they exhibited this tendency to form a precipitate after an even shorter time -- less than one half hour. These solutions were abandoned due to the undesirable prospect of precipitation in the apparatus during the runs. While this use of Na\(_2\)SO\(_4\) to vary the Schmidt number of ferricyanide, ferrocyanide solutions seems to be quite promising, this tendency toward precipitation is clearly undesirable, and for experiments of lengthy duration, perhaps less concentrated solutions (~1M) might prove more practical.

The presence of the large amount of Na\(_2\)SO\(_4\) had no apparent effect upon either the limiting current curves or the ferricyanide titration results.
E. Experimental Results

The data gathered for the runs performed are given in tables 5a and 5b. Dimensionless mass-transfer rates are presented as Stanton numbers

\[ St = \frac{i}{nFR_i \Omega c} \]

where \( i \) is the average current density, \( n \) the number of electrons exchanged per ion reacting, \( F \) Faraday's constant, and \( c \) the bulk concentration of the reacting species.

III.3 Theory

If shear induced turbulence is postulated, one may expect to describe the friction-factor and mass-transfer behavior with an empirical model, such as the Wasan, Tien, Wilke correlation which was developed to correlate the turbulent mass transfer for flow in pipes and more recently, was used to predict closely the mass transfer to rotating disks in turbulent flow. This model has been chosen for this study. The eddy diffusivity is correlated as a function of a dimensionless distance from the wall; this distance is

\[ y^+ = \frac{y}{\nu} \sqrt{\frac{\tau}{\rho}} \]  \hspace{1cm} (60)

Near the inner cylinder \( y_1 = r - \kappa R_o \) and the shear stress at the wall \( \tau = \tau_1 \); \( r \) is the radial distance from the center of rotation.
Table 5a: Experimental Results for Mass Transfer between Rotating Cylinders; Sc = 1661.

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<th>CONC. (GMUL/CC)</th>
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XBL 754-1061
Table 5b: Experimental Results for Mass Transfer between Rotating Cylinders; Sc = 5780.

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Near the outer cylinder, \( y_o = R_o - r \) and \( \tau = \tau_o \). An angular momentum balance leads to

\[
\kappa R_o^2 \tau_i = R_o^2 \tau_o .
\]  

(61)

Since the eddy diffusivity is continuous across the gap, we must determine the value of \( r \) at which \( y_i^+ = y_o^+ \). From equations 60 and 61

\[
y_{\text{max}}^+ = \kappa R_o \frac{1 - \kappa \sqrt{\frac{\tau_i}{\rho \nu}}}{1 + \kappa} , \quad \text{where} \quad y_{\text{max}}^+
\]

is the value of \( y^+ \) at the radial position where \( y_i^+ = y_o^+ \).

Introducing the friction factor

\[
f = \frac{1}{\frac{1}{2} \rho \kappa \frac{2}{R_o^2 \Omega^2}}
\]

(63)

and using the gap-distance based Reynolds number, equation 58, we find from equation 62 that

\[
y_{\text{max}}^+ = \frac{\kappa}{1 + \kappa} \text{Re} \frac{\sqrt{\tau}}{2} .
\]  

(64)

The shear stress expression for cylindrical coordinates is, when turbulence is included,

\[
\tau_{r\theta} = \frac{\tau_i (\kappa R_o)^2}{r^2} = -(\mu + \mu(t)) \frac{\partial}{\partial r} \left( \frac{\dot{\gamma}}{r} \right) ,
\]

(65)
where \( \mu \) and \( \mu(t) \) are the absolute and eddy viscosities and \( \bar{v}_\theta \) is the time-averaged \( \theta \)-velocity at radial position \( r \). The expression for \( y^+ \) and \( f \) may be introduced, and equation may be integrated across the gap (considering the outer cylinder stationary) to yield

\[
\sqrt{2/f} = \int_0^{y_{max}} \frac{dy^+_1}{(1 + \frac{1 - \kappa}{1 + \kappa} \frac{y^+_1}{y_{max}})^3 \left(1 + \frac{v(t)}{v}\right)} + \int_0^{y_{max}} \frac{dy^+_o}{(1 + \frac{1 - \kappa}{1 + \kappa} \frac{y^+_o}{y_{max}})^3 \left(1 + \frac{v(t)}{v}\right)}
\]

where the eddy kinematic viscosity is \( v(t) = \mu(t)/\rho \). The development of the expressions for the mass-transfer rate proceeds in an analogous manner. When the equation for turbulent mass transport in cylindrical coordinates is integrated across the gap, the resultant expression, in terms of the Stanton number, is

\[
\frac{1}{St} \sqrt{f/2} = \int_0^{y_{max}} \frac{dy^+}{\left(1 + \frac{1 - \kappa}{1 + \kappa} \frac{y^+}{y_{max}}\right)\left(\frac{1}{Sc} + \frac{\rho(t)}{v}\right)}
\]

\[
+ 2 \int_0^{y_{max}} \frac{\frac{1 - \kappa}{1 + \kappa} \frac{y^+}{y_{max}} dy^+}{\frac{1}{Sc} + \frac{\rho(t)}{v}} + \int_0^{y_{max}} \frac{\left(\frac{1 - \kappa}{1 + \kappa} \frac{y^+}{y_{max}}\right)^2 + \frac{1 + \kappa}{1 + \kappa} \frac{y^+}{y_{max}} dy^+}{1 - \left(\frac{1 - \kappa}{1 + \kappa} \frac{y^+}{y_{max}}\right)^2} \left(\frac{1}{Sc} + \frac{\rho(t)}{v}\right)
\]

\( \rho(t) \) is the eddy diffusivity; \( \rho(t)/v \) is correlated as a function of \( y^+ \) in empirical treatments of turbulent transport.\(^{(29,30)}\)
For arbitrary values of $\text{Sc}$ and $y_{\text{max}}^+$, these integrals must be evaluated numerically due to the complicated nature of the expressions relating $D(t)/\nu$ to $y^+$. However, in the limit as $\text{Sc} \to \infty$, a singular perturbation expansion of these integrals is possible. When the Wasan, Tien, Wilke (29) eddy-diffusivity correlation is used, the result is

$$\frac{1}{S_{\text{T}}} \sqrt{f/2} = \frac{2\pi \text{Sc}^{2/3}}{3\sqrt{3} A^{1/3}} + \text{Sc}^{1/3} \left[ \frac{2\pi}{3\sqrt{3}} \frac{y^+}{y_{\text{max}}^{2/3}} + \frac{B}{3A} \Gamma \left( \frac{5}{3} \right) \Gamma \left( \frac{1}{3} \right) \right]$$

$$- \frac{2\pi}{3\sqrt{3}} + \frac{1}{3} \left( \frac{\alpha^2}{A} + \frac{\beta^2}{A^3} - \frac{\alpha\beta}{A^2} + \frac{B}{y_{\text{max}}^2} \right) \log \text{Sc} + O(1) , \quad (68)$$

where $A$ and $B$ are constants appearing in the eddy-diffusivity correlation ($A = 9.39 \times 10^{-4}$ and $B = 1.65 \times 10^{-5}$) and $\alpha = \frac{1 - \kappa}{1 + \kappa} \frac{1}{y_{\text{max}}^+}$.

This expression converges rapidly for Schmidt numbers on the order of 1000. For $\text{Sc} = 1000$ and $y_{\text{max}}^+ = 100$, the term of order $(\log \text{Sc})$ contributes only approximately one percent of the leading term. The derivation of equation 68 is outlined in Appendix C.

