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Publication Date
1980-11-01
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(Ph.D. thesis)

November 1980

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CORROSION OF IRON

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ABSTRACT

In this dissertation three problems relevant to the electrochemical aspects of iron are treated. In the first problem, a model was developed for the anodic dissolution of iron in a sulfuric acid solution. Current and potential distribution validate experimentally obtained z-shaped polarization curves. In the second problem mass-transfer rates on rotating disks and rings are calculated when the flow regime may vary from laminar near the center to fully developed turbulent flow near the periphery. These results are subsequently used in a model which calculates corrosion rates on a disk rotating in sea water.

On a completely different topic, the current and potential distributions on a dropping-mercury electrode are calculated below the limiting current. Results are generated in terms of two dimensionless parameters.
Acknowledgments

I would like to thank Professor John Newman for his guidance, patience, and friendship. Fortunately, I have learned much more than what is expressed on these few pages.

My friends and colleagues have contributed to my education for which I am appreciative. I will always appreciate the kind deed performed by Gary Trost of filing this thesis.

And finally, I would like my family to know that I have truly appreciated their love, encouragement, and endurance. They made it all possible.

This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. W7405-Eng-48.
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1. INTRODUCTION

In this dissertation models are developed for different aspects relevant to the corrosion of iron from an electrochemical viewpoint. In the first model, the anodic dissolution of an iron disk rotating in a sulfuric acid is considered. Potential and current distributions are presented for a partially passivated rotating disk electrode where a discontinuous local polarization relation is used to reflect the change from the active to the passive state. Results of the model yield a z-shaped polarization curve similar to curves measured experimentally. The limiting cases of mass-transfer control and ohmic control are treated. Comparison of previous experimental results with the model is in harmony with the conclusion that the electrode is mass transfer controlled in the transition region.

In the second model, mass-transfer rates are calculated to rotating disks and rotating rings when laminar, transition, and fully developed flow exist upon different portions of the surface. Good agreement of data and the model is obtained for rotating disks and relatively thick rotating rings. Results of the calculations for thin rings generally exceed the experimental data measured in transition and turbulent flow. A $y^+$ form for the eddy diffusivity is used to fit the data. No improvement is noticed with a term involving both $y^+$ and $y^+$. 

In the final model relevant to corrosion, the corrosion rate is calculated on a disk rotating in sea water. The rotation speed and
the disk size are such that the periphery may be in transition and turbulent flow whereas the center is in laminar flow. Corrosion rates are calculated for a variety of conditions which correspond to the experiments performed by LaQue. Using an expression for the iron current density which varies discontinuously with potential, the experimental observations made by LaQue are obtained qualitatively. The effect of oxygen concentration, conductivity, rotation speed, and disk size on the results is presented.

On a completely different topic, a model is developed to describe the characteristics of the dropping-mercury electrode below the limiting current. The combined effect of electrochemical kinetics, ohmic potential drop, and mass transfer on a metal deposition reaction is addressed. Current, potential, and surface concentrations are expressed in terms of two parameters which characterize the results. Even in the presence of an excess of supporting electrolyte, current densities larger than the mass transfer limit calculated by Ilković may exist.
2. A MODEL FOR THE ANODIC DISSOLUTION OF IRON IN SULFURIC ACID

Introduction

Passivation of iron in sulfuric acid has been noticed by investigators for some time. In his experiments Flade$^1$ observed a potential characteristic of the passive-active state transition. Somewhat later, Osterwald$^2$ considered the potentiostatic measurements of Franck.$^3$ An explanation was presented which relates the oscillating current-potential behavior to an ohmic drop in the solution and the stability of an iron oxide film. In a series of papers, Hurlen$^{4-6}$ presented kinetic parameters important for the description of the iron electrode. In this paper a model is developed which corresponds to the experimental results obtained with an iron rotating disk electrode in sulfuric acid solution.

More recently, Epelboin et al.$^7$ showed the importance and validity of an electronic device for obtaining polarization curves. Briefly, they explained the hysteresis of the current-potential curve observed with potentiostatic control in terms of the operating characteristic of the potentiostat. They also introduced a negative impedance converter (NIC). This device was used to control the current-potential behavior of the iron electrode without hysteresis but with a continuous, reversible transition from the active to the passive state. Because of its shape, the curve is referred to as a z-shaped curve.

In this paper the portion of the polarization curve which descends from the limiting current plateau to a very small current is called the
transition region. In the transition region, active and passive states exist on different portions of the disk electrode.

The polarization curves obtained by Epelboin et al. with a NIC are given in Fig. 1. The limiting current varies with the square root of rotation speed. The dotted region of the plateau is not a stable region; here the measured currents were reported to have large fluctuations.

In their paper Epelboin et al. suggest the applicability of a local polarization relation which decreases sharply to a low current density.

Model Development

A simple model is presented for the passivation of iron in 1 molar sulfuric acid which accounts for the kinetic resistance in the double layer and the nonuniform ohmic potential across the disk surface. The model does not consider mass transfer of chemical species explicitly. However, the effect of mass transfer limitations is included in the kinetic expression.

To characterize the overall response of a disk electrode undergoing anodic polarization, a local polarization curve is needed. There are many kinetic expressions from which to choose; however, we have considered an expression which shows a discontinuous change from the active to the passive state. For example, in the active region a modified Butler-Volmer relationship is presumed to apply:

\[ i = nFk_a \exp\left( \frac{\alpha_a F}{RT} (V - \phi_o) \right) - nFk_c c_{Fe^{++}} \exp\left( \frac{-\alpha_c F}{RT} (V - \phi_o) \right). \]  \hspace{1cm} (2-1)

At a characteristic value of the driving force, \( V - \phi_o = (V - \phi_o)_* = 0.28 \text{ V}, \)
Fig. 2-1. Current-voltage behavior of a rotating disk electrode obtained by Epelboin et al.
a passive film is presumed to form; and the current density changes discontinuously to an extremely low value that remains constant with further increases in $V - \phi_o$.

The electric driving force is the local potential difference $V - \phi_o$, where $V$ is the potential of the iron rotating disk electrode and $\phi_o$ is the potential measured by a saturated calomel electrode immediately adjacent to the surface but outside the double layer. The state of the electrode can be characterized by the value of $V - \phi_o$. If $V - \phi_o$ at the edge is equal to or less than $(V - \phi_o)_* = 0.28$ V, then the active state prevails. The passive state exists over the entire disk when $V - \phi_o$ at the center of the disk is greater than $(V - \phi_o)_*$. In the transition region which exists between these conditions, both states exist simultaneously on the disk. Figure 2 is a description of the local polarization relationship.

It is possible to include the effects of mass transfer limitations without explicitly calculating the mass transfer of chemical species. This is accomplished by including the concentration dependence of the limiting reactant in the kinetic expression. An applicable expression is

$$i = nFk_e \left( \frac{c_{R,o}}{c_{R,\infty}} \right)^p \exp \left[ \frac{a_0^F}{RT} (V - \phi_o) \right] - nFk_c c_{Fe}^{++} \exp \left[ \frac{-c_{Fe}^F}{RT} (V - \phi_o) \right].$$

(2-2)

The ratio $c_{R,o}/c_{R,\infty}$ is equivalent to $1 = i/i_{lim}$. The electrode is still presumed to passivate locally for values of $V - \phi_o$ greater than $(V - \phi_o)_*$. However, the shape of the local polarization curve is noticeably different. Figure 3 schematically illustrates the local polarization curve when the
Fig. 2-2. Local polarization behavior for kinetic control.
Fig. 2-3. Local polarization behavior when mass transfer limitations are considered. While this curve qualitatively represents the behavior for a range of parameters, the curve was actually drawn with $nFk_a = 1.0 \times 10^6$ A/cm$^2$, $p = 0.01$, and $\Omega = 4500$ rpm.
effect of a limiting species is included. Results will be presented which indicate the merits of the two polarization relations discussed here.

We must mention that the model presented here considers only one of the possible arrangements of the active and passive state. In addition to an active disk with a passive ring outside it, one could also consider a passive disk with an outer active ring, and an active ring between an inner passive disk and an outer passive ring. All three possibilities were observed experimentally by Epelboin et al.

**Analysis**

Laplace's equation is solved for the region between the electrode surface and a counterelectrode well removed from the surface. The equations describing the problem are

\[ \nabla^2 \phi = 0 \]  
\[ r = 0 \quad \phi \text{ is well behaved} \]  
\[ r = r_p \quad i = f(V - \phi_0) \]  
\[ r_0 > r > r_p \quad V - \phi_0 = (V - \Phi_0)_z \]  
\[ r > r_0 \quad i = i_p = 10^{-4} \text{ A/cm}^2 \]  
\[ z = 0 \quad \frac{\partial \phi}{\partial z} = 0 \]  
\[ z \to \infty \quad \phi \to 0 \]
where \( i = f(V - \Phi_0) \) refers to Eq. (2-1) without mass transfer limitations and to Eq. (2-2) when mass transfer limitations are considered.

One does not hope to find a solution to Laplace's equation subject to these boundary conditions in the literature. A solution is obtained by superimposing solutions to Laplace's equation subject to boundary conditions which are algebraically equivalent to those given above. The three solutions are:

\[
\phi = \phi^I + \phi^{II} + \phi^{III}, \tag{2-10}
\]

where \( \phi^I, \phi^{II}, \) and \( \phi^{III} \) all satisfy Eqs. (2-3), (2-4), (2-8) and (2-9); while on the disk electrode at \( z = 0 \), they satisfy the following

\[
r \leq r_p: i^I = f(V - \Phi_0) , \quad i^{II} = I_p, \quad i^{III} = I_p, \tag{2-11}
\]
\[
r > r_p: i^I = 0 \quad , \quad i^{II} = I_p, \quad i^{III} = 0. \tag{2-12}
\]

A solution for \( \phi^I \) subject to the boundary conditions specified has been given in rotational elliptic coordinates by Newman and takes the form

\[
\phi = \sum_{n=0}^{\infty} B_n P_{2n}(\eta) M_{2n}(\xi) \tag{2-13}
\]

where

\[
r = r_p \sqrt{(1 - \eta^2)(1 + \xi^2)} , \quad z = r_p \eta \xi .
\]

The current density at the working electrode is given by

\[
i = -\kappa \frac{\partial \phi}{\partial z} \bigg|_{z=0} \tag{2-14}
\]
From the orthogonal properties of Legendre polynomials, the $B_n$ coefficients can be expressed as

$$B_n = \frac{(4n + 1)r_p}{M_{2n(0)K}} \int_0^1 i(\eta)\eta P_{2n}(\eta) d\eta \quad (2-15)$$

It is convenient to use the results of Nanis and Kesselman$^9$ for solutions to the second and third terms in Eq. (2-10). The potential just outside the double layer is the potential of most concern and is given as

$$\phi^{II} = \frac{2}{\pi} \left( \frac{ip_0}{\kappa} \right) \frac{r}{r_0} \left\{ E \left[ \left( \frac{r_0}{r} \right)^2 \right] - \left[ 1 - \left( \frac{r_0}{r} \right)^2 \right] K \left[ \left( \frac{r_0}{r} \right)^2 \right] \right\}, \quad r > r_0 \quad (2-16)$$

$$\phi^{II}_0 = \frac{2}{\pi} \left( \frac{ip_0}{\kappa} \right) \frac{r}{r_0} \left\{ E \left[ \left( \frac{r_0}{r} \right)^2 \right] - \left[ 1 - \left( \frac{r_0}{r} \right)^2 \right] K \left[ \left( \frac{r_0}{r} \right)^2 \right] \right\}, \quad r > r_0 \quad (2-17)$$

where $K[(r_0/r)^2]$ and $E[(r_0/r)^2]$ are respectively the complete elliptic integrals of the first and second kind as defined by Abramowitz and Stegun.$^{10}$ (Newman$^{11}$ quoted the results of Nanis and Kesselman without realizing the difference in the definition of the elliptic integrals.) A similar expression applies for $\phi^{III}$ but with $r_0$ replaced by $r_p$.

**Solution Technique**

The current and potential distributions on the active portion of the disk are determined from the $B_n$ coefficients given by Eq. (2-15). To calculate the $B_n$ coefficients, the $n$ coupled equations are solved
using a multi-dimensional Newton-Raphson iteration procedure.

To obtain a satisfactory initial guess for the most important $B$ coefficient, $B_0$, this coefficient was made equivalent to the ohmic potential given by the primary resistance relationship for a disk electrode. Thus we set $B_0 = \pi r_p i_{lim}/4\kappa$.

In the transition from active to passive state, the point of passivation, $r_p$, is unknown. However, a constraint in addition to the $n$ orthogonal constraints for $B_n$ is obtained. The value of $V - \Phi_0$ is specified at the edge of the active region. Computationally it is convenient to replace the unknown $r_p$ with $V$. Therefore, the point of passivation is presumed to occur at a specified location, and the potential, $V$, of the working disk electrode is calculated. Now the $n + 1$ equations are calculated using the same Newton-Raphson technique.

In the completely passive region, no detailed calculations are needed as the current density is uniformly equal to $i_p$. The potential distribution is simply given by Eqs. (2-16) and (2-17).

The Newton-Raphson method was found to be efficient, as convergence was obtained within a few iterations. For the transition region, calculations were also done using a method of successive approximations. Excellent agreement was obtained. However, convergence was very slow for this method and it was necessary to damp the calculations strongly.

Results and Discussion

The principal value of the model and the analysis is an overall description of the total current from the rotating iron electrode during anodic polarization. The kinetic parameters used to fit the model to
the experimental results are included in Table 1. The solution conductivity from the literature is also given.\textsuperscript{13} To obtain an adequate comparison of the experimental results and the model, it is necessary to decide exactly how the comparison should be made. For example, different results and different values of $k_a$ are used if one decides to match the experimental and calculated currents at the point of passivation versus a good comparison of the kinetically controlled regime.

\textbf{Kinetic considerations}

Figure 4 presents a comparison of the experimental results of Epelboin et al. at a rotation speed of 4500 rpm and the model when the value of $k_a$ is such that $I_{calc} = I_{expr}$ at the point where the disk begins to passivate. The highest rotation speed was chosen since mass transfer limitations were less than at the lower speeds. A good agreement in the transition region is obtained at the expense of poor agreement in the active kinetic region.

The transition region shown in Fig. 4 does not normally occur for an active electrode. Normally increases in $V - \phi_{ref}$ result in further increases in $I$. However, from the viewpoint of the model, the transition region occurs as a result of boundary condition 6 and the ohmic potential drop. As one travels along the transition region from A to B, the size of the active portion decreases, and the total disk current drops. To see how the electrode potential varies in this region it is helpful to recall the simple relationship for the primary resistance for a disk electrode given by Newman,\textsuperscript{12}

$$\frac{\phi_0}{I} = \frac{1}{4k\tau_0}.$$  \hfill (2-18)
TABLE 1. Parameters for the model.†

\[ \alpha_a = 1.0 \ , \quad \alpha_c = 1.0 \ , \quad n = 2.0 \]

\[ nFk_a^\ddagger = 1.00 \times 10^7 \text{ A/cm}^2, \quad c_{Fe^{++}} \cdot Fk_c = 8.32 \times 10^{-16} \text{ A/cm}^2 \]

\[ (V - \phi_0)^* = 0.28 \text{ V} \]

\[ i_p = 1.0 \times 10^{-4} \text{ A/cm}^2 \]

\[ \kappa = 0.40 \text{ (ohm cm)}^{-1} \]

\[ c_{Fe^{++}} = 4.0 \text{ mole/litre} \]

\[ \beta = 0.17496 \frac{\text{A-sec}^1}{\text{cm}^2} \]

†The reference electrode is positioned in the bulk position. [Claude Gabrielli, personal communication]

‡This value of \( k_a \) corresponds to an exchange current density of \( 9.1 \times 10^{-5} \text{ A/cm}^2 \) at \( c_{Fe^{++}} = 4.0 \text{ mole/liter} \).
$nFk_a = 3.162 \times 10^{-4} \text{ A/cm}^2$

$nFk_c = 6.569 \times 10^{-27} \text{ A/cm}^2$

Fig. 2-4. Comparison of experimental results and calculations when kinetic factors control: (solid line) calculations, (dashed line) experimental results. The lines marked uniform and primary refer to the transition region behavior of a completely active disk which passivates at $(V - \Phi_o)_* = 0.28 \text{ V}$ at its edge for the respective current density distributions.
Since \( V - \phi_o \) is specified at \( r = r_p \), the value of \( V - \phi_{\text{ref}} \) approaches 0.28 V as \( I \) and \( r_p \) approach zero. However, since \( r_o \) should here be replaced by \( r_p \) in Eq. (2-18), the decreasing part of the transition is not linear but is bowed outward as shown in Fig. 4.