III.4 Results and Conclusions

The experimental data for $\text{Sc} = 1661$ are presented on figure 23 as the Stanton number versus the inner cylinder-radius based Reynolds number $\text{Re}_1$. A comparison of the data gathered for two different Schmidt numbers, $\text{Sc} = 1661$ and $\text{Sc} = 5780$, is shown on figure 24 as $\text{StSc}^{2/3}$ as a function of Reynolds number $\text{Re}_1$ for two gap ratios,
Figure 23. Mass-transfer Rate for Turbulent Flow Between Rotating Cylinders.
Figure 24. Comparison of Data for Two Schmidt Numbers for Turbulent Flow in a Rotating Cylinder Cell.
\[ \kappa = 0.9829 \quad \text{and} \quad \kappa = 0.9608 \]. Except for three points taken with \( \kappa = 0.9829 \) and \( \text{Sc} = 1661 \), the curves for each gap ratio seem to agree closely. The three errant points differ from the suggested data fit by approximately ten percent (maximum). We may thus conclude that the \( \text{Sc}^{2/3} \) dependence suggested by the empirical model and verified by Eisenberg \((43, 44)\) and others \((42, 46, 49, 50)\) provides a good fit of these data. The Reynolds-number dependence of the Stanton number, however, does not seem to agree with these previous studies. It appears from figure 23 that Reynolds number alone does not suffice for an accurate correlation. The systematic trend of reduced transfer rates with reduced gap size would seem to indicate that the influence of the presence of the outer cylinder is beginning to be felt. Figure 25 shows the mass-transfer behavior predicted by equations 66 and 67 when the Wasan, Tien, Wilke \((29)\) eddy diffusivity model is used. While the results seem in reasonable agreement for the larger gaps used, it is important to note that they predict a trend that is opposite to that given by the data - an increase in transfer rate as the gap size diminishes rather than the observed decrease. The slope of the predicted curves is considerably less than that found for the data, approximately \(-0.12\) rather than \(-0.2\). The disagreement between predicted and observed transfer rates is more extreme for lower Reynolds numbers. These results suggest that the shear-induced turbulent behavior, upon which the empirical model is based, is not the dominant factor even for the small gaps used in this study. If one adopts the concept that the centrifugal instabilities,
Experimental data

$\Delta K = 0.9829$

$\square K = 0.9608$

$\times K = 0.9394$

$+ K = 0.9161$

$Sc = 1661$

Figure 25. Comparison of Predicted and Experimental Mass-transfer Rates for Small Gap Conditions with $Sc = 1661$. 

$Re_i$
such as cause Taylor vortices\(^{(47)}\) to form as the laminar couette flow becomes unstable, are the cause of the turbulence, then it appears that the effect of decreasing the gap between the cylinders serves to dampen the propagation of these turbulent eddies; hence the reduced transfer rate.

As a purely empirical fit of the lines defined by the results for large Reynolds numbers, the data on figure 25 lead to (for \(Sc = 1661\))

\[
St = (0.0292 - 0.088 \kappa)Re^{-0.2}
\]

which is accurate to within approximately four percent. This curve is of interest only in displaying the uniform trend that appears for this range of Reynolds numbers and gap ratios. It is also interesting to note that the experimental results of both Eisenberg (for mass transfer) and Theodorsen and Regier (for friction factors) agree with these large \(Re\) asymptotes in that they display a Reynolds number dependence of approximately \(Re^{-0.2}\) for this range of Reynolds numbers, even though their correlations are given as \(Re^{-0.3}\), which provides a better fit for smaller values of \(Re\). The modeling based upon a "universal eddy diffusivity" profile has not proven successful for this geometry. While one may speculate that the shear-induced turbulence must dominate for sufficiently small gaps\(^{(45)}\), the construction of electrodes with which to test this hypothesis does not seem feasible. It would appear that further progress in modeling this system must involve a more thorough knowledge of the structure of turbulence in rotating flows.
IV. AN IMPROVED SOLUTION FOR THE HYDRO_DYNAMIC
FLOW DUE TO A ROTATING DISK

IV.1 Introduction

Accurate knowledge of the flow field near a disk rotating in a
body of otherwise stationary fluid is required in order to determine
the mass-transfer rates to portions of this disk in certain diffusion
studies, as illustrated in section I of this dissertation. The
values given for certain important parameters describing this flow
field have undergone periodic revision for approximately the last
fifty years, beginning with von Kármán (13) who in 1922 first proposed
the variable transformations that rendered the Navier-Stokes equations
solvable in this geometry. In 1934 Cochran (14) revised von Kármán's
solution and reported improved values for the parameters of interest:
the tangential and radial normal velocity derivatives at the disk
and the asymptotic fluid velocity toward the disk at large distances
from it. Rogers and Lance (53) further refined the results of
Cochran while also considering the effect of bulk rotation of the
fluid far from the disk. Still more accurate results have been
generated by Benton (54) who, unlike the other investigators, did
not rely upon a finite-difference based solution of the coupled
nonlinear ordinary differential equations which result when the
von Kármán transformation is applied to the Navier-Stokes equation.
Benton also determined the time-dependent solution for an impulsively
started rotating disk and credited his numerical method to Fettis (55),
who also considered this problem but did not generate results of
the same order of accuracy as did Benton. Newman and Hsueh (9) were
able to calculate very accurate values for the desired parameters using a finite-difference based routine by extrapolating their results to zero mesh size in their work on the effect of variable (concentration dependent) solution properties.

Due to the approximate nature of such schemes, the use of finite-difference routines for numerical integration of the appropriate equations would seem to place a limit on the accuracy that may be economically achieved. While the method proposed by Benton seems capable of extreme accuracy in principle, he found it necessary to employ double precision computer arithmetic and reports results only to an accuracy of five significant figures, suggesting that convergence was rather slow for the series method that he used. It thus seems that a refined technique for the solution of this problem is of interest for both the numerical results that it would generate and the basis of comparison that it would provide to evaluate the accuracy of other methods used for this and similar numerical studies. (See also reference 57, from this laboratory, which compares the present technique with boundary-value finite-difference methods and with a Runge-Kutta initial-value procedure.)
IV.2 Extension of Cochran's Method

Cochran (14) has shown that the system of equations derived by von Kármán (13) for the hydrodynamics due to a disk rotating in a semi-infinite fluid,

\begin{align}
2F + H' &= 0 \\
F^2 - G^2 + HF' &= F'' \\
2FG + HG' &= G''
\end{align}

(70) (71) (72)

together with the appropriate boundary conditions

\begin{align}
F(0) = H(0) &= 0, \quad G(0) = 1, \\
F(\infty) = G(\infty) &= 0
\end{align}

(73)

can be satisfied by two sets of series expansions. Near the disk, the power-series expansions

\begin{align}
F_i(Z) &= \sum_{n=1}^{\infty} f_i^n Z^{n-1} \\
G_i(Z) &= \sum_{n=1}^{\infty} g_i^n Z^{n-1} \\
H_i(Z) &= \sum_{n=1}^{\infty} h_i^n Z^{n-1}
\end{align}

(74) (75) (76)

converge and represent the solution to equations 1 to 4 for suitably chosen coefficients \(f_i^n, g_i^n,\) and \(h_i^n\) \(n = 1, 2, \ldots\). Sufficiently
far from the disk, it becomes convenient to use a different set of "asymptotic" expansions

\[
F_0(Z) = \sum_{n=1}^{\infty} f_n e^{-c(n-1)Z} \quad (77)
\]

\[
G_0(Z) = \sum_{n=1}^{\infty} g_n e^{-c(n-1)Z} \quad (78)
\]

\[
H_0(Z) = \sum_{n=1}^{\infty} h_n e^{-c(n-1)Z} \quad (79)
\]

The parameter \( c \) is undetermined at the outset and is found to be the asymptotic velocity toward the disk as \( Z \rightarrow \infty \),

\[
c = \lim_{Z \rightarrow \infty} H_0(Z) \quad (80)
\]

We anticipate that since three of the five boundary conditions apply at the surface of the disk, the power-series expansions (valid near the disk) should contain two undetermined coefficients. Similarly the asymptotic expansions will contain three undetermined coefficients since only two of the boundary conditions may be directly applied to them.

Cochran solved equations 70 to 73 by assuming values for the two unknown coefficients in the power-series expansion, taken to be \( F'(0) = a \) and \( G'(0) = b \), and integrated numerically the set of equations 70 to 72 out to \( Z = Z_{\text{max}} \approx 2.5 \) where he then determined the three unknown coefficients in the asymptotic expansions that
minimized the discontinuities in functions $F$, $G$, $H$, $F'$, and $G'$. He could determine numerically the effect of varying the parameters $a$ and $b$ upon these discontinuities, and, together with the directly calculated derivatives $\partial F/\partial c$, $\partial F/\partial A$, $\partial F/\partial B$, ..., $\partial G'/\partial B$ (fifteen total) given by six-term asymptotic series, he applied a 5-dimensional Newton-Raphson iteration $^9$ to generate successively better values for the five parameters. While he did not specify explicitly his method for integrating equations 70 to 73 out to a value of $Z = 2.5$, his method bears strong resemblance to a Runge-Kutta "shooting" technique with asymptotic outer boundary conditions.$^{(39)}$

We propose here to employ a method similar to this, but we will use the power-series expansions directly rather than a numerical solution in the region near the disk. Then our goal will be to make $F$, $G$, $H$, $F'$, and $G'$ continuous at some value of $Z$, for which both series converge, by using a five-dimensional non-linear equation solving scheme to determine the five unknown coefficients in the two series. We anticipate that the accuracy of this method will depend only upon the convergence criterion in the equation solving routine, the number of terms retained in each series, and the accuracy to which the coefficients in the different series, $f_n^i$, $f_n^o$, $g_n^i$, ..., and $h_n^o$, $n = 1, 2, ...$, can be generated (given values for the five unknown parameters) via recursion relationships. The critical cause of error will probably be the last mentioned above, but even this should be completely negligible.
for a computer that retains an accuracy of fourteen significant figures. We thus expect to be able to determine the values of the five unknown parameters to an accuracy of at least eight significant figures, a feat which would seem to be difficult to duplicate economically with a numerical scheme based upon a finite-difference approach. A desire for greater accuracy could be satisfied by employing double precision arithmetic in the computer programs, a refinement that was not used here.

The development of two series, one for small $Z$ and one for large $Z$, and the subsequent adjustment of parameters to assure that the dependent variables and their derivatives are continuous at a certain value of $Z$ bears a strong resemblance to the use of matched asymptotic expansions to solve a singular-perturbation problem. The similarity is enhanced by the fact that the rotating disk shows a boundary layer, and such boundary layers are frequently encountered in singular-perturbation problems.

However, Cochran's method is not a singular-perturbation solution. In equations 70 to 73 there is no parameter which takes on a small value; in fact, their are no parameters at all. Cochran uses coordinate expansions rather than parameter expansions. There is no asymptotic matching; rather the functions and their derivatives are made continuous at a selected value of $Z$. There is no term by term matching -- carrying ten terms in a series instead of five changes, in principle, the values of all the parameters and coefficients involved in the expansions.
Method

Recursion relationships for the coefficients in each set of series must be developed, for while Cochran gave explicitly the first few terms in each, he did not outline their general form (although he undoubtedly derived this himself). We will now do this for both the power series and the asymptotic series.

A. Power series:

From equation 74 we notice that

\[ F_i' = \sum_{n=1}^{\infty} (n-1)f_i^1Z^{n-2} \]  \hspace{1cm} (81)

and

\[ F_i'' = \sum_{n=1}^{\infty} (n-1)(n-2)f_i^2Z^{n-3} \]  \hspace{1cm} (82)

with similar expressions for G and H (H'' is not required). By inserting these forms into equation 70 we find

\[ 2 \sum_{n=1}^{\infty} f_i^1Z^{n-1} + \sum_{n=1}^{\infty} (n-1)h_i^1Z^{n-2} = 0 \]  \hspace{1cm} (83)

or, equating terms of order k in Z

\[ h_{k+1}^i = -\frac{2f_k^i}{k} \]  \hspace{1cm} (84)

Immediately from the boundary conditions we may conclude that

\[ f_1^i = h_1^i = 0 \text{ and } g_1^i = 1 ; \]  \hspace{1cm} (85)
thus equation 84 informs us that $h^1_2 = 0$ as well.

Inserting forms similar to equations 81 and 82 into equation 71 yields

\[
\left( \sum_{n=1}^{\infty} f_n^1 z^{n-1} \right) \left( \sum_{m=1}^{\infty} f_m^1 z^{m-1} \right) - \left( \sum_{n=1}^{\infty} g_n^1 z^{n-1} \right) \left( \sum_{m=1}^{\infty} g_m^1 z^{m-1} \right)
+ \left( \sum_{n=1}^{\infty} h_n^1 z^{n-1} \right) \left( \sum_{m=1}^{\infty} (m-1)f_m^1 z^{m-2} \right)
= \sum_{n=1}^{\infty} (n-1)(n-2)f_n^1 z^{n-3} \tag{86}
\]

Matching terms of order $k$ in $Z$ yields

\[
f^1_{k+3} = \frac{1}{(k+1)(k+2)} \sum_{n=1}^{k+1} \left[ \frac{f_n^1}{n^{k+2-n}} - g_n^1 g_{k+2-n} + h_n^1 (k-n+2)f^1_{k-n+3} \right]
\]

for $k > 0$. \tag{87}

Finally, insertion of the appropriate series into equation 72 leads in an analogous manner to

\[
g^1_{k+3} = \frac{1}{(k+1)(k+2)} \sum_{n=1}^{k+1} \left[ \frac{2f_n^1}{n^{k+2-n}} + (k-n+2)h_n^1 g_{k-n+3} \right] \tag{88}
\]

for $k > 0$. We notice that $f^1_2$ and $g^1_2$ are not given in these relationships but are required for the calculation of higher order coefficients. These are the two unknown parameters in the region near the disk:

\[
f^1_2 = F'(0) = a \tag{89}
\]

\[
g^1_2 = G'(0) = b
\]
with the values of \( a \) and \( b \) yet to be determined.

B. Asymptotic series:

For the expansions in the region far from the disk, equation 77 leads to

\[
F'_o(Z) = \sum_{n=1}^{\infty} -c(n-1)f^o_n e^{-c(n-1)Z} \quad (90)
\]

and

\[
F''_o(Z) = \sum_{n=1}^{\infty} c^2(n-1)2f^o_n e^{-c(n-1)Z} . \quad (91)
\]

Substituting the appropriate expansions into equation 70 yields

\[
2 \sum_{n=1}^{\infty} f^o_n e^{-c(n-1)Z} - \sum_{n=1}^{\infty} c(n-1)h^o_n e^{-c(n-1)Z} = 0 . \quad (92)
\]

Equating terms of order \( e^{-c(n-1)Z} \) leads to

\[
h^o_n = \frac{2f^o_n}{(n-1)c} \quad (n > 1) . \quad (93)
\]

Equation 71 leads to

\[
k^2 c^2 f^o_{k+1} = \sum_{n=1}^{k+1} \left[ f^o_n f^o_{k-n+2} - g^o_n g^o_{k-n+2} - c(k - n + 1)h^o_k f^o_{k-n+2} \right] . \quad (94)
\]

Since, from the boundary conditions, \( f^o_1 = g^o_1 = 0 \), this may be simplified to

...
Similarly, equation 72 leads to

\[ f^o_{k+1} = \frac{1}{k^2 c^2 + kch^o_1} \sum_{n=2}^{k} \left[ f^o_n f^o_{k-n+2} - g^o_n g^o_{k-n+2} \right] - c(k - n + 1) h^o_n f^o_{k-n+2} \], \quad k \geq 2 . \tag{95} \]

Similarly, equation 72 leads to

\[ g^o_{k+1} = \frac{1}{k^2 c^2 + kch^o_1} \sum_{n=2}^{k} \left[ 2f^o_n g^o_{k-n+2} - c(n - 1) g^o_n h^o_{k-n+2} \right] , \quad k \geq 2 . \tag{96} \]

We notice that \( h^o, f^o, \) and \( g^o \) are not given by these expressions. These are the three unknowns in the asymptotic expansions and are taken to be \( c, A, \) and \( B \) respectively.