The shape of the transition can be seen in view of the current density specified at the edge and Eq. (2-18). The measured driving force can be written as

\[
V - \phi_{\text{ref}} = V - \phi_o(r = r_p) + (\phi_o(r = r_p) - \phi_{\text{ref}})
\]

or alternatively

\[
V - \phi_{\text{ref}} = 0.28 + \phi_o(r = r_p) - \phi_{\text{ref}}
\]

It is convenient to express \( \phi_o(r = r_p) \) as

\[
\phi_o(r = r_p) = \frac{\epsilon I}{4\kappa r_p}
\]

where \( \epsilon \) is a number which varies from 1 for a primary distribution to \( 8/\pi^2 = 0.810569 \) for a uniform distribution. Since \( r_p \) is unknown, let us replace it with the average current density \( i_{\text{avg}} \) according to

\[
I = \pi r_p^2 i_{\text{avg}}
\]

(with neglect of the small current on the passivated part of the disk). The electrode polarization in the transition region can now be expressed as

\[
V - \phi_{\text{ref}} = 0.28 + \frac{\epsilon \sqrt{\pi I i_{\text{avg}}}}{4\kappa} - \phi_{\text{ref}}
\]
In the experimental system, the reference electrode is in the bulk solution, and $\Phi_{\text{ref}}$ is essentially zero. Then, this relationship shows that the calculated transition region curve should be a parabola if the average current density on the active portion and $\varepsilon$ remain constant. The experimental curves have approximately this shape, and deviations can be explained in terms of variations in $i_{\text{avg}}$ and $\varepsilon$.

Returning to Fig. 4, we observe that both the experimental and calculated curves deviate from a parabolic shape over the range of the transition. If point A' represents an entirely active electrode, then the difference between A and A' is attributable to different current distributions. Point A' has a more uniform distribution than that at the calculated point A.

Near point B the calculated results approach a disk of uniform current density, since the current density approaches are given by Eq. (2-6). Using Eq. (2-22) we can determine that the current density at the bottom is greater than at the top of curve B-A. One can also conclude that the distortion from a parabola is caused by an increase in $i_{\text{avg}}$ from A' to B in addition to changes in $\varepsilon$.

To show the calculated variation in current distribution that occurs over the course of the transition region, Fig. 5 is presented. Following Newman,\textsuperscript{14} we have normalized the ohmic potential with respect to the primary resistance for a disk of radius $r_p'$. The uniform current density limit is provided for reference. One notices that as the active surface area decreases the current density on the active portion becomes more nearly uniform. For example, the ratio of the current density at the center to that at the edge varies from 0.07 when $r_p/r_o = 1.0$ to 1.
Fig. 2-5. Variation of the ohmic potential across the active portion of the disk.
when \( r_p/r_o = 0 \). The current distribution approaches the uniform limit as \( r_p/r_o \to 0 \) and the primary limit when \( r_p = r_o \).

**Mass transfer limitations**

If one considers mass transfer limitations, a local polarization relation given by Eq. (2.2) is valid. The results of the model using this equation are given in Fig. 6. Parameters are again given in Table 1. \( \beta \) is determined from the data and the defining relation

\[
  i_{\text{lim}} = \beta \sqrt{\omega}.
\]  

(2-23)

It is also necessary to specify the reaction order, \( p \), of the limiting reactant. Levich\(^{15}\) has indicated the effect of the reaction order on the approach to a limiting current plateau; for smaller values of \( p \) the curve follows more closely the kinetic and limiting-current limits. Figure 7 shows the effects of varying the reaction order \( p \) of the limiting reactant.

The calculated transition region shown in Figs. 6 and 7 is substantially mass transfer controlled. As one proceeds from the completely active to the completely passive state, the current density is uniform across the disk and given by Eq. (2-23). The decrease in current is completely attributable to the decrease of the active area.

A discrepancy between the model and the experiments is revealed in Fig. 6. The model yields four distinct curves in the transition which are characteristic of the four rotation speeds. In the lower portion of the transition, the experimental curves overlap. The four distinct curves of the model indicate four different average or limiting current
Fig. 2-6. Comparison of measured and calculated polarization curves: (solid line) calculations (p = 0.01), (dashed line) experimental results.
Fig. 2-7. Comparison of calculated polarization curves for different reaction orders of the limiting reactant. The four curves for any given value of $p$ correspond to rotation speeds of 750, 1600, 3000, and 4500 rpm.
densities, although the superimposed experimental curves give evidence of the same uniform current density existing for all four rotation speeds. The experimental curves also reflect an increase in the average current density as one travels toward the passive state.

Epelboin et al. made measurements of the total current from the disk electrode and the dimensions of the active electrode. Figure 8 presents the results of these measurements and calculations from the model. However, it should be emphasized that some of the experimental results indicated that the current was restricted to a thin ring and no noticeable faradaic reaction occurred inside the inner radius or beyond the outer radius of the ring, whereas the model considers an active disk whose radius decreases as the passive state is approached. Therefore, comparison of the model with the experimental results for equivalent areas may compare the results of rings with those of a disk.

The upper curve on Fig. 8 refers to the situation where kinetic factors determine the current distribution on the disk (as was the case for the calculations shown in Fig. 4). Here the average current density on the disk in the transition region increases markedly as the size of the active disk approaches zero, although the increase is gradual for relatively large values of the active area.

The horizontal line on Fig. 8 is characteristic of a mass transfer controlled active-disk region (as was the case for calculations shown in Figs. 6 and 7). The experimental results of Epelboin et al. appear to resemble closely the behavior typical of a mass transfer region. In fact, their results look like two mass transfer regions coupled by a steep transition. Most of their experimental curve is for ring shapes. It is
Fig. 2-8. Current density on the active portion of the disk electrode in the transition region: (---) = experimental results of Epelboin et al., (----) = results of the model when mass transfer effects are included, (-----) = results of the kinetic model.
remarkable that a mass transfer-controlled ring region would have a lower average current density than a disk region. One is also surprised that the experimental curve and the horizontal line do not meet when the disk is completely active, as this shows an inconsistency between $i_{\text{avg}}$ obtained from $\beta \sqrt{\Omega}$ and $i_{\text{avg}}$ obtained from $I$ and measurements of the active dimensions. An explanation could be given in terms of a region existing near A' (Fig. 6) where the disk remains active and a decrease in the current density occurs. Of course, the model presented here cannot substantiate this.

**Consideration of ring shapes**

Since a significant portion of the transition region is a ring and not a disk, one should consider whether a consideration of rings can account for the average current density decreasing as the passive state is approached (Fig. 8). A comparison of the measured potential and current with that calculated for rings may clarify this matter. Consider a normalized resistance function, $g(r_i/r_p)$, which contains the important measured parameters

$$g\left(\frac{r_i}{r_p}\right) = \frac{\kappa \Phi_o(r = r_p)}{\sqrt{i_{\text{lim}}} \sqrt{I}}$$  \hspace{1cm} \text{(2-24)}$$

where

$$\Phi_o(r = r_p) = V - \Phi_{\text{ref}} - 0.28$$

Therefore, with choice of a rotation speed, measured potential, and current, a value of $g(r_i/r_p)$ is defined. This measured value of $g$ can be compared with functions defined for rings of various current distri-
butions. Namely, consider $g^o$ defined by a ring of uniform current, $i_{avg} = \beta \sqrt{\Omega}$; $g^*$ defined by a ring of average current density, $i_{avg} = \beta \sqrt{\Omega} f(r)$; $g^+$ defined by a ring of average current density, $i_{avg} = \beta \sqrt{\Omega} f(r)$, and the primary resistance of a ring given by Miksis and Newman.\textsuperscript{16} $f(r)$ is defined by Newman\textsuperscript{17} as

$$f(r) = \sqrt[3]{\frac{1 - \left(\frac{r_1}{r_p}\right)^2}{1 - \left(\frac{r_1}{r_p}\right)^3}}.$$  

$\phi_o(r = r_p)$ for $g^o$ and $g^*$ are calculated using the results of Nanis and Kesselman. $g^*$ can be related to $g^o$ by

$$g^*(\frac{r_1}{r_p}) = g^o\left(\frac{r_1}{r_p}\right)^{\sqrt{f(r)}}. \quad (2-25)$$

Figure 9 illustrates the behavior of these functions. It is important to compare values of $g$ obtained experimentally with $g^o$, $g^*$, and $g^+$. For example, if we consider a point where $\Omega$ 4500 rpm, $I = 0.54$ A, $i_{lim} = 2.80$ A/cm, $V - \phi_{ref} = 1.42$ V, then $g(r_1/r_p)$ is calculated to be 0.37. This is the smallest value of $g$ one can obtain from the data. For this example $g$ intersects the $g^+$ curve, $r_1/r_p = 0.85$, which corresponds to a thin ring near the periphery of the disk. However, it is inconsistent to have a $g$ value obtained near the limiting current plateau equivalent to a calculated value of $g$, $g^+$, which corresponds to the primary resistance of a thin ring. An increase in $i_{lim}$ will lower the value of $g$ and it will approach the more appropriate values of $g^o$ and $g^*$. Also, as one travels down the transition region, the current
Fig. 2-9. Correlation of normalized resistance functions.
distribution becomes more uniform and increases in $i_{\text{avg}}$ must occur.

**Summary and Conclusions**

The simple model presented yields a z-shaped curve for the anodic polarization of iron in sulfuric acid, very similar to that obtained experimentally by Epelboin et al. The model accounts for the kinetic resistance at the surface, the ohmic potential, and the effect of mass transfer limitations. In the transition region the model predicts the same general response of the disk electrode for the limit of mass transfer control and for the case of kinetic control. However, the calculated current density remains constant in the transition region when mass transfer limitations are included, whereas the current density increases in the transition region as the passive state is approached, when strictly kinetic factors are considered. Epelboin et al. report current densities which decrease in the transition. Analysis presented here states that the experimentally obtained average current density must increase as the passive state is obtained. The analysis is valid for both disk and ring shapes.
3. CHARACTERISTICS OF THE DROPPING-MERCURY ELECTRODE BELOW THE LIMITING CURRENT

Introduction

Polarographic analysis with a dropping-mercury electrode is usually carried out in the presence of a large excess of indifferent, nonreacting electrolyte. This serves to reduce the ohmic potential drop in the solution and to reduce the effect of the electric field on the movement of reacting ionic species. For a sufficiently large applied potential, the current to the drop is limited by the rate of diffusion and convection and corresponds to a zero concentration of reactant at the surface. In this situation, the cathodic current density is given by the Ilković equation, provided that the volumetric flow rate of mercury through the capillary is constant.

Theoretical equations for polarographic limiting currents have also been developed for a number of systems involving specific combinations of chemical and electrochemical reactions. These studies have focused attention on the interactions between homogeneous and heterogeneous processes and, generally, the importance of ohmic potential drop in the solution and surface overpotentials for the electrochemical reactions has not been evaluated. However, early qualitative studies indicate that if there is insufficient supporting electrolyte, the current due to one discharging species could produce an electric field that enhances the limiting current for other reactants.

The influence of ohmic potential drop on the distribution of current has been analyzed for disk, ring, and ring-disk electrodes.
as well as for planar, tubular, and spherical electrodes. With smaller electrolyte conductivity, the distributions of current and concentration become more nonuniform and, under some circumstances, local current densities can exceed the local limiting current. A review of current and potential distributions for various geometries is given by Newman.

The instantaneous current and the average current to a dropping mercury electrode in a binary salt solution have been calculated. This analysis showed that ohmic potential drop can prevent the attainment of a limiting current during the initial stage of growth of the drop, particularly if the applied voltage is small.

In this paper, a general model is presented for the dropping mercury electrode below the limiting current. The analysis includes the effects of mass transfer, ohmic potential drop in the solution, and electrode kinetics. Factors that govern the relative importance of these effects are identified for the example of a metal deposition reaction.

It is pointed out that the general approach presented here can be used to evaluate experimental situations different from traditional polarography. For example, the potential may not be constant throughout the life of the drop; the drop may not grow with the cube root of time.

Analysis

At currents below, but at an appreciable fraction of, the limiting current, it is necessary to consider the surface overpotential associated with the electrode reaction, the ohmic potential drop in the bulk of the solution, and concentration variations near the drop surface. The analysis
presented here is restricted to a single electrode reaction with stoichiometry represented by:

$$\sum_i s_i M_i^{z_i} + n e^- \quad (3-1)$$

A polarization equation of the form

$$i = i_o \left[ e^{\frac{\alpha_a F \eta_s}{RT}} - e^{\frac{-\alpha_c F \eta_s}{RT}} \right] \quad (3-2)$$

can be used to express the dependence of the reaction rate on the surface overpotential, $$\eta_s = V - \phi_o - U_o$$. The exchange current density can be written as

$$i_o = i_{o,ref} \prod_i \left( \frac{c_{i,o}}{c_{i,ref}} \right)^{\gamma_i} \prod_k a_k^{\gamma_k} \quad (3-3)$$

and the theoretical open circuit cell potential is given by

$$U_o = U^0 - U_{ref}^0 - \frac{RT}{nF} \sum_i s_i \ln \frac{c_{i,o}}{\rho_o} + \frac{RT}{n_{ref}^F} \sum_i s_{i,ref} \ln \frac{c_{i,ref}}{\rho_o} \quad (3-4)$$

provided that activity-coefficient corrections can be neglected. Furthermore, exponents $$\gamma_i$$ for ionic species in Eq. (3) are given the values

$$\gamma_i = q_i + \frac{\alpha_c s_i}{n} \quad (3-5)$$

where $$q_i = -s_i$$ for a cathodic reactant and is zero otherwise. For a metal deposition reaction, and with a reference electrode of the same kind, Eq. (3-4) reduces to
\[ U_0 = -\frac{s_i RT}{nF} 2\ln \left( \frac{\theta_i}{\theta_m} \right), \quad (3-6) \]

where \( \theta_i = c_{i,o}/c_{i,\text{ref}} \) and \( \theta_m = c_{m,o}/c_{m,\text{ref}} \). Here and for the remainder of the paper the subscript \( i \) refers to the metal ion. The activity coefficients of metallic species are assumed to be unity. Consequently, substitution of Eqs. (3-3), (3-5) and (3-6) into Eq. (3-2) gives, on rearrangement:

\[ i = i_{o,\text{ref}} \left[ \theta_m e^{\alpha_A F(V-\Phi_0)/RT} - \theta_i e^{-\alpha_A F(V-\Phi_0)/RT} \right]. \quad (3-7) \]

Furthermore, the bulk solution potential \( \Phi_0 \) can be evaluated at the drop surface from the resistance relationship for a spherical drop in a solution of uniform conductivity,

\[ \Phi_0 = \frac{ir_0}{\kappa}. \quad (3-8) \]

For radial growth of a mercury drop without tangential surface motion, the reactant concentration obeys the equation of convective diffusion in the form

\[ \frac{\partial c_i}{\partial t} + v_r \frac{\partial c_i}{\partial r} = \frac{D_i}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial c_i}{\partial r} \right), \quad (3-9) \]

where the velocity \( v_r \) is determined by the growth rate of the drop:

\[ v_r = \left( \frac{r_0}{r} \right)^2 \frac{dr_0}{dt}. \quad (3-10) \]

Equation (3-9) can be expressed in terms of the normal distance \( y \)
from the surface of the drop, provided that the diffusion layer is thin compared to the drop radius throughout the lifetime of the drop:

\[
\frac{\partial c_i}{\partial t} - \frac{2y}{r_o} \frac{d r_o}{d t} \frac{\partial c_i}{\partial y} = D_i \frac{\partial^2 c_i}{\partial y^2} \quad (3-11)
\]

A similar equation applies inside the sphere, but with the diffusion coefficient \( D_s \) of the discharged reactant in mercury.

The diffusion equation can be solved subject to the conditions

\[
c_i = c_i,\infty \quad \text{for} \quad t \leq 0
\]

\[
c_i = c_i,\infty \quad \text{as} \quad r \rightarrow \infty \quad \text{for} \quad t > 0 \quad (3-12)
\]

\[
c_i = c_i,0(t) \quad \text{at} \quad r = r_o \quad \text{for} \quad t > 0
\]

By superposition, the results can be used to express the concentration derivative at the surface in terms of an integral over the variation of surface concentration during the drop lifetime:

\[
\left. \frac{\partial c_i}{\partial y} \right|_{y=0} = -\frac{2r_o^2}{\pi^2} \int_0^t \frac{dc_i,0}{dt} \left|_{t=t_o} \right. \frac{dt_o}{t_o^2} \left[ 4D_i \int_{t_0}^t r_o^2 dt \right]^{1/2} \quad (3-13)
\]

The surface fluxes, both inside and outside the drop, can be related to the instantaneous current density by an expression of the form:

\[
\frac{s_i}{nF} = D_i \left. \frac{\partial c_i}{\partial y} \right|_{y=0} \quad (3-24)
\]

This equation is restricted not only to the large excess of supporting electrolyte, where the effects of migration can be neglected, but also
to the absence of appreciable charging of the double layer, a process which does not follow Faraday's law. Concentration changes within the drop can be related to external changes by equating the superposition integrals for the two regions through Eq. (3-14). This gives

\[ \theta_m = \theta_m(0) + \left( \frac{D_i}{D_s} \right)^{1/2} \frac{1 - \theta_i}{\theta_s} \]

where \( \theta_s = \frac{c_m, \text{ref}}{c_i, \text{ref}} \).

The model presented here is more general than the approach taken by Ilković since two basic constraints made in his development can be removed. Namely, the potential can vary throughout the life of the drop and can be expressed, for example, as

\[ V = V_{\text{int}} + \beta t \]

where \( \beta \) is the scan rate of the applied potential. Also it is not necessary to maintain a constant flow rate of mercury through the capillary. Removal of the last constraint is particularly important in evaluating the characteristics of modern polarographic equipment. Although results presented here do not evaluate the importance of scan rate and constant flow rate, it is appropriate to indicate the general utility of this model.

When the volumetric flow rate of mercury is constant, the growth rate is given as

\[ r_o = \gamma t^{1/3} \]

With this growth rate, the governing equations (3-7) and (3-13) for the dropping-mercury electrode below the limiting current can be expressed
in dimensionless form as

\[ \phi_o = -N \int_0^{N^{-6}} \frac{d\theta_i}{d(N^{-6})} \bigg|_{N=N_1} \frac{d(N_1^{-6})}{1 - [(N_1^{-6})/(N^{-6})]^{7/3}} \bigg)^{1/2} , \quad (3-17) \]

\[ \phi_o N^2 = K \left( \theta_m - \alpha_0 (E+\phi_o)/\alpha_c - \theta_i e^{E+\phi_o} \right) , \quad (3-18) \]

where \( \phi_o = \alpha_c F r_0 i / \kappa R T \), \( E = -\alpha_c F V / R T \), and \( N^{-6} \) is a dimensionless time given by

\[ N^{-6} = \left[ \left( \frac{\kappa R T}{\alpha_c n F^2 c_i, \omega} \right)^2 \frac{3\pi}{7 D_i} \right]^3 t . \quad (3-19) \]

The dimensionless parameter \( K \) represents a combination of quantities associated with kinetic, ohmic, and mass-transfer effects:

\[ K = \frac{7 i_{0, \text{ref}} (\alpha_c F)^3}{3\pi (F n c_i, \omega)^2 D_i} . \quad (3-20) \]

In Eqs. (3-17) and (3-18), \( \phi_o \) and \( \theta_i \) are dependent variables and \( N^{-6} \) is the independent variable. The parameters \( E \) and \( K \) are expected to have a significant impact on the system behavior, whereas \( \alpha_a / \alpha_c \), \( D_i / D_0 \), and \( \theta_s \theta_m(0) \) are of relatively minor importance and should not influence the results markedly.

The governing equations (3-17) and (3-18) are solved by a stepwise numerical procedure that involves discretization of the integral equation and a Newton-Raphson technique to obtain values for \( \phi_o \) and \( \theta_i \) at each time step. Since the variables may vary very rapidly at short times,
it is necessary to vary the step size to ensure accurate results. In addition, the initial singularity in Eq. (3-17) is avoided by using a short-time series expansion for the concentration derivative over the first time interval.

Results and Discussion

The time dependence of the dimensionless potential $\phi_0$ is presented in Fig. 1 for several values of the parameters $E$ and $K$. This diagram also depicts changes in the instantaneous current density through the relationship, $\phi_0 = \alpha_c F \frac{r_i}{K R T}$.

Lines of slope $1/3$, $0$, and $-1/6$ represent the kinetic, ohmic, and mass-transfer limits, respectively. Figure 1 illustrates that it is not possible to generalize the results for large and small values of $E$ and $K$. Clearly, both parameters are influential in determining $\phi_0$. For large times and moderate to large values of $E$, $\phi_0$ is independent of $K$ and $E$ in accordance with the Ikkovic equation. However, at short times, kinetic factors and, subsequently, ohmic factors can prevent attainment of the mass-transfer limit. These effects are particularly important for small values of $K$ or $E$. A reduction in $K$ corresponds to a smaller exchange current density, bulk reactant concentration, diffusion coefficient, or drop growth rate, or a larger electrolyte conductivity. A larger electrolyte conductivity will also reduce the ohmic potential drop in the solution, and consequently ohmic limitations are less prevalent with small values of $K$, for a specified magnitude of $E$. Furthermore, the effect of $K$ is more pronounced at small values of $E$.

The parameter $E$ is a dimensionless applied potential which includes
Fig. 3-1. Time dependence of dimensionless, instantaneous current density, \( \phi_o = \alpha_c Fr_0 i / \kappa RT \), for a metal deposition reaction at a growing mercury drop. Parameter values: 

- \( D_i / D_s = 1.0; \) 
- \( \alpha_d / \alpha_c = 1.0; \) 
- \( \theta_s = 1.0; \) 
- \( \theta_m(0) = 0.0; \) and 
- \( c_{i,ref} = c_{i,\infty}. \)

(- - - - -): \( K = 10^{-10} \), (---): \( K = 10^{-3} \), 
(- - - - - - - -): \( K = 10^4 \).
the cathodic transfer coefficient for the deposition reaction. As $E$ is increased, ohmic factors have progressively more impact upon the short-time behavior. The ohmic limit is given by

$$\phi_0 = E \quad (3-21)$$

For $E = 80$ the three curves in Fig. 1 are almost horizontal and superimposed upon each other. However, even under these conditions, the curves are not precisely horizontal due to the finite rate of the electrochemical reaction. The mass-transfer limit is represented by

$$\frac{\phi_0}{N} = 1 - e^{(-E)} \quad (3-22)$$

where

$$\frac{\phi_0}{N} = \frac{i_{\text{lim}}}{i} = 1 - \frac{c_{i,0}}{c_\infty} \quad (3-23)$$

At large applied potentials, the intersection of the ohmic and mass-transfer limits can be identified from Eq. (3-21) and Eq. (3-22) as $\phi_0 = N = E$.

Figure 2 shows the time dependence of the average current density defined by

$$i_{\text{avg}} = \frac{1}{T_d} \int_0^{T_d} i \, dt \quad (3-24)$$

for fixed values of $E$ and $K$. This average current is made dimensionless in the same manner as Fig. 1. Total currents can be obtained directly from the relation $I = 4\pi r_o^2 i$. Figures 1 and 2 are analogous, except that the magnitude of the current densities in Fig. 2 have been altered in accordance with Eq. (3-24).
Fig. 3-2. Time dependence of dimensionless average current density, $\frac{a_c}{\text{Fr}_{0}^1 \text{avg}}$, for a metal deposition reaction at a growing mercury drop. Parameters as in Fig. 3-1.
The time dependence of the surface concentration is presented in Fig. 3. Rapid reductions in composition are observed for large values of \( E \) and \( K \), in keeping with the early onset of mass-transfer limitations predicted in Fig. 1 for similar conditions. With small applied potentials, and particularly for small values of \( K \), kinetic factors can control the deposition rate, and the corresponding variations in concentration are less marked.

Figure 4 shows the variations in instantaneous current density normalized with the mass-transfer limiting current density defined by Eq. (3-23). Values in excess of the mass-transfer limit of Ilkovič are obtained. This is similar to results obtained with disk, ring, and plane electrodes. In transient stagnant-diffusion-cell experiments current densities measured and calculated by Hsueh and Newman were found to overshoot the mass transfer limit. Material adjacent to the drop surface that does not react at short times can do so subsequently when kinetic and ohmic factors no longer limit the reaction rate. In contrast, Fig. 5 illustrates the average current density obtained from Eq. (3-24) which rises monotonically to the average limiting current density calculated with the Ilkovič equation. The average current density cannot exceed the average limiting current density.

Figures 1-5 pertain to the behavior of an individual drop. An example of polarographic curves for a metal deposition reaction is presented in Fig. 6. The parameters for the two curves are given in Table 1. The curves result from a number of drops formed sequentially over a range of potentials. The different values of \( i_{\text{o,ref}} \) illustrate their effect on attainment of the mass-transfer plateau.
Fig. 3-3. Time dependence of dimensionless surface concentration, $\theta_1$. Parameters as in Fig. 3-1.
Fig. 3-4. Time dependence of the instantaneous current density normalized with the instantaneous current density in the mass-transfer limit. Parameters as in Fig. 3-1.
Fig. 3-5. Time dependence of the average current density normalized with the average current density predicted with the Ilković equation. Parameters as in Fig. 3-1.
Fig. 3-6. The effect of $i_{o,\text{ref}}$ on attainment of the mass-transfer plateau. Curves are for a number of drops at constant potential formed sequentially.
TABLE 1. Parameters used for Fig. 3-6.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_i$</td>
<td>$5.81 \times 10^{-6}$ mol/cm³</td>
</tr>
<tr>
<td>$\alpha_d$</td>
<td>1.5</td>
</tr>
<tr>
<td>$\alpha_c$</td>
<td>0.5</td>
</tr>
<tr>
<td>$D_i$</td>
<td>$7.5 \times 10^{-6}$ cm²/s</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>0.54373 (ohm-cm)$^{-1}$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.10 cm/s$^{1/3}$</td>
</tr>
<tr>
<td>$t_{\text{drop}}$</td>
<td>1.0 s</td>
</tr>
</tbody>
</table>

Parameters used by R. White and J. Newman.\textsuperscript{42}
The analysis considered above does not account for the capacitive current needed to charge the mercury-solution interface. To assess the effects of the capacitive current the total current can be expressed as

$$ I = I_f + I_{nf} $$

(3-25)

where for linear kinetics

$$ I_f = 4\pi r_o^2 i_{o,ref} \frac{F}{RT} (\alpha_a + \alpha_c) (V - \Phi_o - U_o) $$

(3-26)

The capacitive term is

$$ I_{nf} = \frac{d}{dt} \left[ 4\pi r_o^2 \left\{ q_o + C(V - \Phi_o - U_o) \right\} \right] $$

(3-27)

$q_o$ is the charge on the interface when $V - \Phi_o = U_o$. Substitution of Eq. (3-26) and (3-27) into Eq. (3-25) with use of Eq. (3-8) yields

$$ 4\pi \kappa \gamma t^{1/3} \Phi_o = 4\pi \gamma t^{1/3} i_{o,ref} \frac{F}{RT} (\alpha_a + \alpha_c) (V - \Phi_o - U_o) $$

$$ + \frac{8\pi \gamma^2}{3t^{1/3}} \left[ q_o + C(V - \Phi_o - U_o) \right] - 4\pi \gamma t^{2/3} C \frac{d\Phi_o}{dt} $$

(3-28)

This equation can be rearranged to show the importance of the faradaic and nonfaradaic contribution to the total current

$$ tC \frac{d}{dt} \left( 1 - \frac{\Phi_o}{V - U_o} \right) + \frac{2}{3} C \left( 1 - \frac{\Phi_o}{V - U_o} \right) + \frac{i_{o,ref}(\alpha_a + \alpha_c)Ft}{RT} \left( 1 - \frac{\Phi_o}{V - U_o} \right) $$

$$ = - \frac{2}{3} \frac{q_o}{(V - U_o)} + \frac{\kappa \Phi_o t^{1/3}}{\gamma(V - U_o)} $$

(3-29)

The last term on the left side of Eq. (3-29) is the result of the faradaic
process, the last term on the right side represents the total current, whereas the remaining terms account for the nonfaradaic process.

The charging current, represented by the second term in Eq. (3-29), should be considered for

\[ t < \frac{2}{3} \frac{CRT}{i_{o,ref}(\alpha_a + \alpha_c)F} \]  

For typical values of the parameters \( C = 30 \mu F/cm^2 \), \( i_{o,ref} = 10^{-1} A/cm^2 \), and \( (\alpha_a + \alpha_c) = 1 \), the nonfaradaic current is equivalent to the faradaic current at about 5 ms.

The above criterion expressed in Eq. (3-30) actually apply only for

\[ \frac{i_{o,ref}(\alpha_a + \alpha_c)}{2\kappa} \frac{FY}{RT} \left( \frac{CY}{3\kappa} \right)^{3/2} < 1 \]  

(the usual case). In the contrary case, the charging current (represented by the first term in Eq. (3-29)) would need to be considered for

\[ t < \left( \frac{CY}{3\kappa} \right)^{3/2} \]  

One should be reminded that Eq. (3-29) has not considered mass-transfer effects.

**Summary and Conclusions**

A model is presented for the current and potential distributions of a dropping-mercury electrode below the limiting current. Results are dependent upon a potential parameter \( E \) and an additional parameter \( K \) which reflect the relative importance of the kinetic, ohmic, and mass-
transfer resistances. For relatively large values of these parameters, the instantaneous current density of a metal deposition reaction in the presence of an excess of supporting electrolyte can exceed the mass-transfer limiting value given by Ilković.
4. MASS TRANSFER TO ROTATING DISK AND ROTATING RINGS IN LAMINAR, TRANSITION, AND FULLY DEVELOPED TURBULENT FLOW

Introduction

On rotating disks and rotating rings, the flow regime may vary from laminar near the center to fully developed turbulent flow near the periphery. The fundamentals of fluid flow and mass transfer are well characterized in laminar flow. However, transition flow, existing between laminar and fully developed turbulent flow, along with the developed turbulent flow regime have not been described to the same extent. Correlations of experimental results form the basis of most of the available information concerning the mass-transfer rates for these systems.