**Numerical procedure**

As mentioned previously, we wish to ensure continuity of \( F, G, H, F', \) and \( G' \) at some suitable point, \( Z = Z_o, \) in order to determine the values of the five parameters \( a, b, c, A, \) and \( B. \)

We define "residual" functions of \( Z_o, a, b, c, A, \) and \( B \) as follows

\[
\begin{align*}
R_1(Z_o,a,b,c,A,B) &= F^o(Z_o,c,A,B) - F^o_i(Z_o,a,b) \\
R_2(Z_o,a,b,c,A,B) &= G^o(Z_o,c,A,B) - G^o_i(Z_o,a,b) \\
R_3(Z_o,a,b,c,A,B) &= H^o(Z_o,c,A,B) - H^o_i(Z_o,a,b) \\
R_4(Z_o,a,b,c,A,B) &= F^o_i(Z_o,c,A,B) - F^o_i(Z_o,a,b) \\
R_5(Z_o,a,b,c,A,B) &= G^o_i(Z_o,c,A,B) - G^o_i(Z_o,a,b). 
\end{align*}
\]
The problem now becomes finding the values of the five parameters (with \( Z_0 \) fixed) such that

\[
R_i = 0 \quad i = 1, \ldots, 5.
\]

We have chosen to use a 5-dimensional Newton-Raphson iteration, as discussed by Broyden,\(^{(56)}\) to find successive approximations of the five parameters that should converge to the desired values. Formally, the procedure to be followed is successive solution of the expression

\[
\frac{\partial R}{\partial P} [\Delta P] = -[R]
\]

where the matrices

\[
\frac{\partial R}{\partial P} = \begin{bmatrix}
\frac{\partial R_1}{\partial a} & \frac{\partial R_1}{\partial b} & \cdots & \frac{\partial R_1}{\partial B} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial R_5}{\partial a} & \cdots & \cdots & \frac{\partial R_5}{\partial B}
\end{bmatrix}
\]

\[
[\Delta P] = \begin{bmatrix}
\Delta a \\
\Delta b \\
\Delta c \\
\Delta A \\
\Delta B
\end{bmatrix}
\]

and

\[
[R] = \begin{bmatrix}
R_1 \\
R_2 \\
R_3 \\
R_4 \\
R_5
\end{bmatrix}
\]
The matrix \([\partial R/\partial P]\) will be estimated for approximate values of the five parameters and equation 98 will be solved for \([\Delta P]\) whereupon the new (more accurate) values for the parameters will be given by

\[
a_{\text{new}} = a_{\text{last}} + \Delta a
\]
\[
b_{\text{new}} = b_{\text{last}} + \Delta b .
\] (100)

The residuals will then be calculated for the new values of the parameters, and, if their value has not been reduced to a satisfactory level, the matrix \([\partial R/\partial P]\) will be re-estimated and the procedure repeated. The method used to calculate the required derivatives in the matrix is as follows

\[
\frac{\partial R_i}{\partial P_j} = \frac{R_i(P_1, \ldots, P_j + \delta P, \ldots, P_5) - R_i(P_1, \ldots, P_j, \ldots, P_5)}{\delta P} .
\] (101)

The residuals are found by putting the appropriate values of the parameters into the series expansions for the functions (or derivatives) of interest. The computer scheme for implementing this scheme is given in Appendix D.

IV.3 Results and Discussion

A value of \(Z_o = 1.0\) was chosen for the calculations. To test the effect of this choice, calculations were also made for \(Z_o = 0.9\) and \(Z_o = 1.1\). It was found that when thirty or more terms were
retained in each series, the value of $Z_0$ had no effect upon the eighth significant figure for any of the parameters. For fewer than thirty terms, it appeared that $Z_0 = 0.9$ gave slightly better results. The effect of varying the number of terms retained in each series was also tested. The results for 30, 40, and 50 terms were identical to eight significant figures. The initial values of the parameters used in the calculations were those given by Cochran. All of the results reported in tables 6-11 (twelve different trials) required computer time equal to about 1.3 seconds on a CDC 7600 computer, at a cost of approximately $1.50. Tables 6 to 10 present the calculated values of the five parameters for the various values of $Z_0$ and number of terms considered. The results of Cochran are also given, as are the percent difference between his results and those calculated here. The first few coefficients in the inner and outer expansions may also be of interest and are given in table 11. Since it would seem that this method should yield the results least sensitive to numerical inaccuracies, it is hoped that the final values given herein for the parameters of interest may provide a benchmark for evaluation of other solution techniques as applied to this problem.
Table 6. Values of the parameter "a" for n-term expansions matched at $Z = Z_0$.

<table>
<thead>
<tr>
<th>$Z_0$</th>
<th>0.9</th>
<th>1.0</th>
<th>1.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.50691465</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.51002626</td>
<td>0.50977116</td>
<td>0.50922273</td>
</tr>
<tr>
<td>20</td>
<td>0.51023257</td>
<td>0.51023231</td>
<td>0.51023093</td>
</tr>
<tr>
<td>30</td>
<td>0.51023262</td>
<td>0.51023262</td>
<td>0.51023262</td>
</tr>
<tr>
<td>40</td>
<td>0.51023262</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.51023262</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cochran's Result: 0.510

Percent Difference: 0.0456%
Table 7. Values of the parameter "b" for n-term expansions matched at \( Z = Z_0 \).

<table>
<thead>
<tr>
<th>( Z_0 = )</th>
<th>0.9</th>
<th>1.0</th>
<th>1.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n = 6 )</td>
<td>-0.64800672</td>
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<td></td>
</tr>
<tr>
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<td>-0.61610074</td>
<td>-0.61640266</td>
<td>-0.61693932</td>
</tr>
<tr>
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<td>-0.61592198</td>
<td>-0.61592170</td>
</tr>
<tr>
<td>30</td>
<td>-0.61592201</td>
<td>-0.61592201</td>
<td>-0.61592201</td>
</tr>
<tr>
<td>40</td>
<td>-0.61592201</td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>-0.61592201</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Cochran's Result: -0.616

Percent Difference: 0.0127%
Table 8. Values of the parameter "c" for n-term expansions matched at \( Z = Z_0 \).

<table>
<thead>
<tr>
<th>( Z_0 )</th>
<th>0.9</th>
<th>1.0</th>
<th>1.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>0.87565013</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.88419003</td>
<td>0.88376654</td>
<td>0.88274164</td>
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<td>0.88447405</td>
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<td>0.88447097</td>
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<td>0.88447411</td>
<td>0.88447411</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>0.88447411</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>0.88447411</td>
<td></td>
</tr>
</tbody>
</table>

Cochran's Result: 0.886

Percent Difference: 0.153%
Table 9. Values of the parameter "A" for n-term expansions matched at $Z = Z_0$.

<table>
<thead>
<tr>
<th>$Z_0$</th>
<th>n</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6</td>
<td>0.88056174</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.92429793</td>
<td>0.92325633</td>
<td>0.92067660</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.92486344</td>
<td>0.92486276</td>
<td>0.92485791</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.92486353</td>
<td>0.92486353</td>
<td>0.92486353</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td></td>
<td>0.92486353</td>
<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td></td>
<td>0.92486353</td>
<td></td>
</tr>
</tbody>
</table>

Cochran's Value: 0.934

Percent Difference: 1.16%
Table 10. Values of the parameter "B" for n-term expansions matched at $Z = Z_0$.

<table>
<thead>
<tr>
<th>$Z_0$ =</th>
<th>0.9</th>
<th>1.0</th>
<th>1.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td>1.13257425</td>
</tr>
<tr>
<td>10</td>
<td>1.20161270</td>
<td>1.20029645</td>
<td>1.19710059</td>
</tr>
<tr>
<td>20</td>
<td>1.20221169</td>
<td>1.20221121</td>
<td>1.20220781</td>
</tr>
<tr>
<td>30</td>
<td>1.20221175</td>
<td>1.20221175</td>
<td>1.20221175</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>1.20221175</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>1.20221175</td>
<td></td>
</tr>
</tbody>
</table>

Cochran's Value: 1.208

Percent Difference: 0.481%
Table 11. First five coefficients in the inner and outer series expansions for F, G, and H.