Mohr and Newman\textsuperscript{43} provide experimental results for the Sherwood number in the laminar, transition, and fully developed turbulent regions of a rotating disk. In addition, they considered the transition region to exist for Reynolds numbers from $2 \times 10^5$ to $3 \times 10^5$. This range is similar to values reported by Gregory, Stuart and Walker,\textsuperscript{44} Cobb and Saunders,\textsuperscript{45} Kreith, Taylor and Chong,\textsuperscript{46} Tien and Campbell,\textsuperscript{47} Ellison and Cornet,\textsuperscript{48} and Chin and Litt.\textsuperscript{49} For the transition region Mohr and Newman give

$$\bar{Sh} = (9.7 \times 10^{-15} \, Re^3 + 0.89 \times 10^5 \, Re^{-\frac{1}{2}}) \, Sc^{\frac{1}{2}}$$

(4-1)

and for fully developed turbulent flow

$$\bar{Sh} = (0.0078 \, Re^{0.9} - 1.3 \times 10^5 \, Re^{-\frac{1}{2}}) \, Sc^{\frac{1}{2}}$$

(4-2)

where the Sherwood number is defined for disks or rings as
Additional studies of mass transfer to a rotating disk have been reported by Ellison and Cornet as

\[
\overline{Sh} = \frac{\overline{r_o}}{nFDC_\infty} = \frac{r_o \int_{r_i}^{r_o} 2\pi r \, dr}{\pi (r_o^2 - r_i^2) nFDC_\infty} \quad (4-3)
\]

and also by Daguenet\textsuperscript{50} as

\[
\overline{Sh} = 0.0117 \, Re^{0.896} \, Sc^{0.249} \quad \text{for} \quad Re > 10^6 \quad (4-4)
\]

The different Schmidt and Reynolds number dependences are indicative of the scatter in the data. Modification of the multiplicative constant and the two exponents makes it possible to represent the data, due to scatter, with slightly different expressions. Because of the scatter in the data, it is also difficult to distinguish between a 1/3- and 1/4-power Schmidt number dependence.

Average mass-transfer rates are measured and hence average-Sherwood number correlations are obtained directly. The data must be differentiated to obtain information on local mass-transfer rates. Differentiation of data with considerable scatter may not give reliable information. To model accurately mass-transfer processes on a rotating disk (as in corrosion), reliable local mass-transfer rates are required. Therefore, the approach taken here is to develop a model from which local mass-transfer rates can be calculated. These local rates can then be integrated for comparison with measured average mass-transfer rates. This general approach was used by Kader and Dil'man\textsuperscript{51} in pipe flow.
In the study of corrosion on a rotating disk, local mass-transfer rates are needed when the mass transfer commences at an arbitrary radial position on the surface. This is analogous to rotating rings with different thicknesses. Daguenet\textsuperscript{50} and Delouis and Keddam\textsuperscript{52} have investigated mass-transfer rates on ring electrodes of various dimensions in the transition and turbulent regimes. Data taken by Delouis and Keddam on thick rings support a 0.9 exponent on the Reynolds number, similar to disk correlations. However, for thin rings the data gave rise to an exponent of 0.6. These authors also reported measured values of the limiting current for thin rings in transition and turbulent flow which lie below the Levich\textsuperscript{53} relationship for thin rings. This deviation in limiting currents cannot be explained in terms of radial diffusion. Newman\textsuperscript{54,55} has considered the importance of radial diffusion to a flat plate and to a rotating disk at the limiting current. Radial diffusion is important in a very small region and its effect is to increase the mass-transfer rate.

From an analytic viewpoint, few models exist which describe the mass transfer to rotating disks and rotating rings beyond the laminar flow region. Chin and Litt\textsuperscript{49} express the Sherwood number for thin rings in terms of the shear stress. Cognet and Daguenet\textsuperscript{56} along with Kornienko and Kishinevskii\textsuperscript{57} have presented models for disks and rings in turbulent flow. In the work by Kornienko and Kishinevskii the problem was solved for developed and undeveloped diffusion boundary layers. They also state that it is not possible to distinguish between the 1/3 and 1/4 Schmidt number dependence from rotating ring data due to the different levels of development of the diffusion boundary layer.
An approach to solving heat and mass-transfer problems in turbulent flow without a priori solution of the Navier-Stokes equations was presented by Spalding some time ago. Spalding's results are for a Prandtl number of one. This work has been the subject of further investigation, review, and extension by Kestin and Presen, Kestin and Richardson, and Donovan, Hanna and Yerazunis. Numerical results have been presented by Smith and Shah for low Prandtl numbers and extensive tabulations were presented by Gardner and Kestin for Prandtl numbers up to 1000. Although the model developed herein is based on solving the time averaged convective-diffusion equation in terms of the Lighthill variable, we would be remiss not to mention the applicability of Spalding's transformation for two-dimensional and axisymmetric problems with high Schmidt numbers. However, both approaches are comparable in that the shear stress is required in addition to a form for turbulent transfer near the wall, but solution of the Navier-Stokes equations is not required.

Model Development

The boundary layer form of the time-averaged convective-diffusion equation is the governing equation for mass transfer,

\[ v_r \frac{\partial \Theta}{\partial r} + v_y \frac{\partial \Theta}{\partial y} = \frac{\partial}{\partial y} \left[ (D + D(t)) \frac{\partial \Theta}{\partial y} \right] \]  

\[ \Theta \to 1 \text{ as } y \to \infty , \]

\[ \Theta = 0 \text{ at } y = 0 , \quad r > r_i , \]

\[ \Theta = 1 \text{ at } y = 0 , \quad r < r_i . \]

\( v_r \) can be expressed as
\[ v_r = \beta(r)y \quad , \tag{4-7} \]

and \( v_y \) is given by the equation of continuity as

\[ v_y = -\frac{1}{2}y^2 \frac{(r\beta)'}{r} \quad . \tag{4-8} \]

With the Lighthill variable

\[ \xi = \frac{y\sqrt{r\beta}}{\left[ 9D \int_{r_1}^r \frac{r\sqrt{r\beta}}{dr} \right]^{1/3}} \quad , \tag{4-9} \]

Eq. (4-6) can be expressed as

\[ \frac{\xi}{r\sqrt{r\beta}} \left[ 9 \int_{r_1}^r \frac{r\sqrt{r\beta}}{dr} \right] \frac{\partial \Theta}{\partial r} = 3\xi^2 \frac{\partial \Theta}{\partial \xi} + \frac{\partial}{\partial \xi} \left[ \left( 1 + \frac{D(t)}{D} \right) \frac{\partial \Theta}{\partial \xi} \right] \quad . \tag{4-10} \]

At this point it is appropriate to comment on the form for \( D(t)/D \) or alternatively \( D(t)/\nu \). The concept of the universal velocity profile for fully developed turbulent flow suggests that \( D(t)/\nu \) depends only on a dimensionless distance \( y^+ \) from the wall, in the form

\[ y^+ = \left( \frac{y}{\nu} \right) \sqrt{\frac{\tau_o}{\rho}} \quad , \]

where \( \tau_o \) is the shear stress equal to \( \mu \beta \).

Expansion of the velocity components in terms of \( y^+ \) shows that near the wall \( D(t)/\nu \) must be proportional to the cube of \( y^+ \) or a higher power of \( y^+ \). With this in mind, many researchers\(^{65-72}\) have expressed theoretical or experimental results in terms of

\[ \frac{D(t)}{\nu} = Ky^3 = K \left( \frac{y}{\nu} \sqrt{\frac{\tau_o}{\rho}} \right)^3 \quad , \tag{4-11} \]

whereas other investigators\(^{58,73-77}\) prefer
Levich\textsuperscript{78} initially advocated the $y^3$ form but subsequently\textsuperscript{79} expressed a preference for Eq. (4-12). The form used in Eq. (4-10) will be kept sufficiently general so that a decision concerning the form of $D(t)/\nu$ can be made in view of experimental and theoretical results. For this reason we let

$$\frac{D(t)}{\nu} = K y^3 d(y^+) \quad (4-13)$$

where $d(y^+)$ is a function of $y^+$. For simplicity, $d(y^+)$ can be considered 1, and Eq. (4-11) is recovered. Substitution into Eq. (4-10) with the definitions

$$R = \sqrt{Re} = \frac{\sqrt{\Omega/\nu}}{r} \quad (4-14)$$

$$X = \frac{9K}{\sqrt{\Omega}} \left( \frac{\Omega}{\nu} \right)^{5/4} \sqrt{r \beta} \ dr = 9K \int_{R_i}^{R} \sqrt{R \beta} \ dR \quad (4-15)$$

$$\beta = \frac{\tau_0}{\mu \Omega} \quad (4-16)$$

that simplify the governing equation and boundary conditions to

$$9\xi \frac{\partial \Theta}{\partial \xi} = 3\xi^2 \frac{\partial \Theta}{\partial \xi} + \frac{3}{\partial \xi} \left[ \left( 1 + \frac{X \xi^2 d(X, \xi)}{R^{3/2}} \right) \frac{\partial \Theta}{\partial \xi} \right] \quad (4-17)$$

$$\Theta = 1 \quad \xi = \infty$$
$$\Theta = 0 \quad \xi = 0 \quad X > 0$$
$$\Theta = 1 \quad \xi = 0 \quad X < 0$$
When \( X = 0 \), Eq. (4-17) simplifies to

\[
\frac{d^2 \Theta}{d \xi^2} + 3 \xi^2 \frac{d \Theta}{d \xi} = 0
\]

This equation is analogous to the equation given by Leveque, with the solution

\[
\Theta = \frac{1}{\Gamma(4/3)} \int_0^\infty e^{-y^3} dy
\]

For \( X > 0 \), Eq. (4-17) is solved using a Crank-Nicholson procedure. The procedure is efficient and stable.

The local and average Sherwood numbers can be expressed as

\[
Sh_{\text{loc}} = \frac{ir}{nFDC_\infty_{\omega}} = \left. \frac{\partial \Theta}{\partial \xi} \right|_{\xi=0} R^{3/2} \sqrt{\frac{\beta}{\Omega}} \left( \frac{KSc}{X} \right)^{1/3}
\]

\[
\overline{Sh} = \frac{\int_{R_i}^{R_o} \left. \frac{\partial \Theta}{\partial \xi} \right|_{\xi=0} R^{3/2} \sqrt{\frac{\beta}{\Omega}} \left( \frac{KSc}{X} \right)^{1/3} dR}{(R_o^2 - R_i^2)}
\]

The term \( X \xi^3 d(X, \xi)/R^{3/2} \) in Eq. (4-17) accounts for the turbulent contribution to the mass transfer rate. Equation (4-17) must be modified slightly to describe the three different transport mechanisms on the surface. A function \( f(R) \) is introduced:

\[
9X \xi \frac{\partial \Theta}{\partial \xi} = 3 \xi^2 \frac{\partial \Theta}{\partial \xi} + \frac{2}{\partial \xi} \left[ \left( 1 + \frac{X \xi^3 d(X, \xi) f(R)}{R^{3/2}} \right) \frac{\partial \Theta}{\partial \xi} \right]
\]

where \( f(R) \) is defined as
\[
f(R) = 0 \quad \text{Re} \leq 2.0 \times 10^5 \quad (4-23a)
\]
\[
f(R) = \frac{R - \sqrt{2 \times 10^5}}{\sqrt{3 \times 10^5} - \sqrt{2 \times 10^5}} \quad 2.0 \times 10^5 \leq \text{Re} \leq 3.0 \times 10^5 \quad (4-23b)
\]
\[
f(R) = 1 \quad \text{Re} \geq 3.0 \times 10^5 \quad (4-23c)
\]

For laminar flow, the turbulent contribution to mass transfer disappears, since \(f = 0\). Equation (4-17) is recovered for fully developed turbulent flow. The linear dependence of \(f(R)\) with \(R\) in the transition region was found to describe the data adequately.

The Reynolds-number dependence of the shear stress is different for the three regimes. In laminar flow, the results of Von Karman\(^81\) yield
\[
\frac{B}{\Omega} = aR \quad (4-24)
\]

Such theoretically well established results are not available for the shear stress in fully developed turbulent flow. However, Von Karman's\(^81\) semi-empirical expression is available from a momentum balance using the 1/7-power velocity profile form commonly used in turbulent pipe flow. The result of Von Karman's work is used in the form
\[
\frac{B}{\Omega} = 8.55 \times 10^{-3} R^{1.6} \quad (4-25)
\]

Torque measurements on rotating disks are reported by Schlichting\(^82\) in the form of torque coefficients. The angular shear stress is available from these studies. Surprisingly, its radial counterpart has not been explicitly reported nor correlated. Von Karman's expression is compatible with the torque measurements, the flux expression given in the Appendix, and the results of mass-transfer correlations.
In the transition region, the shear stress is made continuous with the forms for laminar and fully developed turbulent flow. With the experimental results of rotating ring electrodes in mind, the Reynolds-number limits were set as $1.5 \times 10^5$ to $3.0 \times 10^5$ for the transition region shear stress. These limits are slightly different for those for $f(R)$. A graph of the shear stress is given in Fig. 1.

To fit the rotating-disk data for fully developed turbulent flow (Eq. (4-2)), the shear stress and $K$ must be consistent with the experimental mass-transfer correlation. Equation (A-10), developed in the Appendix, for $d(y^+)=1$, expresses the Sherwood number in terms of $K$ and $\beta/\Omega$ as

$$Sh_{loc} = 0.01092 R^{1.8} Sc^{1/3} = R^{(\beta/\Omega)^{1/2}} (K Sc)^{1/3} \frac{1.2092}{1.2092} \quad (4-26)$$

For $\beta/\Omega$ given by Eq. (4-25), $K = 2.9116 \times 10^{-3}$.

It is convenient and helpful to have the mass-transfer flow rate for extremely thin rings. Taking $\beta/\Omega$ as constant and the derivative as $1/\Gamma(4,3)$, Eq. (4-20) can be expanded and rearranged to yield

$$Sh_{loc} = \frac{1}{\Gamma(4/3)} \left( \frac{\beta}{3\Omega} \right)^{1/3} \frac{R^{5/3}}{(R^3 - R_i^3)} \frac{Sc^{1/3}}{1.2092} \quad (4-27)$$

In particular, for laminar flow, this reduces to (see Ref. 53)

$$Sh_{loc, lam} = \frac{(a/3)^{1/3}}{\Gamma(4/3)} \frac{R^2 Sc^{1/3}}{(R^3 - R_i^3)^{1/3}} \quad (4-28)$$

Comparison of Eq. (4-27) with (4-28) shows the importance of the shear stress:
Fig. 4-1. The Reynolds number dependence of the radial shear stress.
To consider average mass-transfer rates, Eq. (4-27) is integrated for thin-ring conditions to give

\[
\frac{Sh_{loc}}{Sh_{loc,\text{lam}}} = \left(\frac{\beta}{aR\Omega}\right)^{1/3}.
\]  

(4-29)

An analogous expression for laminar flow can be obtained so that the ratio of average Sherwood numbers is also given by Eq. (4-29) and is the ratio of the measured current to the current if laminar flow prevailed.

\[
\frac{\overline{Sh}}{Sh_{\text{lam}}} = \left(\frac{\beta}{aR\Omega}\right)^{1/3} \frac{Sc^{1/3}}{6\Gamma(4/3)} = \frac{I}{I_{\text{lam}}}
\]  

(4-31)

The last equality is important from a practical point since total currents are measured from limiting current experiments.

Experimental Data

Data presented in figure 4-4 are the results of limiting current experiments performed by Pierini.\(^{85}\)

Results and Discussion

The results presented in the ensuing figures are for \(d(y^+) = 1\), that is, \(D(t)/\nu = Ky^{+3}\). Subsequent comments will be made concerning a \(y^+\)-dependence of \(D(t)/\nu\).

Figure 2 shows the results for average mass-transfer rates on a
Fig. 4-2. Overall mass-transfer rate vs. Reynolds number for laminar, transition, and turbulent regimes. The Schmidt number for the data of Mohr and Newman: □ 1192, △ 1377, +1636, ○ 1760, × 2465; for the data of Daguenet: ● 1212, ▲ 1980. The calculated results (—) are obtained from the solution of Eq. (4-22) with $K = 2.9 \times 10^{-3}$. 
rotating disk compared to data given by Mohr and Newman\textsuperscript{43} and Daguenet\textsuperscript{50}. Agreement between the two is obtained over a considerable range of Reynolds numbers. The lines marked $f(R) = 0$ or $f(R) = 1$ are provided for reference. Note that absence of the eddy diffusivity term, $f = 0$, may result in an average flux below the corresponding laminar flow value.