<table>
<thead>
<tr>
<th>n</th>
<th>$f_1^n$</th>
<th>$g_1^n$</th>
<th>$h_1^n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2</td>
<td>0.510232619</td>
<td>-0.615922014</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>-0.5</td>
<td>0.0</td>
<td>-0.510232619</td>
</tr>
<tr>
<td>4</td>
<td>0.205307338</td>
<td>0.170077540</td>
<td>0.333333333</td>
</tr>
<tr>
<td>5</td>
<td>0.031613327</td>
<td>-0.109521959</td>
<td>-0.102653669</td>
</tr>
</tbody>
</table>

n | $f_1^o$ | $g_1^o$ | $h_1^o$ |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.884474110</td>
</tr>
<tr>
<td>2</td>
<td>0.924863531</td>
<td>1.20221175</td>
<td>2.09132980</td>
</tr>
<tr>
<td>3</td>
<td>-1.47047294</td>
<td>1.8166x10^{-14}*</td>
<td>1.66253927</td>
</tr>
<tr>
<td>4</td>
<td>0.869229477</td>
<td>-0.376631382</td>
<td>0.655176123</td>
</tr>
<tr>
<td>5</td>
<td>-0.533508583</td>
<td>0.296846990</td>
<td>-0.301596495</td>
</tr>
</tbody>
</table>

*This term should equal 0.0, but does not (probably due to round-off error in the computer).
APPENDIX A: Computer Programs for Eccentric Rotating Disk Calculations

Calculation of the critical eccentricities near $\varepsilon = 1.0$, between which this analysis is not applicable, employed the following computer program which is written in Fortran II compatible with the XDS-910 computer operated by the College of Chemistry, University of California (Berkeley):

```fortran
X = ATAN [.616,.51]
Calf = COS [X]
PI = 3.1415926536
EPS = 1.0
DOLK = 1,3,2
DIN = K-2
DOLI = 1,50
AA = SQRT [1.-[Calf/EPS]**2]/Calf*EPS
AC = ATAN [AA]
A = .51/.154*[PI+AC]
DK = EXP [A]
C1 = COS [X-AC]
C2 = COS [X+AC]
B = DK*C1 - C2
EPS = [B + DIN*SQRT[B*B-[DK-1.]*2]]/[DK-1.]
1 PRINT 2, EPS
2 FORMAT [F12.8]
END
```

The program used for calculating the mass-transfer rates for $\varepsilon < 1.0$ follows. Program "MAIN" partitions the disk into strips and sums the contribution from each to the total transfer rate. It makes use of subroutine "TFIND" to locate the tangent points,
subroutine "TRAJ" to determine the points at which a trajectory which leaves the disk at (RMIN, TMIN), where RMIN is the radial coordinate and TMIN is the \( \theta' \) coordinate, re-enters (RMIN, TMID) the electrode and (RMAX, TMAX) where it leaves the electrode for the last time, and subroutine "NCALC", which calculates the parameter \( N \) from equation 21.

The programs used to calculate the numerical results for \( \varepsilon > 1.0 \) follow. Subroutine TFIND was eliminated in favor of direct use of equations 14. Subroutine TRAJ is simplified, since now only one point must be found rather than two when the ring-disk analogy applies. Subroutine NCALC has been eliminated, of course, since the Levich formula for mass transfer to a ring electrode, equation 23, is simple enough to use directly.
PROGRAM MAIN( INPUT, OUTPUT )

COMMON / PATH / EPS, ALFA, TMIN, TMID, TMAX, RMIN, RMID, RMAX
FINDR( X, Y ) = Y * COS( X ) + SORT( ( Y * COS( X ) ) ** 2 + 1. - Y ** 2 )
ALFA = ATAN( 1.208 )

1 READ 100, EPS IF( EPS .EQ. 0. ) STOP

100 FORMAT( F3.2 )

CALL TFIND $ DELT=( TMID-TMAX )/ 200.
RILAS=RMIN $ R2LAS=RMIN $ RLAST=RMAX
T=TMAX $ AREA=0. $ SUM=0. $ DO21=1, 199 $ T=T+DELT
R=FINDR( T, EPS ) $ CALL TRAJ( T, R, T1, R1, T2, R2 )

IF( R2.GT. R1.OR.R1.RT. R2 ) GOTO 20
RLIT=( R2+R2LAS )/ 2. $ RM=( R1+RILAS )/ 2. $ RBIG=( R+RLAST )/ 2.
CALL NCALC( RLIT, RM, RBIG, DN )

ZZ=ABS( R-RLAST )/RLAST/$B.828
ZZ=DELT- ZZ
A=ZZ/2.* ( RBIG-RM ) *( RBIG+RM ) $ AREA=AREA+A
SUM=SUM+ZZ/2.* ( RBIG**3-RM**3)**.6666667-RLIT**2*DN)

RILAS=R1 $ R2LAS=R2

2 RLAST=R

20 CONTINUE

TRAN=( 3.14159-AREA+SUM )/ 3.14159
PRINT 101, EPS, TMIN, TMID, TMAX, AREA, TRAN, T

101 FORMAT( 5X, 6E18.6, 6I6 )
GOTO 1 $ END

SUBROUTINE TFIND

COMMON / PATH / EPS, ALFA, TMIN, TMID, TMAX, RMIN, RMID, RMAX
FINDR( X, Y ) = Y * COS( X ) + SORT( ( Y * COS( X ) ) ** 2 + 1. - Y ** 2 )
RAD( X, Y, Z ) = X * EXP( .828 *( Y-Z ) )

FUN( T, R, EPS ) = T * ACOS( EPS - R * COS( T ) ) - 1.57079
X=0.5 $ INDEX=0 $ BIGT=1.57079 $ BIGR=FINDR( BIGT, EPS )
BIGAL=FUN( BIGT, BIGR, EPS ) $ SMAT=0.010 $ SMAR=FINDR( SMAT, EPS )
SMAAL=FUN( SMAT, SMAAL, EPS )

20 DO1=1, 100 $ T=( BIGT+SMAT )/ X $ R=FINDR( T, EPS ) $ ALF=FUN( T, R, EPS )
IF( ALF.GE. ALFA ) GOTO 2 $ BIGT=T $ BIGR=R $ BIGAL=ALF $ GOTO 3
2 SMAT=T $ SMAR=R $ SMAAL=ALF
3 IF( ABS( ALFA-ALFA ) .LE. 1.E-9 ) GOTO 4

1 CONTINUE $ PRINT * $ RETURN
5 FORMAT( 5X*NO GO*)
4 IF( INDEX .EQ. 1 ) GOTO 10 $ TMID=T $ RMID=R $ INDEX=1 $ GOTO 11
10 TMIN=T $ TMIN=R $ GOTO 12

11 BIGT=1.57079 $ BIGR=FINDR( BIGT, EPS ) $ BIGAL=FUN( BIGT, BIGR, EPS )
SMAT=3.14158 $ SMAR=FINDR( SMAT, EPS ) $ SMAAL=FUN( SMAT, SMAAL, EPS )
GOTO 20

12 TS=TMID $ DO61=1, 110 $ TS=TS-0.05 $ RS=FINDR( TS, EPS )
RTEST=RAD( RMIN, TMID, TS ) $ IF( RS.LE.RTEST ) GOTO 62
61 CONTINUE $ PRINT 68 $ RETURN
68 FORMAT( * CANNOT FIND TMAX*)

62 T=TS $ R=RS $ TT=TS+0.05 $ RR=FINDR( TT, EPS ) $ DO63=1, 110
TM=( T+TT )/ 2. $ RM=FINDR( TM, EPS ) $ RTEST=RAD( RMIN, TMID, TM )
IF( RTEST .LE. RM ) GOTO 64 $ T=TM $ R=RM $ GOTO 65

64 TT=TM $ R=RR
65 IF( ABS( RTEST-RR ) .LE. 1.E-9 ) GOTO 66

63 CONTINUE

66 TMAX=TM $ RMAX=RM $ RETURN $ END
SUBROUTINE TRAJ(T,P,T1,R1,T2,R2)
COMMON/PATH/EPS,ALFA,TMIN,TMID,TMAX,PMIN,P MID,RMAX
FINDR(X,Y)=Y*COS(X)+SORT(Y*XOS(X))**2+1.-Y**2
RAD(X,Y,Z)=X*EXP(.A28*(Y-Z))
X=0.5 $ TT=TMID+.001 $ RR=FINDR(TT, EPS) $ RT1=RAD(R,T,TT)
INDEX=0
1 DO21=1,100 $ TS=TT $ PS=RR $ RT2=RT1 $ TT=TT+.05
RR=FINDR(TT, EPS) $ RT1=RAD(P,T,TT)
IF((RT1 .GE. PR. AND. RT2 .LE. RS). OR. (RT1 .LE. RR. AND. RT2 .GE. RS)) GOTO3
2 CONTINUE $ PRINT4 INDEX $ RETURN
4 FORMAT(* INDEX= [I* NOGO)*
3 DO51=1,100 $ TM=X*(TS+TT) $ RM=FINDR(TM,EPS)
RT3=RAD(R,T,TM)
IF((RT3 .GE. RM. AND. RT1 .LE. RR). OR. (RT3 .LE. RM. AND. RT1 .GE. RR)) GOTO6
5 CONTINUE
6 TS=TM $ RS=RM $ RT2=RT3
7 IF(ABS(RT2-RM).LE.8.E-7) GOTO8
8 IF(INDEX.EQ.1) GOTO9 $ T1=TM $ R1=RM $ INDEX=1 $ TT=TMID+.001
RR=FINDR(TT, EPS) $ RT1=RAD(R,T,TT) $ GOTO1
9 T2=TM $ R2=RM $ RETURN $ END

SUBROUTINE NCALC(R,R1,R2,DN)
A=R2/R $ B=R1/R $ C=(B**3-1.)* (1./3.) $ S3=SORT(3.)
PI=3.14159
$1=1.0$2=0.0$3=2.0
D=(A**3-B**3)**(1./3.) $ PSI=D/A/C
DN=D*D*(S3/4.)*PI*ALOG((1.+C**3)/(1.+C)**3)-1.5/PI*ATAN((2.*C-1.) /
1.S3)+.75)*S3/4.1*PI*ALOG((1.+A*PSI)**3)/(1.+A*PSI)**3+1.5/PI*ATAN
2(2.*A*PSI-1.)/S3)+.25
DN=DN-A*PSI**(S3/4.)*PI*ALOG((1.+PSI)**3)/(1.+PSI)**3+1.5/PI*ATAN(2.*
1PSI-1.)/S3)+.25 $ RETURN $ END
PROGRAM MAIN(INPUT, OUTPUT)
COMMON TMIN, RMIN, TMAX, RMAX
ALFA=ATAN(1./.028) $ PI=3.141592654
1 READ100,EPS $ IF(EPS.EQ.0.)STOP
100 FORMAT(F5.2)
TMIN=ALFA-PI/2.+ASIN(COS(ALFA)/EPS) $ TMAX=2.*ALFA-TMIN
RMIN= SORT(EPS**2+1.0-2.*EPS*COS(TMIN))
RMAX= SORT(EPS**2+1.0-2.*EPS*COS(TMAX))
PRINT101, TMIN, RMIN, TMAX, RMAX, EPS
101 FORMAT(5E18.6)
DEL=(TMAX-TMIN)/200. $ T=TMIN-DEL/2. $ AREA=0.0 $ TPAN=0.0
DO1=1,200 $ T=T+DEL
ZZ=(EPS*COS(T-ALFA)/COS(ALFA)-1.0)/2./PI*DEL
CALL TRAJ(T, EPS, X)
TRAN=TRAN+((T+0.+X)**1.5-1.0)**(1.0/3.)*ZZ
AREA=AREA+*ZZ
2 CONTINUE $ PRINT103, AREA, TRAN
103 FORMAT(5X,3F18.8//)
GOTO 1 $ END

SUBROUTINE TRAJ(T, EPS, X)
COMMON TMIN, RMIN, TMAX, RMAX
11 DT=THETA=ATAN(SIN(T)/(EPS-COS(T)))-ATAN(SIN(T1)/(EPS-COS(T1)))
F=2.0*EPS*(COS(T)-COS(T1))/(EPS**2+1.0-2.0*EPS*COS(T))-EXP(DTHETA*
1.656)/1.0
DF=2.0*EPS*SIN(T1)/(EPS**2+1.0-2.0*EPS*COS(T1))+1.656*EXP(DTHETA*
1.656)*((EPS*COS(T1)-1.)/(EPS**2+1.0-2.0*EPS*COS(T1)))
IF(F.GT.0.0) T1MAX=T1 $ IF(F.LT.0.0) T1MIN=T1 $ IF(FG.0.0) T1=T1-F/DF
IF(ABS(F/DF).LT.1.E-6) GOTO12
IF(T1.GT.T1MIN AND T1.LT.T1MAX) GOTO11 $ T1=0.5*(T1MAX+T1MIN)
IF(T1MAX-T1MIN.GT.1.E-6) GOTO11
12 X=2.0*EPS*(COS(T)-COS(T1))/(EPS**2+1.0-2.0*EPS*COS(T1))
RETURN $ END
APPENDIX B: Modification of Daguenet's Correlation for Turbulent Mass Transfer to a Rotating Disk Electrode

The determination of a correlation appropriate for mass transfer in the turbulent flow regime on a rotating disk is necessary for utilization of the results of section II, in which the transfer rate in the transition region is derived. While the results of Daguenet, equation 47, seem immediately useful, they suffer from a flaw in the interpretation of the data presented therein. We expect the asymptotic transfer rate to be proportional to $Re^n$, where $n$ is a constant that has been found to equal approximately 0.9 by Daguenet and others, but it may not be appropriate to determine the constant of proportionality by a direct best fit of data for $Re < 10^6$. Ellison and Cornet have stated that for $Re < 10^6$, the overall Nusselt number is still significantly dependent upon transfer in the laminar and transition zones, and only for $Re > 10^6$ is the asymptotic limit for the turbulent flow regime approached closely by the data. Figure B-1 demonstrates that Daguenet assumed the asymptotic limit was reached as early as $Re \approx 6 \times 10^5$, and the correlation

$$\frac{Nu}{Sc} - \frac{1}{3} = 0.00725 Re^{0.9}$$

(B-1)

agrees well with his data for Schmidt numbers of 1212 and 1980 (values chosen for comparison here because of their close approximation to the Schmidt numbers encountered in this study). It would seem better to approximate the transfer rate as

$$\frac{Nu}{Sc} = a Re^{0.9} - \frac{1}{3} + b Sc^{-1/3} Re^{-1/2}$$

(B-2)
Figure B-1. Correlation of Turbulent Mass Transfer to a Rotating Disk.
and determine coefficients \( a \) and \( b \) from the data presented. The expression \( b \text{Sc}^{1/3} \text{Re}^{-1/2} \) is chosen so that the local transfer rate is proportional to \( \text{Re}^{0.9} \text{Sc}^{1/3} \) for all \( \text{Re} \). While the value of \( a \) should depend only on the asymptotic behavior in the turbulent regime, \( b \) is expected to depend on the transfer rate in the laminar and transition zones and also on the Reynolds numbers taken as the limits of the transition region. Choosing Reynolds numbers \( \text{Re} = 4 \times 10^5 \) and \( \text{Re} = 8 \times 10^5 \), we find that the data of Daguenet suggest \( \overline{\text{Nu Sc}}^{-1/3} = 640 \) and \( \overline{\text{Nu Sc}}^{-1/3} = 1470 \) respectively. This leads to

\[
a = 7.80 \times 10^{-3}
\]

and

\[
b = 1.38 \times 10^5 \tag{B-3}
\]

when the two equations are solved simultaneously. The resultant transfer rate is shown as a dashed line on figure B-1. The expression

\[
\overline{\text{Nu Sc}}^{-1/3} = 0.0078 \text{Re}^{0.9} - 1.38 \times 10^5 \text{Re}^{-1/2} \tag{B-4}
\]

is seen to provide an excellent fit of Daguenet's data, but will not be used in this form with \( b = 1.38 \times 10^5 \) since the results of this study will be used to determine the value of \( b \). Equation 55, derived using the experimental results of this investigation, leads to \( b = 1.30 \times 10^5 \), a slightly different value, but one which still provides an excellent fit of Daguenet's turbulent-flow data.
APPENDIX C: Asymptotic Expression for Turbulent Mass Transfer

Asymptotic expressions valid as $\text{Sc} \to \infty$ are to be derived for the integrals appearing in equation 29. These may be anticipated to be singular perturbation expansions since there are two regions in which different approximations are valid. Far from the wall, turbulent diffusion predominates, so that

$$\frac{D(t)}{\nu} \gg \frac{1}{\text{Sc}}, \quad (C-1)$$

while close to the wall, due to the damping of eddy transport, there is a small region in which eddy transport and molecular diffusion are the same order of magnitude. As $\text{Sc} \to \infty$, this region diminishes in size and the approximation

$$y^+ < 1 \quad (C-2)$$

becomes valid.