In Fig. 3 the local value of the mass-transfer rate from the calculations is given. At a Reynolds number of $1.5 \times 10^5$, the local Sherwood number drops below the laminar prediction due to the influence of the shear stress. However, at $2.0 \times 10^5$ the importance of turbulence in the transition region is seen as the eddy diffusivity term causing the local rate to increase. Finally, the full impact of turbulence exists at $3.0 \times 10^5$ and beyond.

The data from Pierini's experiments with rotating ring electrodes are given in Fig. 4. The current is made dimensionless with the current calculated as though laminar flow conditions existed. This normalization is particularly convenient for thin rings. Data are from the experiments described above. Agreement of the data with the calculations is adequate at low Reynolds numbers; however, at higher values the calculated results exceed the measurements. The rotating rings considered here are quite thin. Even so, the calculated current very rapidly approaches the rotating-disk result with increases in rotation speed. Somewhat surprisingly, the measured flux is below the laminar flow relationship, in transition and fully developed turbulent flow.

This fact led to our choice of Von Karman's expression for the radial shear stress, since it also lies below the laminar flow value for a certain range of Reynolds numbers, and it was anticipated that this
Fig. 4-3. Local mass-transfer rate on a disk electrode vs. Reynolds number.
Fig. 4-4. The results of Pierini's mass transfer experiments on rotating rings compared to the results of the calculations (Eq. (4-22) with $K = 2.9 \times 10^{-3}$.
could lead to a similar behavior for the mass-transfer rate in the thinring limit. On the other hand, expressions for the shear stress available from torque measurements always lie above laminar flow results and differ substantially from the measurements made on thin ring electrodes.

From the data presented in Fig. 4 and from the lines representing thin rings, it is clear that mass transfer in transition and turbulent flow can be less than that given by the laminar-flow expression. The results of the analysis show that the mass-transfer rate normalized with the laminar rate depends only upon the shear stress value.

Epelboin and his coworkers have performed mass transfer experiments with thin rings in the presence of small amounts of drag-reducing compounds. Their results indicate qualitatively that small changes in the concentration of drag-reducing compounds cause a decrease in the mass-transfer rate, as well as the angular shear stress (torque), in transitional and turbulent flow. A representation of one of their graphs is given in Fig. 5.

Figure 6 is a comparison of the data taken by Delouis and Keddam for a relatively thick ring, \( r_1/r_0 = 0.6 \). The comparison is good for all three regions.

Local mass-transfer rates representative of a number of different conditions are presented in Fig. 7.

From the curves in Fig. 7, the local mass-transfer rate on rotating rings is high at the beginning of the mass-transfer region and approaches the rotating disk results downstream of the inner radius. This is true whether the diffusion boundary layer begins in laminar, transition, or fully developed turbulent flow. However, it is interesting
Fig. 4-5. Qualitative illustration from Ref. 41 denoting the effect of increasing concentration of drag reducing agent on the mass transfer rate for thin rotating rings.
Fig. 4-6. Comparison of the mass-transfer data of Delouis and Keddam\(^5\) on a rotating ring for dimensions \(r_1/r_0 = 0.6\) with the results of the calculations (Eq. (4-22) with \(K = 2.9 \times 10^{-3}\)).
Fig. 4-7: Local mass-transfer rate for rotating rings of various dimensions. The Reynolds number designation on the respective curves denotes the point at which mass transfer begins.
to note that the sharp decline in the local Sherwood number observed near the inner edge of the ring is more pronounced in fully developed turbulent flow than in laminar flow. The mass-transfer entry length region in fully developed turbulent flow is shorter than in laminar flow. Newman comments on this with regard to pipe flow.

It is worth mentioning that the discrepancy between measured and calculated values observed in Fig. 4 occurs in the development of the turbulent mass-transfer boundary layer. However, from Fig. 6 it is clear that the model does a good job of describing the average flux for thick rings, where the turbulent diffusion layer is more developed.

The results presented above are for \( \frac{D(t)}{\nu} = 2.9 \times 10^{-3} (y^+)^3 \). In an attempt to obtain a better fit of the thin-ring data in transition and turbulent flow, \( d(y^+) \) can be modified so that \( \frac{D(t)}{\nu} = Ky^+^3(1 + K_1y^+) \). With the value of \( K \) from Lin, Moulton and Putnam, the disk results are fit reasonably well with the expression

\[
\frac{D(t)}{\nu} = 3.28 \times 10^{-4} y^+^3(1 + 19.3 y^+) \quad (4.32)
\]

In Fig. 8, \( \frac{D(t)}{\nu} \) is presented for these two forms in addition to the expression by Wasan, Tien and Wilke. The form by Wasan, Tien and Wilke would fit the thin-ring data better than the two alternative forms, at the expense of a worse fit of the rotating-disk data in fully developed turbulent flow.

Only for very small values of \( y^+ \) is the \( y^+^3 \), \( y^+^5 \) form smaller than the \( y^+^3 \) form \( (y^+ \leq 0.41) \). However, even with this more involved form, the thin-ring results in transition and turbulent flow are substantially the same. It is not possible to distinguish between
Fig. 4-8. Dependence of the eddy diffusivity upon the form used near the wall. $2.9 \times 10^{-3} y^3$: ——,
$3.3 \times 10^{-4} y^3 (1 + 19.3 y^+)$: ————, form used by Wasan, Tien and Wilke: ————.
these two forms from the data on rotating disks and rotating rings. Due to the simplicity of the governing equation with $Ky^+^3$, this form is preferred.

**Summary and Conclusions**

A model is presented for the mass-transfer rate to rotating rings and rotating disks when laminar, transition, and turbulent flow exist upon different portions of the surface. The model compares well to rotating-disk data and to data for relatively thick rotating rings, existing in the literature. For the data presented herein on thin rotating rings, the calculated results may exceed the measured mass-transfer rate in the transition and fully developed turbulent flow regimes. The contribution of the eddy diffusivity term to the overall mass transfer is too high, even for these thin rings. A $y^+^3$ form for the eddy diffusivity is used. However, no improvement in the comparison with the thin ring data was obtained for a $y^+^3$, $y^+^4$ form.
5. CORROSION OF IRON

Introduction

The rotating disk is an excellent system for the study of localized corrosion. Much is known about fluid flow, mass transfer, and electrochemical kinetics on a rotating disk in laminar flow. However, because the mass transport rate is uniform across the surface in laminar flow, a uniform corrosion rate occurs. Consequently, laminar flow results do not reveal much information concerning the interaction of ohmic drop, electrochemical kinetics, and mass transfer to determine overall corrosion rates. Whereas, in transition flow and fully developed turbulent flow, the nonuniform mass transfer rate is compatible with a non-uniform heterogeneous reaction rate distribution. In Chapter 4, the mass transfer rates in transition and turbulent flow were calculated, which can be used here to calculate corrosion rates on a disk in transition and fully developed turbulent flow.

LaQue reports the results of corrosion experiments with rotating disks in sea water. The interesting feature of the results is the difference in behavior between iron and copper disks. For copper disks the most severe corrosion attack occurred near the periphery with the central region almost unattacked. But the iron disks were corroded near the center and not near the edge. In photographs of iron disks given by LaQue, one can see the clear demarcation between the attacked region in the center and the low corrosion rate region near the edge.

For the 3, 4, and 5 inch iron disks rotated at 122/sec by
LaQue, portions near the periphery of the disks can be in fully developed turbulent flow. In their calculations, Vahdat and Newman obtained results qualitatively similar to LaQue's experimental results with iron disks. However, due to the form of the kinetic expression used and without the benefit of detailed mass transfer calculations, their results show the possibility of the experimental observations. However, the conditions are not the same as in the experiments. Results presented here are aimed at removing some of the limitations of the earlier work in an effort to match the experimental results more closely.

Model Development

In an oxygenated salt solution, the corrosion reactions can be expressed as:

\[
\text{Fe} \rightarrow \text{Fe}^{++} + 2e^- \quad (5-1)
\]

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (5-2)
\]

The rates of each reaction vary across the surface. For corrosion to occur the total current from the anodic reaction must balance the total cathodic current, hence

\[
I = 0 = I_{\text{Fe}} + I_{\text{O}_2} \quad (5-3)
\]

Since iron is an active-passive metal, the electrochemical reaction is dependent upon the potential range under consideration. For values of \(V - \phi_0 \leq (V - \phi_0)_*\), the reaction is considered active, whereas the disk is covered by a passive film at larger potentials. From Pourbaix's results it is possible to obtain the current density at \((V - \phi_0)_*\).
(V - \Phi_0)_* is the value used by Vahdat corresponding to the maximum iron current possible.

**Electrochemical Kinetics**

Corrosion of an iron rotating disk in an oxygenated salt solution is an example of the occurrence of simultaneous electrochemical reactions. An individual reaction can be written in the general form

$$ \sum_i s_{ij} M_i^{z_i} + n_j e^- $$

(5-4)

where $n_j$ is the number of electrons transferred, $s_{ij}$ is the stoichiometric coefficient for species $i$ in reaction $j$, $M_i$ represents chemical species $i$ with charge $z_i$. The local rate of each individual reaction is given by $i_j$ and is related to the total rate by

$$ i_T = \sum_j i_j $$

(5-5)

The flux of an individual species at the surface is related to its participation in each reaction by

$$ N_i(r) = -\sum_j s_{ij} \frac{i_j}{n_j F} $$

(5-6)

A Butler-Volmer expression can be used to express the local current density of each reaction $i_j$ in terms of the local value of the surface over potential.

$$ i_j = i_{0,j} \left[ \frac{\alpha_a F}{e RT} \eta_s - \frac{-\alpha_c F}{e RT} \eta_s \right] $$

(5-7)

The exchange current density can be written as
\begin{equation}
\nu_{0,j}^{\text{cat}} = \nu_{0,j}^{\text{ref}} \prod_i \left( \frac{C_i^{\text{cat}}}{C_i^{\text{ref}}} \right)^{\gamma_{ij}} \tag{5-8}
\end{equation}

\begin{equation}
\gamma_{ij} = q_{ij} + \frac{\alpha_{ij}s_{ij}}{n_j} \tag{5-9}
\end{equation}

where \( q_{ij} = -s_{ij} \) for a cathodic reactant and zero otherwise. The surface overpotential is defined by

\begin{equation}
\eta_j = V - \phi_0 - U_j^{\text{ref}} \tag{5-10}
\end{equation}

\( V \) is the potential of the iron disk; \( \phi_0 \) is the potential in the solution just outside the double layer; and \( U_j^{\text{ref}} \) is the theoretical open circuit cell potential for reaction \( j \). \( U_j^{\text{ref}} \) is expressed as

\begin{equation}
U_j^{\text{ref}} = U_j^{\theta} - U_{\text{ref}}^{\theta} - \frac{RT}{n_jF} \sum_i s_{ij} \ln \left( \frac{C_i^{\text{cat}}}{\rho_0} \right) + \frac{RT}{n_{\text{ref}}F} \sum_i s_{i,\text{ref}} \ln \left( \frac{C_i^{\text{ref}}}{\rho_0} \right) \tag{5-11}
\end{equation}

provided that activity-coefficient corrections can be neglected. For the work given here the saturated calomel electrode is chosen as the specific reference electrode. With the definitions given above, the expressions for the iron and oxygen current densities can be expressed as
The expression for the iron current density applies only to the active region where $V - \Phi_0 \approx (V - \Phi_0)^* = 0.20$ for the passive region existing for larger $V - \Phi_0$.

Note that the transfer coefficients are not subscripted for the respective reactions, but are of course different for each.

Potential Distribution

From previous work on rotating disk systems, the solution of Laplace's equation for the potential can be expressed as

$$\phi(\eta, \xi) = \sum_{n=0}^{\infty} Q_n P_{2n}(\eta) M_{2n}(\xi)$$

(5-15)
where \( n \) and \( \xi \) are rotational elliptic coordinates. These are related to cylindrical coordinates by

\[
y = r_0 \xi \eta
\]

\[
r = r_0 \sqrt{(1 + \xi^2)(1 - \eta^2)}
\]

(5-16)

(5-17)

\( P_{2n}(\eta) \) is the Legendre polynomial of order \( 2n \). \( M_{2n}(\xi) \) is the Legendre function of imaginary argument defined so that \( M_{2n} = 1 \) at \( \xi = 0 \).

The diffusion layer is also considered thin enough so that the local current density can be obtained from the sum of the partial currents or from the potential derivative at the surface. An additional equality is added to equation 5 to give

\[
i_T = \sum_j i_j = -K_{\infty} \frac{\partial \phi}{\partial y} \bigg|_{y=0}
\]

(5-18)

From the orthogonal properties of Legendre polynomials the constants in the series solution for the potential distribution are given as

\[
Q_n = \left[ P_{2n}(0) \right]^2 \frac{(4n+1)\pi r_0}{2K_{\infty}} \int_0^1 n_i_T P_{2n}(\eta) \, d\eta
\]

(5-19)

To obtain the potential distribution when the iron current density can discontinuously change from the value given by equation 12 at \( V = \Phi_0 = (V - \Phi_0)^* \) at position \( r_p \) to \( i = i_p \), it is convenient to consider the potential associated with each reaction differently.

From equation 18 we can write

\[
i_T = (i_{Fe^{2+}} - i_p) + (i_{O_2} + i_p)
\]

(5-20)

The potential distribution is
\[ \Phi(\eta, \xi) = \sum_{n=0}^{\infty} B_n P_{2n}(\eta_p) M_{2n}(\xi_p) + \sum_{n=0}^{\infty} D_n P_{2n}(\eta) M_{2n}(\xi) \]  

(5-21)

where \( \eta_p \) and \( \xi_p \) are defined in equations 16 and 17 with \( r_0 \) replaced with \( r'_p \).

\[ B_n = \left[ P_{2n}(0) \right]^2 \frac{(4n+1)\pi r_p}{2K_\infty} \int_0^1 \eta_p (i_p^{Fe^{++}} - i_p) P_{2n}(\eta) d\eta_p \]  

(5-22)

\[ D_n = \left[ P_{2n}(0) \right]^2 \frac{(4n+1)\pi r_0}{2K_\infty} \int_0^1 \eta P_{2n}(\eta) d\eta \]  

(5-23)

The potential on the surface of the disk is given by

\[ \Phi_0(\eta, \xi = 0) = \sum_{n=0}^{\infty} B_n P_{2n}(\eta_p) M_{2n}(\xi_p) + \sum_{n=0}^{\infty} D_n P_{2n}(\eta) \]  

(5-24)

**Diffusion Layer**

In laminar flow for an excess of supporting electrolyte, the flux of minor species at the surface can be expressed in terms of a superposition integral. This result has been given by Smyrl and Newman\(^90\) in addition to others as

\[ \left. \frac{\partial C_i}{\partial \xi} \right|_{\xi=0} = -r \int_0^r \frac{dC_0}{dr} \left. \frac{dr'}{(r^3-r'^3)^{1/3}} \right|_{r=r'} \]  

(5-25)

When the flow regime departs from laminar flow, the integral must be modified to account for the effect of the hydrodynamics upon the mass transfer. In Chapter 4, a model was developed from which local mass transfer rates to a rotating disk are presented, in the absence of kinetic and ohmic limitations, when laminar, transition, and fully developed turbulent flow occur upon the surface. This solution can be
superimposed to obtain a superposition integral which is valid when ohmic and kinetic effects are relevant. A form of the integral is

\[
C_i = C_{i,\infty} + \int_0^z \frac{dC_i}{dz} \left|_{z=z'} \right. 1 - \Theta \left[(z, z', \zeta) \right] dz'
\] (5-26)

where

\[
z = 9K \int_0^R R \sqrt{R \frac{\beta}{\Omega}} dR
\] (5-27)

\[
R = \frac{r}{\sqrt{\Omega/v}}
\] (5-28)