The model chosen for the eddy diffusivity profile is that of Wasan, Tien, and Wilke:(29)

$$\frac{D(t)}{\nu} = \frac{Ay^3 - By^4}{1 - Ay^3 + By^4} \quad \text{for} \quad y^+ \leq 20, \quad (C-3)$$

$$\frac{D(t)}{\nu} = \frac{y^+}{2.5} - 1 \quad \text{for} \quad y^+ \geq 20, \quad (C-3)$$

where

$$A = 4.3888 \times 10^{-4}$$

and

$$B = 1.6475 \times 10^{-5}.$$
The first term to be considered is

\[
I_1(y^+) = \int_0^{y_m} \frac{y^+}{y_m} dy^+ \left( \frac{1}{\nu} + \frac{\nu}{\nu} \frac{d}{d} \right) .
\]  

(C-4)

We wish to expand this integral in the two regions of interest. By then matching the expansions in a region where both are valid, we can then form a composite expansion valid in both regions. As discussed above, the first region, called the "outer region," is far from the wall where the eddy diffusivity predominates, equation C-1. An appropriate variable for this region is simply \( y^+ \) as it appears in equation C-4. Expanding this integral considering \( 1/\text{Sc} \) to be small leads to

\[
I_1(y^+) = \frac{1}{y_m} \int_0^{y^+} y^+ \left( \frac{\nu}{d} \right) \left[ 1 - \frac{\nu}{d} \frac{\nu}{\nu} + \left( \frac{\nu}{d} \frac{\nu}{\nu} \right)^2 - \ldots \right] dy^+ 
\]

\[
= I_1(20) - \frac{1}{y_m} \int_0^{20} y^+ \left[ -1 + \frac{1}{A y^+ 3 - B y^+ 4} \right] dy^+ + O(1) .
\]  

(C-5)

In the region near the wall, the "inner region," \( d/\nu = O(\text{Sc}^{-1}) \), thus from equation C-3 since \( y^+ \) is small (equation C-2),
\( \alpha y^+ = 0(Sc^{-1})' \) \hspace{1cm} (C-6)

This suggests that a convenient "inner variable" would be

\[ y^+ = (A \cdot Sc)^{1/3} y^+ \] \hspace{1cm} (C-7)

thus "stretching" the thickness of the inner region so that

\[ y^+ = 0(1). \]

Equation C-4 becomes

\[
\bar{I}_1(y^+) = \frac{Sc^{1/3}}{y_m^{2/3}} \int_0^{y^+} \frac{y^+}{(1 + y^+^3)^2} \left[ 1 - \frac{Sc(T)}{v} \left( \frac{1}{y^+^3} - Ay^+^3 \right) \right] dy^+
\]

\[ = \frac{Sc^{1/3}}{y_m^{2/3}} \left[ \int_0^\infty \frac{y^+}{(1 + y^+^3)^2} dy^+ - \int_{y^+}^\infty \frac{y^+}{(1 + y^+^3)^2} dy^+ \right] \] \hspace{1cm} (C-8)

\[
\frac{Sc^{4/3}}{y_m^{2/3}} \int_0^{y^+} \frac{y^+ dy^+}{(1 + y^+^3)^2} \left[ -By^+^4 + A^2 y^+^6 - ABy^+^7 \right] [1 + (Ay^+^3 - By^+^4) + ...]
\]

\[ = \frac{Sc^{1/3}}{y_m^{2/3}} \left[ \frac{2\pi}{3\sqrt{3}} - \frac{1}{y^+} + 0\left( \frac{1}{y^+^4} \right) \right] + \frac{B}{y_m^{1/2}} \left[ \frac{1}{3} \log (1 + y^+^3) + 0\left( \frac{y^+^2}{Sc^{2/3}} \right) \right].
\]

Since these two expansions are required to match in an intermediate region, following Kaplun (57) we determine the inner limit of the outer expansion and require that it equal the outer limit of the inner expansion

\[
\lim_{y^+ \to 0} \left[ I_1(y^+) \right] = \lim_{y^+ \to \infty} \left[ \bar{I}_1(y^+) \right]. \] \hspace{1cm} (C-9)
These required limits are, from equations C-5 and C-8,

\[
\lim_{y^+ \to 0} \left[ I_1(y^+) \right] = I_1(20) - \frac{1}{Ay_y} + \frac{B}{A^2 y_m} \log y^+ + 0(1) \tag{C-10}
\]

and

\[
\lim_{y^+ \to \infty} \left[ I_1(y^+) \right] = \frac{2\pi Sc^{1/3}}{3\sqrt{3} y_m^{+2/3}} - \frac{Sc^{1/3}}{y_m^{+2/3}} + \frac{B}{y_m^{+2}} \log y^+ . \tag{C-11}
\]

Reintroduction of the outer variable \( y^+ \) into equation C-11 and matching leads to

\[
I_1(20) = \frac{2\pi Sc^{1/3}}{3\sqrt{3} y_m^{+2/3}} + \frac{B}{3y_m^{+2}} \ln Sc + 0(1) . \tag{C-12}
\]

The next integral of interest is

\[
I_2(y^+) = \int_y^y \frac{dy^+}{0 (1 + \alpha y^+) \left( \frac{1}{Sc} + \frac{\nu^{(t)}}{\nu} \right)} . \tag{C-13}
\]

Again expanding this considering \( 1/Sc \) to be small compared to \( \nu^{(t)}/\nu \) (the outer expansion) leads to

\[
I_2(y^+) = I_2(20) - \frac{1}{\alpha} \log (1 + \alpha y^+) - \frac{1}{2Ay_y^+} + \frac{\alpha B}{2A^2} \log \frac{y^{+2}}{1 + \alpha y^+ (A - By^+)}
+ \frac{\alpha A - B}{A^2 y^+} - \frac{(\alpha A - B)^2}{2A^3} \log \frac{(1 + \alpha y^+)(A - By^+)}{y^{+2}} + 0(1) . \tag{C-14}
\]
The inner expansion with the same inner variable, equation C-7, leads to

\[
I_2(y^+) = \frac{2\pi Sc^{2/3}}{A^{1/3}3^{2/3}} - \frac{1}{2Ay^+} \frac{Sc^{1/3}}{A^{2/3}} \left[ a \frac{2\pi}{3\sqrt{3}} - \frac{B}{3A} \frac{\Gamma(5/3)\Gamma(1/3)}{\Gamma(2)} - \frac{a}{y^+} + \right.
\]

\[
\left. \frac{B}{Ay^+} + \frac{1}{A^{1/3}} \left[ \frac{\alpha^2}{2A^{2/3}} \ln \left(1 + \frac{y^+}{3}\right) + \frac{B^2}{A^{8/3}} \left\{ \frac{1}{3} \ln \left(1 + \frac{y^+}{3}\right) + \frac{2}{1 + \frac{y^+}{3}} - \frac{1}{2\left(1 + \frac{y^+}{3}\right)} \right\} - \frac{\alpha B}{A^{5/3}} \left\{ \frac{1}{3} \ln \left(1 + \frac{y^+}{3}\right) + \frac{1}{1 + \frac{y^+}{3}} \right\} \right] + O(1). \quad (C-15)
\]

Matching the appropriate limits of equations C-14 and C-15 results in

\[
I_2(20) = \frac{2\pi Sc^{2/3}}{3^{2/3}A^{1/3}} + \frac{Sc^{1/3}}{A^{2/3}} \left[ \frac{B}{3A} \frac{\Gamma(5/3)\Gamma(1/3)}{\Gamma(2)} - \frac{2\alpha^2\pi}{3\sqrt{3}} \right]
\]

\[
+ \frac{1}{3A} \ln \frac{Sc}{\left[ \alpha^2 + \frac{B^2}{A^2} - \frac{\alpha B}{A} \right]} + O(1). \quad (C-16)
\]

Equation 67 also contains a third integral,

\[
\int_0^{y^+} \frac{\alpha y^+ + 2(1 + \kappa^2 + \alpha y^+)dy^+}{(1 - \alpha^2y^2)(\frac{1}{Sc} + \frac{\varepsilon}{\nu})},
\]

but this is found to contribute terms of order unity only, and it is thus insignificant when compared to the first two integrals at large Schmidt numbers.

Equations C-12 and C-16 have been developed using only the inner portion \((y^+ \leq 20)\) of the Wasan-Tien-Wilke eddy-diffusivity profile.
While we anticipate that for $Sc$ large, the diffusion layer will reside very close to the wall, it is not immediately apparent that we are justified in neglecting the contribution to these integrals that occurs between $y^+ = 20.$ and $y^+ = y_m^+$. Fortunately we find that

$$I_1(y_m^+) + I_2(y_m^+) - I_1(20) - I_2(20) = O(1) , \quad (C-17)$$

so that the complete integrals are not needed. Combining equations C-12 and C-16 we find

$$St = \frac{\sqrt{f/2}}{I_1(20) + I_2(20) + O(1)} . \quad (C-18)$$
APPENDIX D: Numerical Calculations for Solution of Rotating Disk Hydrodynamics

The subroutines used are: MATINV, which solves the set of equations 98 once the matrix and residuals are known; DERIV which defines the matrix \( \frac{\partial \mathbf{R}}{\partial \mathbf{P}} \); RESID which calculates the residuals, \( R_i \), for a given set of parameters; and COEF which calculates the coefficients in the two sets of expansions, equations 74 through 79, via the recursion relationships, equations 84, 87, 88, 93, 95, and 96.
PROGRAM MAIN(INPUT,OUTPUT)
DIMENSION DUM(5),XY(5)
COMMON/DUM/DUM(5),XY/PA/A1+CC+AA+BB/DESE/CC/C
READ100,A+CC+AA+BB,TEST=1*E-12
10 READ200,N+Z,IF(N+EQ+0),GOTO300$PRINT201,N+Z
201 FORMAT(1H1* N+*13* MATCHED AT Z =*F5.2)
PRINT202
202 FORMAT(/11X*A$14X*B$14X*C$14X*AA$13X*BB$/) PRINT110,A$B+CC$AA$BB,M=1,INDEX=0$CALL COEF(N)
100 FORMAT(5F10.5)
200 FORMAT(I3,F5.0)
CALL RESID(N+Z)
L=5
1 CALL DERIV(N+Z)$INDEX=INDEX+1$DO201=1*5
20 XY(I+1)=R(I)$$CALL MATINV(L+INDEX)$IF(DETERMINATE=0*1)$PRINT120
120 FORMAT(* DETERMINATE = 0*1)
IF(DETERMINATE=0*1)STOP$A=A+XY(I+1)$B=R+XY(2+1)
CC=CC+XY(3+1)$AA=AA+XY(4+1)$BB=BB+XY(5+1)
CALL COEF(N)$CALL RESID(N+Z)
RP=ABS(R(1))$ABS(R(2))+ABS(R(3))+ABS(R(4))+ABS(R(5))$PRINT110,A$B+CC$AA$BB$IF(RPGE.TEST)GOTO2
PRINT111*(R(K)+K=1*5)
111 FORMAT(/13*SE15.5)
110 FORMAT(I3,F5.15*8)
GOTO10
2 IF(INDEX.LE.20),GOTO1
PRINT112
112 FORMAT(/13*ITERATION LIMIT EXCEEDED*)
PRINT111*(R(K)+K=1*5)$GOTO10
300 PRINT302=MM=10$CALL COEF(MM)$DO301 I=1*10
301 PRINT303*(C(J+I),J=1*6)$DO303
303 FORMAT(/6E10.8)
302 FORMAT(1H1*)
STOP $END

XBL 754.1059
SUBROUTINE MATINV(N,M,DETERM)
DIMENSIONA(5,5),B(5,5),C(5,5),D(5,5),JCOL(5),X(5,11)
COMMON/MUD/A,B,C,D
 NM1=N-1 $ DETERM=1.0 $ DO 1 I=1,N $ JCOL(I)=I $ DO 1 K=1,M
 1 X(I,K)=D(I,K) $ DO 6 II=1, NM1 $ IP1=II+1 $ SMAX=ABS(B(II,II))
    JC=II $ DO 2 J=IP1,N $ IF(ABS(B(II,J))<SMAX) GO TO 2 $ JC=J
    RMAX=ABS(B(II,J))
 2 CONTINUE $ DETERM=DETERM*B(II,JC) $ IF(DETERM.EQ.0.0) RETURN
    IF(JC.EQ.11) GO TO 4 $ JS=JCOL(JC) $ JCOL(JC)=JCOL(II)
    JCOL(II)=JS $ DO 3 I=1,N $ SAVE=B(I,JC) $ B(I,JC)=B(I,II)
 3 B(I+II)=SAVE $ DETERM=-DETERM
 4 DO 6 I=IP1,N $ F=B(I,II)/B(II,II) $ DO 5 J=IP1,N
 5 B(I+J)=B(I+J)-F*B(I+J) $ DO 6 K=1,M
 6 X(I,K)=X(I,K)-F*X(I,K) $ DETERM=DETERM*B(N,N)
    IF(DETERM.EQ.0.0) RETURN $ DO 7 II=2,N $ IR=N-II+2 $ IM1=IP-1
    JC=JCOL(IR) $ DO 7 K=1,M $ F=X(IR,K)/B(IR,IR) $ D(JC,K)=F
    DO 7 I=1,IM1
 7 X(I,K)=X(I,K)-B(I,IR)*F $ JC=JCOL(II) $ DO 8 K=1,M
 8 D(JC,K)=X(I,K)/B(1,1) $ RETURN $ END

XBL 754-1055
SUBROUTINE DERIV(N,Z)
DIMENSIONDM(5,5),R(N),S(N),DUM1(5,5),DUM2(5,5),XY(N,5)
COMMON/MUD/DUM1,DUM2,XY,RES/R,PAR/A,B,C,AA,BB
D=0.000001 $ DO1J=1,N
1 R2(J)=R(J)
   A=A+D $ CALL COEF(N) $ CALL RESID(N,Z) $ DO2I=1,N
2 DM(I+1)=(R(I)-R2(I))/D $ A=A-D $ B=B+D $ CALL COEF(N) $ CALL RESID(N,Z)
   DO3I=1,N
3 DM(I+2)=(R(I)-R2(I))/D $ B=B-D $ CC=CC+D $ CALL COEF(N)
   CALL RESID(N,Z) $ DO4I=1,N
4 DM(I+3)=(R(I)-R2(I))/D $ CC=CC-D $ AA=AA+D $ CALL COEF(N)
   CALL RESID(N,Z) $ DO5I=1,N
5 DM(I+4)=(R(I)-R2(I))/D $ AA=AA-D $ BB=BB+D $ CALL COEF(N)
   CALL RESID(N,Z) $ DO6I=1,N
6 DM(I+5)=(R(I)-R2(I))/D $ BB=BB-D $ RETURN $ END

XBL 754-1057
SUBROUTINE RESID(N,Z)
DIMENSION R(5),C(6,50)
COMMON/C0/C/PAR/A*B*CC*AA*BB/RES/R
DO1 I=1,N
  1 R(I)=C(I+3*I)-C(I+1)
  R(4)=0. $ R(5)=0. $ R2I=2+N $ X=1./EXP((I-1)*CC*Z) $ Y=Z**(I-1)
  R(1)=R(1)+C(4+I)*X-C(1+I)*Y
  R(2)=R(2)+C(5+I)*X-C(2+I)*Y
  R(3)=R(3)+C(6+I)*X-C(3+I)*Y
  R(4)=R(4)-(I-1)*CC*C(4+I)*X-(I-1)*C(1+I)*Y/Z
  R(5)=R(5)-(I-1)*CC*C(5+I)*X-(I-1)*C(2+I)*Y/Z $ RETURN $ END
SUBROUTINE COEFCN
DIMENSION C(6,50)
COMMON/CO/C/PAR/A,B,C,AA,BB
C(1,1)=0  C(2,1)=1  C(3,1)=0  C(4,1)=0  C(5,1)=0
C(6,1)=CC  C(6,2)=AA
C(5,2)=BB  C(6,2)=2*AA/CC  DO11=3,N
C(3,1)=2*C(I+1,N)/I  X=O  Y=O  IN=I-2  DO2J=1,N
C(3,1)=X+X+C(1,J)*C(1,N)-C(2,J)*C(2,N)+IN*C(3,J)*C(3,N+1)
2 Y=Y+2*C(1,J)*C(2,N)+IN*C(3,J)*C(2,N+1)
C(1,1)=X/(I-1)/(I-2)  C(2,1)=Y/(I-1)/(I-2)  IN=I-1
X=O  Y=O  DO3J=2,N  IN=I-J+2
X=X+C(4,J)*C(5,N)-C(5,J)*C(5,N)-IN-1*C(4,N)*C(6,J)
7 Y=Y+2*C(4,J)*C(5,N)-C(5,J)*C(5,N)-IN-1*C(4,N)*C(6,J)
C(4,1)=X/CC**2/(I-I-1)*3+2)
C(5,1)=Y/CC**2/(I-I-1)*3+2)
1 C(6,1)=2*C(4,1)/CC/(I-1)
RETURN  $  END

XBL 754-1058
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