\(\beta/\Omega\) is the radial shear stress. The forms for the three regions are

\[
\frac{\beta}{\Omega} = \frac{\alpha R}{R_0} \quad \text{Re} \leq 1.5 \times 10^5
\] (5-29a)

\[
\frac{\beta}{\Omega} = 97.47 R^{0.116} \quad 1.5 \times 10^5 \leq \text{Re} \leq 3.0 \times 10^5
\] (5-29b)

\[
\frac{\beta}{\Omega} = 8.55 \times 10^{-3} R^{1.6} \quad \text{Re} \geq 3.0 \times 10^5
\] (5-29c)

\(\Theta (z, z', \zeta)\) is the solution to the mass transfer problem governed by

\[
9xz \frac{\partial \Theta}{\partial x} = 3\zeta^2 \frac{\partial \Theta}{\partial \zeta} + \frac{\partial}{\partial \zeta} \left[ \left( 1 + \frac{xz^3 f(R)}{R^{3/2}} \right) \frac{\partial \Theta}{\partial \zeta} \right]
\] (5-30)

with boundary conditions

\[
\Theta = 1 \quad \zeta = \infty
\] (5-31a)

\[
\Theta = 0 \quad \zeta = 0 \quad x > 0
\] (5-31b)

\[
\Theta = 1 \quad \zeta = 0 \quad x < 0
\] (5-31c)

where

\[
x = 9K \int_{R_i}^R R \sqrt{R \frac{\beta}{\Omega}} dR
\] (5-32)
The function \( f(R) \) is defined by the following

\[
f(R) = \begin{cases} 
0 & \text{Re} \leq 2.0 \times 10^5 \\
\frac{R - \sqrt{2.0 \times 10^5}}{\sqrt{3.0 \times 10^5 - 2.0 \times 10^5}} & 2.0 \times 10^5 \leq \text{Re} \leq 3.0 \times 10^5 \\
1 & \text{Re} \geq 2.0 \times 10^5
\end{cases}
\]

\( \zeta \) is the Lighthill variable and is conveniently expressed in terms of \( x \) or \( z \) as

\[
\zeta = \left( \frac{\Omega^{1/2} \ K^{1/3}}{\nu^{1/3} \ D_1^{1/3}} \right) \frac{\sqrt{R / \Omega}}{x} \frac{1}{(z-z')^{1/3}}
\]

To obtain the concentrations at the surface and the current density distribution, the expression for the concentration derivative at the surface is the most useful form of the integral

\[
\frac{\partial C_i}{\partial y} \bigg|_{y=0} = - \left( \frac{\Omega^{1/2} \ K^{1/3}}{\nu^{1/3} \ D_1^{1/3}} \right) \sqrt{R / \Omega} \int_0^z \frac{dC_i}{dz} \bigg|_{z=z'} \frac{\Theta(z,z',z=0)dz'}{(z-z')^{1/3}}
\]

\( \Theta(z,z',z=0) \) represents \( \frac{\partial \zeta}{\partial \zeta} \bigg|_{\zeta=0} \) evaluated at position \( z \) for a step change in concentration that occurs at position \( z' \). Once should note that the integral in equation 35 is a stieltjes integral. In terms of a Riemann integral

\[
\frac{\partial C_i}{\partial y} \bigg|_{y=0} = - \left( \frac{\Omega^{1/2} \ K^{1/3}}{\nu^{1/3} \ D_1^{1/3}} \right) \sqrt{R / \Omega} \int_0^z \frac{dC_i}{dz} \bigg|_{z=z'} \frac{\Theta(z,z',z=0)dz'}{(z-z')^{1/3}}
\]

\[
- \left( \frac{\Omega^{1/2} \ K^{1/3}}{\nu^{1/3} \ D_1^{1/3}} \right) \Theta(z,z'=0,z=0) \left[ C_i(0) - C_i,\infty \right]
\]
Solution Technique

Equation 36 governs the mass transfer rate and equation 24 the potential distribution. As in earlier work\(^3\) one alternates between reviving the concentration distribution obtained from the mass transfer equation and the potential distribution, from the \(R_n\) and \(D_n\) constants.

The integral equation is divided evenly in \(r_0^3\). For each mesh point in \(r_0^3\) a corresponding value of \(z\) exists defined by equation 27. If laminar flow prevailed across the surface, the integral equation could be discretized in the efficient manner described by Acrivos and Chambré. However, since the flow regime varies across the surface it is necessary to evaluate the following integral between adjacent mesh points.

\[
\int_{Z_i}^{Z_{i+1}} \frac{\Theta'(Z_i, Z', \zeta=0)}{(Z-Z')^{1/3}} \, dZ' \tag{5-37}
\]

By considering the logarithm of the integrand to be linear in log \(R\), an analytic form is

\[
\ln \left[ \frac{Z-Z_{i+1}}{Z-Z_i} \right] - \ln \left[ \frac{\Theta'(Z, Z_{i+1}, \zeta=0)(Z-Z_{i+1})^{2/3}}{\Theta'(Z, Z_{i-1}, \zeta=0)(Z-Z_i)^{2/3}} \right] \tag{5-38}
\]

The discretized form of the integral equation is similar to the form
of Acrivos-Chambre\textsuperscript{40} except that the constants are expressed in terms of the factor given above.

Initially, one chooses the mesh point at which passivation occurs in addition to values for $B_n$ and $D_n$. The potential of the disk is obtained from specifying $(V-\Phi_0) = (V-\Phi_0)_\ast$ at $r = r_p$. Subsequently, one must alternate between calculating the concentration and current distribution from the mass transfer equation; and from calculating the potential distribution (actually $B_n$ and $D_n$) from the orthogonal properties of Legendre polynomials. This procedure is continued until the values of $B_n$ and $D_n$ do not vary. To ensure convergence, it was also necessary to damp the values from one iteration to another. After convergence for a specific point of passivation, the position was changed in a systematic manner and the procedure described above was repeated. The proper point of passivation for corrosion to occur is when $I_{Fe} + I_{O_2} = 0$.

**Results and Discussion**

In Figure 1 the results of the calculations are compared to the data presented by LaQue. The values for parameters and physical properties are given in Table 1. The comparison of the data with the model is qualitatively good. For comparable disk, passivation phenomena occurs; however the positions are not quite in harmony.

Figure 2 shows the local variation of oxygen and iron current densities in addition to the ohmic potential variation across the surface. The dip in the oxygen current density is due to the onset of transition flow. The point of passivation occurs at $r/r_0 = 0.86$. For the total iron current to balance the total oxygen current, the
Fig. 5-1. Comparison of the measured (---) and calculated (—) points of passivation for disks of different sizes.

\[ C_{O_2}, \alpha = 10^{-4} \text{ moles/litre} \]
\[ \kappa = 0.0462 \text{ (ohm cm)}^{-1} \]
\[ \Omega = 122/\text{sec} \]
Table 1

Parameters used in figures

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{O_2}$</td>
<td>$1.3 \times 10^{-5}$ cm$^2$/sec</td>
</tr>
<tr>
<td>$D_{OH^-}$</td>
<td>$5.26 \times 10^{-5}$ cm$^2$/sec</td>
</tr>
<tr>
<td>$D_{Fe^{++}}$</td>
<td>$0.739 \times 10^{-5}$ cm$^2$/sec</td>
</tr>
<tr>
<td>$C_{OH^-,\infty}$</td>
<td>$1.0 \times 10^{-7}$ moles/litre</td>
</tr>
<tr>
<td>$C_{Fe^{++},\infty}$</td>
<td>0</td>
</tr>
</tbody>
</table>
Fig. 5-2. Current and potential distributions.

\[ C_{O_2} = 10^{-4} \text{ moles/litre} \]
\[ \kappa = 0.0462 \text{ (ohm cm)}^{-1} \]
\[ \Omega = 122/\text{sec} \]
\[ r_0 = 6.35 \text{ cm} \]
iron current density is larger than the oxygen current density near the center to compensate for \( r_p < r_0 \) and for the oxygen current density being greater near the periphery.

The surface concentrations corresponding to the curves in Figure 2 are presented in Figure 3. Since oxygen is at the limiting current, its concentration is zero across the surface. The bulk concentration of \( \text{OH}^- \) is low. Therefore, the surface concentration is obtained from the bulk oxygen concentration. The iron concentration is obtained so as to obey the current distribution.

In Figure 4, the parameters remain the same as in Table 1 except the concentration is half as large. For the smaller concentration and hence smaller mass transfer rate the point of passivation moves inward since the iron reaction must be equivalent to a decreased oxygen rate. The curve for \( \phi_0 \) exhibits a minimum beyond the point of passivation. This is due to the difference in sign for the contribution from each reaction.

Figure 5 shows that an envelope exists beyond which only an entirely passive surface exists. For large disks the rotation speed must be low to avoid the region where only one solution exists.

The two curves representing two values of conductivity are as one would expect them to be (Figure 6). The current distribution is higher at the center and more uniform than the lower conductivity. Consequently, the value of \( r_p/r_0 \) is lower for the higher conductivity. It is interesting that for conductivity values lower than about 0.035 \((\text{ohm-cm})^{-1}\) corrosion will not occur since the iron current can not match the oxygen current due to the large ohmic potential.
Fig. 5-3. Dimensionless concentration distribution.

\[ \frac{c_{i,0}}{c_{O_2,0}} \]

- \( C_{O_2,0} = 10^{-4} \) moles/litre
- \( \kappa = 0.0462 (\text{ohm cm})^{-1} \)
- \( \Omega = 122/\text{sec} \)
- \( r_0 = 6.35 \text{ cm} \)
Fig. 5-4. Current and potential distributions.
Fig. 5-5. Envelope indicating region of passivity.
Fig. 5-6. The effect of conductivity on the corrosion rate distribution.
Summary and Conclusions

Results are presented for the electrochemical corrosion of an iron rotating disk when portions of the disk are not in laminar flow. The importance of solution conductivity, oxygen bulk concentration, and disk size on the overall results is illustrated. Good agreement is obtained between the results of this model and the experimental observations reported by LaQue.
Nomenclature

\( a \) 0.51023262

\( a_k \) relative activity of species \( k \)

\( B_n \) coefficient in the expansion for the potential

\( c_{Fe^{++}} \) concentration of ferrous ions at the electrode surface, mole/litre

\( c_{R,o} \) concentration of the limiting reactant at the electrode surface, mole/litre

\( c_{R,\infty} \) concentration of the limiting reactant in the bulk solution, mole/litre

\( C \) capacity of the double layer; \( c/V\text{-cm}^2 \)

\( c_i \) concentration of species \( i \), mole/cm\(^3\)

\( c_{i,o} \) surface concentration of species \( i \), mole/cm\(^3\)

\( c_{i,\text{ref}} \) reference concentration of species \( i \), mol/cm\(^3\)

\( c_{i,\infty} \) bulk concentration of species \( i \), mole/cm\(^3\)

\( c_{m,o} \) surface concentration of discharged metal, mol/cm\(^3\)

\( c_{m,\text{ref}} \) reference concentration of discharged metal, mol/cm\(^3\)

\( C_{\infty} \) bulk concentration, mol·cm\(^{-3}\)

\( D_i \) diffusion coefficient of species \( i \) in the electrolyte, cm\(^2\)/s

\( D_s \) diffusion coefficient of discharged metal in mercury, cm\(^2\)/s

\( d(y^+) \) function defined in equation (4-13)

\( D \) diffusion coefficient, cm\(^2\)·s\(^{-1}\)

\( D(t) \) eddy diffusivity, cm\(^2\)·s\(^{-1}\)

\( E \) complete elliptic integral of the second kind
E  dimensionless applied voltage, \( E = -\alpha_c \frac{F V}{RT} \)

F  Faraday's constant (96487 C/mol)

f  dimensionless ratio defined in reference 2-17

\( f(R) \)  function defined in equation (4-23)

\( g \)  normalized resistance, figure 2-24

\( g^0 \)  normalized resistance, figure 2-9

\( g^* \)  normalized resistance, figure 2-9

\( g^+ \)  normalized resistance, figure 2-9

\( g \)  function defined in equation (A-6)

i  local current density, A/cm²

\( i \)  instantaneous current density, A/cm²

\( i_j \)  local current density of reaction j, A/cm²

\( i_{\text{avg}} \)  average current density, A/cm²

\( i_{\text{avg}} \)  average current density defined by eq. (3-24)

\( \bar{i} \)  average current density, A·cm²

\( i_{\text{lim}} \)  current density in mass-transfer limit, as predicted with the Ilković equation, A/cm²

\( i_{\text{lim}} \)  limiting current density, A/cm²

\( i_{\text{lim,avg}} \)  average current density in mass transfer limit, A/cm²

\( i_p \)  current density on the passive portion of the disk, A/cm²

\( i_o \)  exchange current density, A/cm²

\( i_{o,\text{ref}} \)  exchange current density at reference concentrations of reactants and products, A/cm²

\( i_{o,j,\text{ref}} \)  reference exchange current density for reaction j, A/cm²

\( i_T \)  total current density, A/cm²
total current on the disk, $A$

$I$

total current, $A$

$I_{Fe}$

total current from the iron reaction, $A$

$I_{O_2}$

total current from the oxygen reaction, $A$

$K$

complete elliptic integral of the first kind

$K$

dimensionless parameter defined by eq. (3-20)

$K$

constant defined in equation (4-11)

$K_1$

constant defined in equation (4-32)

$k_a$

anodic rate constant, mole/sec cm$^2$

$k_c$

cathodic rate constant, cm/sec

$M_i$

symbol for the chemical formula of species $i$

$M_{2n}$

Legendre function of imaginary argument

$n$

number of electrons transferred

$n_j$

number of electrons transferred in reaction $j$

$n_{ref}$

number of electrons transferred in reference electrode reaction

$N_i$

flux of species $i$, mole/cm$^2$-sec

$N$

dimensionless parameter defined by eq. (3-19)

$p$

reaction order of limiting reactant, Chapter 2

$P_{2n}$

Legendre polynomial of order $2n$

$q_i$

reaction order for cathodic reactants

$q_o$

charge on the mercury-solution interface at open circuit, C/cm$^2$

$Q$

constant used in equation (A-1)
Q_n \quad \text{coefficient in the expansion for the potential, V}

r \quad \text{radial coordinate, cm}

r_i \quad \text{inner radius of the ring, cm}

r_o \quad \text{electrode radius, cm}

r_p \quad \text{drop radius, cm}

r_p \quad \text{radius of the active portion, cm}

R \quad \text{universal gas constant (8.2143 J/mol·K)}

R \quad \text{dimensionless radius, } r\sqrt{\Omega/v}

Re \quad \text{Reynolds number, } r^2\Omega/v

s_i \quad \text{stoichiometric coefficient of species i in electrode reaction}

s_i,\text{ref} \quad \text{stoichiometric coefficient of species i in reference electrode reaction}

S_{i,j} \quad \text{stoichiometric coefficient of species i in reaction j}

Sc \quad \text{Schmidt number, } \nu/D

Sh \quad \text{Sherwood number, } \nu/nFDC_o

t \quad \text{time, s}

T \quad \text{absolute temperature, K}

T_d \quad \text{drop lifetime, s}

U_o \quad \text{theoretical open-circuit potential for electrode reaction at the composition prevailing locally at the drop surface, relative to a reference electrode of a given kind, V}

U_{j,0} \quad \text{theoretical open circuit potential for electrode reaction j of the composition prevailing locally at the disk surface relative to a reference electrode of a given kind, V}
\[ V_M = \frac{U_0}{\Delta V} + \frac{F}{RT} \ln \left( \frac{C_{Cl_{ref}}}{} \right) \]

- \( V \): applied voltage, V
- \( V_r \): radial velocity, cm/s
- \( V_y \): axial velocity, cm/s
- \( (V-\phi_o)^* \): passivation potential, 0.28 V
- \( X \): dimensionless variable defined in eq. (4-15)
- \( y \): distance from drop surface, \( y = r - r_o \); cm
- \( y \): axial coordinate, cm
- \( y^+ \): dimensionless axial position
- \( Z \): stretched boundary layer variable defined in eq. (A-4)
- \( z \): axial coordinate, cm

**Greek Letters**

- \( \alpha_a \): transfer coefficient in anodic direction
- \( \alpha_c \): transfer coefficient in cathodic direction
- \( \beta \): constant in eq. (2-23), A·sec\(^{1/2}\)/cm\(^2\)
- \( \beta(r) \): proportionality of \( v_r \) with \( y \), s\(^{-1}\)
- \( \Gamma(4/3) \): 0.89298, the gamma function of 4/3
- \( \gamma \): constant defined by eq. (3-16)
- \( \gamma_i \): exponent in eq. (3-3) and defined by eq. (3-6)
- \( \gamma_k \): exponent in eq. (3-3)
- \( \varepsilon \): defined by eq. (2-21)
- \( \eta \): rotational elliptic coordinate
- \( \kappa \): bulk solution conductivity, ohm\(^{-1}\)·cm\(^{-1}\)
\[ \theta_i \quad \text{dimensionless reactant concentration, } \frac{c_{i,0}}{c_{i,\text{ref}}} \]

\[ \theta_m \quad \text{dimensionless product concentration, } \frac{c_{m,0}}{c_{m,\text{ref}}} \]

\[ \theta_m(0) \quad \text{initial dimensionless product concentration} \]

\[ \theta_s \quad \text{ratio of reference concentrations, } \frac{c_{m,\text{ref}}}{c_{i,\text{ref}}} \]

\[ \Theta \quad \text{dimensionless concentration} \]

\[ \mu \quad \text{viscosity, g cm}^{-1}\text{s}^{-1} \]

\[ \nu \quad \text{kinematic viscosity of the solution, cm}^{2}\text{s}^{-1} \]

\[ \rho_o \quad \text{density of pure solvent, g/cm}^3 \]

\[ \rho \quad \text{solution density, kg cm}^{-3} \]

\[ \xi \quad \text{rotational elliptic coordinate} \]

\[ \xi \quad \text{Lighthill variable} \]

\[ \tau_o \quad \text{shear stress at the surface, g cm}^{-1}\text{s}^{-2} \]

\[ \phi_o \quad \text{electric potential in the solution, immediately adjacent to the drop surface, V} \]

\[ \phi_o \quad \text{dimensionless electric potential, } \phi_o = \frac{\alpha}{c} \frac{F_r i}{\kappa RT} \]

\[ \phi^I, \phi^{II}, \phi^{III} \quad \text{potential in the solution, V} \]

\[ \phi_o \quad \text{solution potential immediately adjacent to the electrode surface, V} \]

\[ \Omega \quad \text{rotation speed of the disk} \]

**Subscripts**

i \quad \text{inner radial position}

o \quad \text{outer radial position}
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APPENDIX A
FULLY DEVELOPED MASS TRANSFER RATE IN FULLY DEVELOPED FLOW

The intent is to obtain an expression for the local flux in fully developed turbulent flow (as R approaches infinity). The governing equation is given in the text as Eq. (4-6). For fully developed turbulent flow at high Schmidt numbers, it is appropriate to use a form for the velocity near the wall which is compatible with torque measurements made in fully developed turbulent flow and the results of Von Karman,

\[ v_r = \frac{Qr^{1.6}y^{1.8}}{v^{0.8}} \]  \hspace{1cm} (A-1)

and from the equation of continuity

\[ v_y = -1.3Qr^{0.6}y^{0.8}y^2 \]  \hspace{1cm} (A-2)

Substitution of these two expressions into Eq. (4-6) gives

\[ \frac{Qr^{0.6}y^{1.8}}{v^{0.8}} r \frac{\partial \Theta}{\partial r} - 1.3y \frac{\partial \Theta}{\partial y} = \frac{\partial}{\partial y} \left[ (1 + D(t)) \frac{\partial \Theta}{\partial y} \right] \]  \hspace{1cm} (A-3)

A stretched variable can be defined as

\[ z = \frac{y^+(KSc)^{1/3}}{g(R)} \]  \hspace{1cm} (A-4)

which changes Eq. (A-4) to

\[ \frac{g^3 z}{\sqrt{Q} R^{1.8}} \left[ \frac{\partial \Theta}{\partial R} - R \frac{\partial \Theta}{\partial Z} \frac{Z}{g} \frac{d g}{d R} - 1.3 Z \frac{\partial \Theta}{\partial Z} \right] = K \frac{\partial}{\partial Z} \left[ 1 + g^3 z^3 \right] \frac{\partial \Theta}{\partial Z} \]  \hspace{1cm} (A-5)
If \( g \) becomes small as \( R \) increases, \( g^3 Z^3 << 1 \). Then we can use the Lighthill similarity solution (compare Eq. (4-18)), which gives

\[
g = \frac{9K}{3.3} \left[ \frac{R^{3.3} - R_{i}^{3.3}}{R^{1.5}} \right]. \tag{A-6}
\]

This is contradictory because here \( g \) increases with \( R \).

If \( g \) becomes large as \( R \) increases, \( g^3 Z^3 >> 1 \) and \( g \) can be cancelled on the left and right sides of the equation. The left side is then negligible for large \( R \), and the equation reduces to

\[
\frac{\partial}{\partial Z} \left( Z^3 \frac{\partial \Theta}{\partial Z} \right) = 0 \tag{A-7}
\]

which has no satisfactory solution near \( Z = 0 \).

Hence we are left with the conclusion that \( g \) must be constant as \( R \) increases, say \( g = 1 \). The left side is still negligible for large \( R \), and the equation reduces to

\[
\frac{\partial}{\partial Z} \left[ (1 + Z^3) \frac{\partial \Theta}{\partial Z} \right] = 0 \tag{A-8}
\]

The solution is

\[
\Theta = \frac{\int_{0}^{Z} \frac{dZ}{1 + Z^3}}{\int_{0}^{\infty} \frac{dZ}{1 + Z^3}} = \frac{\int_{0}^{Z} \frac{dZ}{1 + Z^3}}{1.2092} \tag{A-9}
\]

This then yields
\[
\text{Sh}_{10c} = r \left. \frac{\partial \Theta}{\partial y} \right|_{y=0} = r \left. \frac{\partial \Theta}{\partial z} \right|_{z=0} \left( \frac{\partial z}{\partial y^+} \right) \left( \frac{\partial y^+}{\partial y} \right)
\]

\[
= \frac{r(KSc)^{1/3}}{1.2092 \nu} \sqrt{\frac{\tau_0}{\rho}} = \frac{R(KSc)^{1/3}}{1.2092} \cdot \sqrt{\frac{\beta}{\Omega}} \quad \text{(A-10)}
\]

Equation (A-10) is a very useful relationship. Both the shear stress and the eddy diffusivity are involved in the expression for the transfer rate in fully developed mass transfer.
APPENDIX B

PROGRAM FOR THE ANODIC DISSOLUTION OF IRON IN SULFURIC ACID

The program SECLIN calculates the secondary current distribution to an electrode which is in the active state. In the program PASSIV the current-potential distributions in the transition region are calculated. In the duplicate program SECLIN, a method of successive approximation was used to check the results obtained in the first program, which uses a Newton-Raphson procedure.
PROGRAM SECLIN ( INPUT, OUTPUT)
C PROGRAM FOR SECONDARY CURRENT DISTRIBUTION TO A DISK ELECTRODE WITH
C BUTLER-VOLMER KINETICS
C MASS TRANSFER LIMITATIONS ARE INCLUDED IN THE KINETIC EXPRESSION
C THE OVERPOTENTIAL IS DEFINED WITH RESPECT TO A SATURATED CALOMEL ELECT.
C EX1 IS NFKC=OMEGA IS THE ROTATION SPEED IN RPM
C T IS THE EXPONENT ON THE FACTOR (1-I/ILIM)
DIMENSION X(96), W(96), R(20,96), P0(20), PM(20), G(20), A(20,20), CJR(96)
DIMENSION ACOEF(20,46), M2N(20)
DIMENSION PHIZ(96), SURF(96)
DIMENSION CR(20)
COMMON A, B
COMMON/RED/ X, WM, R, PM, EX, RO, COND, AA, V, CFE, BETA, OMEGA
COMMON/RED/ CR, T, IM
REAL ILIM
REAL M2N
101 FORMAT (1H1, 3X,*J*)
103 FORMAT (4X)
104 FORMAT (6E14.5)
105 FORMAT (5F12.6)
106 FORMAT (6E14.5)
108 FORMAT (2X,F13.16,2X,F19.16)
1E12.5, * POTENTIAL = *,E12.5)
110 FORMAT(* THE DIFFERENCE MEASURED BY A REFERENCE ELECTRODE AT THE
1E1 AT THE POSITION GIVEN ABOVE IS*,E12.5)
111 FORMAT(* INPUT PARAMETERS ARE J = *,E12.5, * CONDUCTIVITY = *,E12.5,
1E12.5, * RZERO = *,E12.5)
112 FORMAT(* AVERAGE CURRENT ON THE DISK = *,E12.5)
113 FORMAT(* slopes POTENTIAL, V =*,E12.5, *RADIAL POSITION OF REFERENCE
1ELEC., RR = *,E12.5, *DISTANCE FROM DISK, Z = *,E12.5)
114 FORMAT(* TOTAL CURRENT ON THE DISK, LAPLACE =*,E12.5, *KINETIC =*,E12.5)
115 FORMAT(* ADDITIONAL PARAMETERS * / * ROTATION SPEED IN RPM =
1E12.5, * IRON CONCENTRATION (MOL/LITRE) = *,E12.5)
1E12.5)
118 FORMAT(* THE LOCAL CURRENT DENSITY IS GIVEN FOR VALUES OF THE DEFI
1E NED OVERPOTENTIAL*>* CURRENT DENSITY, *X*, OVERPOTENTIAL*)
119 FORMAT( 4X,E12.5, 10X,E12.5)
120 FORMAT(* THE NUMBER OF ITERATIONS NEEDED TO CALCULATE THE LOCAL
1E CURRENT DENSITY = *,I4)
121 FORMAT(* THE NUMBER OF MESH POINTS = *,I4, * THE NUMBER OF B COEF =*,I4)
122 FORMAT(* THE EXCHANGE CURRENT DENSITY AT THE CONCENTRATION CFE =
1E12.5)
123 FORMAT(* THE NUMBER OF ITERATIONS NEEDED TO GET B(I) = *,I4)
210 FORMAT ( F12.5)
C THE ARRAY OVER IS A*A*TETAS + LN(X/ILIM)
DATA (OVER(I), I = 1,20) / 31.82043,1.00,6.100,3.500,0.60,9.050,1.00,9.050,0.60,9.050,0.60,9.050,0.60,9.050,2.00,4.00,8.00 /
READ 103,NMAX,IM,IM $ IMPI = I4 + 1
READ 108, (X(I),M(I),I=IMPI,IM)
DO 3 IN=1,IN $ IF(I*LY+IMPI) GO TO 1 $ X(I)=0.5*0.5*X(I) $ GO TO 2
1 IM=IM+1 $ X(I)=0.5*0.5*X(IR) $ M(I)=M(IR)
2 XX=SQRT(1.0-X(I)**2) $ DO 3 NN=1,NMAX $ N=NN-1 $ P6(INN)=P6(N,XX)
3 R(INN,1)=P(Z,N,XX) $ DO 4 NN=1,NMAX $ N=NN-1 $ P6(INN)=P6(N,0.0)
4 PM(NN) = -0.5366197723/P0(NN)**2
FEE = -30.00
RATIO = 0.00
DO 16 K = 2,NMAX
16 B(K) = 0.00
5 READ 104,CFE,COND,R0 $ IF(CFE.EQ.0.30) STOP
   PI = 3.14159 $ RFT = 36.92317859 $ CCLRF = 4.17
   U = -0.7076 $ ALOG1SQRT(CFE)*CCLRF)/RFT
   OMEGA = 7.53E2
   BET = 0.040035258
   EX = 1.0 E+7
   T = 1.00
   AA = 1.00 $ AC = 2.00 -AA
   EX1 = EX/CFE*EXP(RFT*U)**(AA+AC)
   ILIM = BET*SQRT(OMEGA)
C THE LOCAL POLARIZATION CURVE IS CALCULATED THROUGH FORMAT 11.
C OVER(I) = AA*FRF*(V+ETAS) + LN(EX/ILIM)
C OVER(I) HELPS IDENTIFY THE INTERSECTION OF THE MASS TRANSFER PLATEAU
C AND THE THE KINETIC LIMITATION ASYMPOTOTE.
C OVER(I) = 0.0 IS THIS INTERSECTION
   ILOC = 20 $ ICOUNT = 0 $ NLOOP = 56 $ DO 11 I = 1,ILOC
   Q1 = CFE*EX1/ILIM*EXP(-AC*OVER(I)/AA)*EX/ILIM)**(AC/AA)
   IF(Q1.LT.1.20E-11 AND T.LT.0.25) GO TO 9
   C THIS LOOP IS FOR SMALL VALUES OF C1. F+Q1=((1-F)*Q2)**T
   Q2 = EXP(OVER(I))
   C1 = 0.0 $ P1 = 1.0-C1
   DO 14 JJ = 1,NLCP
      IF(C1.GE.1.0) GO TO 13
      Q4 = Q2**((1.0-C1)**T
      DF = (Q4-Q1-C1)/(1.0-C1)**T*Q4)
      C1 = C1 + DF $ P1 = P1 -DF
      IF(DF.LT.0.00) DF = -0.50*ABS(C1)
      PRINT 106,Q1,Q2,DF,P1
      ICOUNT = ICOUNT + 1
      IF(ABS(DF).LT.1.00E-8*ABS(C1)) GO TO 10
   14 CONTINUE
C THIS LOOP IS FOR LARGE VALUES OF C1. USING THE FORM (F+Q1)**T/(1-F)Q2
   Q2 = EXP(OVER(I))**((1.0/T)
   DO 20 JJ = 1,NLCP
      Q3 = C1 + Q1 $ Q4 = Q3**((1.0/T)
      DF = (P1*Q2-Q4)/(Q4/T/Q3 + Q2)
      IF(DF.GT.0.3) DF = P1*0.50
      PRINT 106,Q1,Q2,DF,P1
      C1 = C1 + DF $ P1 = P1 -DF
      ICOUNT = ICOUNT + 1
      IF(ABS(DF).LT.1.00E-8) GO TO 10
   20 CONTINUE
10 CRO(I) = C1*ILIM
IF(P1.LT.0.50) CRO(I) = (1.0-P1)*ILIM
11 CONTINUE
EXCHG = EX*EXP(FRT*U)
   AJ = R0*FRF/CONC*EXP(AA*FRF*U)**(AA+AC)
   PRINT 111,AJ,$COND,R0
   PRINT 115,OMEGA,BET,ILIM $ PRINT 116, EX,EX1,U,CFE
   PRINT 117,AA,AC,T
   PRINT 122,EXCHG
   PRINT 123,IM,NMAX
   PRINT 118
   PRINT 119,(CRO(I),OVER(I)), I = 1,ILOC
C THE NEWMON-RAPHSON THROUGH FORMAT 19 CALCULATES THE FIRST B COEFFICIENT
C THE PRIMARY RESISTANCE RELATION IS USED AND ALSO B(0) = V-ETAS. T = 1.
C TWO OTHER FORMS OF THE EQUATION WERE TRIED UNSUCCESSFULLY. THE FORM
C USED IS
C LN((AA*FRT*V-FEE)*(COND/FRT*ILIM/PI/RO/AA/EX)*(1+EXP(FEE/ILIM)))
A1 = AA*FRT*V - FEE & A2 = 1.0 + EXP(FEE/ILIM)
A3 = 4.0*COND/FRT/PI/RO/AA/EX & A4 = EXP(FEE/ILIM)
AS = -1.0/A1 + AA/(1.0 + A4)
IF(A1*GT. 0.0) GO TO 21
B(1) = 0.03 & GO TO 22
21 CONTINUE
FEE1 = ( ALOG(A1*A2*A3) -FEE*A5)/(1.0 -A5)
IF( ABS(( FEE1-FEE)/FEE1) ,LT. 1.00E-5) GO TO 19
PRINT 210, FEE1
IF ( ICOUNT .EQ. 20) STOP
FEE = FEE1 & ICOUNT = ICOUNT + 1 & GO TO 15
19 PRINT 123, ICOUNT & B(1) = V-FEE/FRT/AA
22 CONTINUE
PRINT 210,B(I)
C INITIAL GUESS FOR THE CURRENT DENSITY WITH T = 1.0
ETAS = V-B(1)
PRINT 106,ETAS
DO 8 I = 1,IM
8 CRD(I) = ( EX*EXP(AA*FRT*ETAS) -EX1*CFE*EXP(-AC*FRT*ETAS))/(1.0 +
1 EX/EX/ETAS/EXPM(OMEGA)*EXP(AA*FRT*ETAS))
IF ( RATIO .GT. 1.0) GO TO 17
GO TO 18
17 B(2) = 0.3125*B(1) & B(3) = 0.52734*B(1) & B(4) = 0.61983*B(1)
B(5) = -0.00993*B(1) & B(6) = 0.005796*B(1)
18 CONTINUE
CALL SRCNV(NMAX)
PRINT 210, (3(I), I = 1,NMAX)
FAC = 0.5/B(1)/PM(1)
PRINT 106,v,v,CFE
TOTIL = 0.00
TOTIK = 0.00 & DO 7 I = 1,IM & SUM1 = 0.00
SUM = 0.00 & DO 6 K = 1,NMAX & SUM = SUM + B(K)*R(K)*PM(K)
SUM = SUM + R(K)*B(K)
ETAS = V-SUM
PHIZ(I) = SUM & SURF(I) = ETAS
XX= SQRT(1.0-(X(I)**2)
CUR(I) = -COND/RO/XX*SUM1
TOTIL = TOTIL + CUR(I)*X(I)*R(I)*PI*RO**2
7 TOTIK = TOTIK + CRD(I)*X(I)^2*R(I)*PI*RO**2
RATIO = TOTIL/ILIM/RO**2/PI
PRINT 106,* PHIZ(K), K = 1,IM)
PRINT 106,* SRVF(I),SURF(I)
PRINT 114,TOTIL,TOTIK
FEE = SURF(IM)*AA*FRT
C THIS PART OF THE PROGRAM CALCULATES THE POTENTIAL MEASURED BY A REFERENCE
C ELECTRODE AT VARIOUS POSITIONS FROM THE SURFACE OF THE DISK
C CALL COEF(NMAX,40,ACOE)
AVCUR = -COND/RO/FAC
ETA = SQRT((ISQRT((K/R0)**2 - 1.0 +((Z/R0)**2 + 4.0*(Z/R0)**2) &
1 - ((RR/RO)**2 - 1.0 + (Z/RJ)**2))/2.0
XI = Z/RJ/ETA
CALL DISK(XI,M2N,ACOEF,NMAX)
PHI = 0.0
DO 12 I = 1,NMAX
12 PHI = PHI + B(I)*M2N(I)*P(Z*(I-1),ETA)
PRINT 109,Z,RR,PHI
DIFF = V-PHI
PRINT 110,DIFF
PRINT 112,AVCJR
99 CONTINUE
GO TO 5 END
SUBROUTINE SRCNV(N)
COMMON SC,SCM
COMMON/YELL/C,A,FOLD
DIMENSION B(20,20),D(20),F3L3(2),A(23),ERR(23),C(20,20),SIM(20)
100 FORMAT (* THE FRACTIONAL ERROR FOR EACH VARIABLE*, F9.6/9E12.5)
101 FORMAT (* THE CONVERGED VALUE FOR EACH VARIABLE*, F9.6/9E12.5)
102 FORMAT (* THE NUMBER OF ITERATIONS =*, I4)
103 FORMAT (8E15.6)
104 FORMAT (* JCOUNT =*, I3,* DAMPING FACTOR =*, F9.6)
DO 1 J = 1,N
1 A(J) = 0.0
JCOUNT = 0
CALL DRVF(N)
8 IF ( JCOUNT .GE. 30) RETURN
FAC = 1.00
JCOUNT = JCOUNT + 1
SUMERR = 0.0
DO 2 M = 1,N
SIGN(M) = 1.0 IF ( FOLD(M) .LT. 0.0) SIGN(M) = -1.0
SUM(M) = SUMERR + FOLD(M)**2
D(M) = -FOLD(M)
2 J = 1,N
2 B(M,J) = C(M,J)
CALL MAININV(N,1,DETERM)
DO 4 M = 1,N
A(M) = A(M) + FAC*O(M)
4 ERR(M) = ABS(D(M)/A(M))
PRINT 103,FOLD(K), K = 1,N,SJM.ERR
PRINT 104,JCOUNT,FAC
DO 5 M = 1,N
5 IF ( ERR(M) .LT. 1.0E-6) GO TO 3
6 CALL DRVF(N) & SUM = 0.0 & FACOLD = FAC
FLIP = 0.0
3 SUM = SUM + FOLD(M)**2
IF ( SUM.LT. 0.05*SUMERR) GO TO 9
IF (FLIP.GT. 0.0) GO TO 9
IF (SUM.LT. SJM.ERR .AND. FAC.LT. 0.99999) GO TO 8
FAC = (1.0+SQR(D(1)+4.0))/2)
3 DO 7 M = 1,N
7 A(M) = A(M) + (FAC-FACOLD)*D(M)
PRINT 103,FOLD(K),K = 1,N,SJM
PRINT 104,JCOUNT,FAC
GO TO 6
9 DO 10 K = 1,N
10 D(K) = A(K)
PRINT 102, JCOUNT
RETURN $ END
SUBROUTINE DRVF(N)
C EX = NFKA
COMMON/RED/ X, W, R, PM, EX, RO, COND, AA, V, CFE, BETA, OMEGA
COMMON/RED/ CRJ, ILM
DIMENSION CR(96)
COMMON/YELL/ Q, O, FOLD(20)
REAL ILIM
DIMENSION X(96), M(96), R(20, 96), W(20), Q(20, 20), D(20)
99 FORMAT(5X, 020)
100 FORMAT( 8E10.4)
101 FORMAT( 28H INNER LOOP NOT CONVERGED AT, I4, 4E20.5)
NLOOP = 50
AC = 0.0
U = -0.7076 & ALOG(SQRT(CFE)*CCLR)/FRT
EX1 = EX/CFE*(EXP(FRT*U)**(AA+AC))
ILIM = BETA*SQRT(OMEGA)
DO 7 M = 1, N & FOLD(M) = D(M) & DO 7 J = 1, N
7 QIM(J) = 0.00
DO 1 I = 1, IM
SUM = 0.00 & DO 2 K = 1, N
2 SUM = SUM + D(K)*R(K, I)
ETAS = V-SUM
C THIS PORTION CALCULATES A NEW GUESS FOR THE CURRENT DENSITY AT THE IM
C MESH POINTS
Q1 = CFE*EX1/ILIM*EXP(-AC*FRT*ETAS)
IF(Q1.LT. 1.20E-11, AND. T.LT. 0.25) GO TO 8
Q2 = EX/ILIM*EXP( AA*FRT*ETAS)
C THIS LOOP IS FOR SMALL VALUES OF C1. F*Q1= (1-F)*Q2)**T
C1 = 0.0 & P = 1.0-C1
DO 9 JJ = 1, NLOOP
IF(C1.GE.1.0) GO TO 10
Q4 = Q2*(1.00-C1)**T
IF(C1.GE.1.0) PRINT 99, C1
DF = (Q4 -Q1/C1)/(1.0 + Q4/(1.0-C1))
C1 = C1 + DF & P = P-DF
IF((DF.LT. 0.0) OR (DF.GT. 0.5)) Q1 = Q2
DO 10 JJ = 1, NLOOP
9 CONTINUE
C THIS LOOP IS FOR LARGE VALUES OF C1, USING THE FORM (F+Q1)**1/T=(1-F)Q2
8 IF(Q1.GT. 5.0E-12) GO TO 11
C1 = 1.0 & P = 1.0-C1 & GO TO 6
10 C1 = 1.0 & P = 1.0-C1
Q2 = (EX/ILIM*EXP( AA*FRT*ETAS))**((1.0/T)
DO 11 JJ = 1, NLOOP
Q3 = (C1 + Q1) & Q4 = Q3**((1.0/T)
DF = (P*Q2-Q4)/(Q4/T*Q3 +Q2)
IF((DF.LT. 0.0) OR (DF.GT. 0.0)) Q1 = Q2
C1 = C1 +DF & P = P-DF
IF((ABS(DF).LT. 1.00E-8) GO TO 6
4 CONTINUE
6 CRD(I) = C1*ILIM
IF(P.LT. 0.5) CRD(I) = (1.0-P)*ILIM
DO 5 M = 1, N
5 FOLD(M) = FOLD(M) + FLOAT(4*M-3)/PM(M)*RO/COND*R(M, I)*X(I)*4(I)*
10.50*CRD(I)
DC10ES = FRT*(AA*(C1+Q1) +AC*Q1)*(1.0-C1)/(1.0-C1) *(C1+Q1)*F
DO 1 J = 1, N
DO 1 M = 1, N
1 QM(J) = QM(J) + FLOAT(4*M-3)/PM(M)*RO/COND*ILIM*M(I)*X(I)*R(M, I)
1*0.50*(DC10ES*RJ, I))
DO 3 M = 1, N
3 QM(M) = 1.00 + QM(M)
RETURN & END
SUBROUTINE MATINV(N, M, DETERM)
DIMENSION B(20,20),D(20,1),IO(21)
COMMON B,O
DETERM = 1.0
DO 1 I=1,N
1 ID(I)= 0.0
DO 18 NN=1,N
BMAX= 0.0
DO 6 I=1,N
IF (ID(I)) 2,2,6
2 DO 5 J=1,N
IF (ID(J)) 3,3,5
3 IF (ABS(B(I,J)) .gt. BMAX) 5,5,4
4 BMAX = ABS(B(I,J))
IROW= I
JCOL= J
5 CONTINUE
6 CONTINUE
IF (BMAX) 7,7,8
7 DETERM= 0.0
RETURN
8 ID(JCOL)= 1
IF (JCOL=IROW) 9,12,9
9 DO 10 J=1,N
SAVE= B(IROW,J)
B(IROW,J) = B(JCOL,J)
10 B(JCOL,J) = SAVE
DO 11 K=1,N
SAVE= D(IROW,K)
D(IROW,K) = D(JCOL,K)
11 D(JCOL,K) = SAVE
12 F= 1.0/B(JCOL,JCOL)
DO 13 J=1,N
13 B(JCOL,J) = B(JCOL,J)*F
DO 14 K=1,N
14 D(JCOL,K) = D(JCOL,K)*F
DO 18 I=1,N
IF (I-JCOL) 15,18,15
15 F= B(I,JCOL)
DO 16 J=1,N
16 B(I,J) = B(I,J) - F*B(JCOL,J)
DO 17 K=1,N
17 D(I,K) = D(I,K) - F*D(JCOL,K)
18 CONTINUE
RETURN
END
FUNCTION P(N,X)
C CALCULATION OF
LEGENDRE
POLYNOMIALS
P1= 1.0
P2= X
IF (N.1) 1,2,3
1 P= P1
RETURN
2 P= P2
RETURN
3 NM1= N - 1
DO 4 NU=1,NM1
P= X*FLOAT(2*NU+1)*P2-FLOAT(NU)*P1/FLOAT(NU+1)
P1= P2
4 P2= P
RETURN
END
SUBROUTINE COFIT(NMAX,KMAX,A) & DIMENSION A(20,40)
!$116$

A(1,1) = 1.0/1.5707963267949 & DO 1 K = 2,KMAX & DO 1 N = 1,NMAX 
1 A(N,K) = 0.00 & DO 3 N = 2,NMAX & QN = N-1 
A(N,1) = 4.0*QN/2*A(N-1,1)/(4.0*QN+1.0)/(4.0*QN-1.0) 
DO 3 KK = 2,KMAX & QK = KK-1 & SUM = 0.00 & PFAC = 1.00 
SIGNP = -1.0 & DO 2 LP = 1,KK & P = LP-1 & SIGNP = -SIGNP 
FACM = 1.0 & IF(LP.GT.1) PFAC = PFAC*(2.0*P+1.0)*2.0*P 
SIGN = SIGNP & DO 2 MM = LP,KK & QM = MM-1 
IF(MM.GT.LP) FACM = FACM*(2.0*(QM-P))*(2.0*QM-2.0*P+1.0) 
SUM = SUM + A(N,KK-MM+1)*SIGN*3.0*(QM+QN+0.5)*(QM+QN+QN)/PFAC/ 1FACM 
2 SIGN = -SIGN 
3 A(N,KK) = -SUM/4.0/QK/(2.0*QN+QK+0.5) & RETURN & END 
SUBROUTINE DISK(CXI,PE,A2N,NH) 
DIMENSION PE(20),A2N(20,40),YM(60) 
C CALCULATES M(XI), THE LEGENDRE FUNCTION OF IMAGINARY ARGUMENT 
C Y = PI/2.-ATAN(XI), WHERE XI IS NOT RESTRICTED TO ETA = 0. THEREFORE 
C XI IS DEFINED BY Z = RQ*ETA*XI AND R/R0 = SQRT((1+XI**2)*((1-ETA**2)) 
Y = 3.14159/2.0- ATAN(XI) & YM(1) = Y & Y2 = Y*Y & MAX = NH+38 
DO 1 M = 1,MAX 
1 YM(M+1) = YM(M)*Y2 & DO 3 N = 1,NH & PE(N)=0.0 & DO 2 M = 1,40 
ADD = A2N(N,M)*YM(M+N-1) & PE(N) = PE(N) +ADD 
IF(ABS(ADD) .LT. 1.0 E-7*ABS(PE(N))) GO TO 3 
2 CONTINUE 
3 CONTINUE & RETURN & END
PROGRAM PASSIVITY( INPUT, OUTPUT )

PROGRAM FOR TRANSITION FROM ACTIVE TO PASSIVE REGION-BUTLER-VOLMER

DIMENSION R(2),96), PC(20), PM(20), Q(20, 20), A(21, 21), B(21), X(35),
1(96), CUR(96)

DIMENSION CR(96)

COMMON A, B

COMMON/RED/X*, R, PM, EX, RQ, RP, COND, SET, AA, PASS, CFE, BETA, OMEGA

COMMON/RED/CR01T, IM

REAL ILIM

REAL MZN

101 FORMAT (1H1, 3X, "J'"

104 FORMAT (414')

135 FORMAT (F12.6, 10X, "RAOIAL POSITION OF PASSIVATION = ", F12.6)

166 FORMAT (8E14.3)  

188 FORMAT (2X, F19.1&.2X, F19.1&)

189 FORMAT (1H20.7' .

Z:..o FORMAT (10F1Z.5)

Z1Z FORMAT(2C8X,E1Z.6"

COMHONIYELLOW/ETA1, ETA2

DIMENSION ETU (100) , EU2 (100) , JHM (100)

311 FORMAT ( * CURRENT DISTRIBUTION * )

322 FORMAT(10X, * PARAMETER SUMMARY * )

323 FORMAT( * ALFA A = , E12.5) * ALFA C = , E12.5, * NFKA = , E12.5,
1* NFKC = , E12.5)

334 FORMAT( * CURRENT DENSITY OF THE DISK CONTRIBUTED BY THE ACTIVE

1 PORTION = , E10.4)* PASSIVE = , E10.4)* DISK AVER CUR- DEN = , E10.4
2)

350 FORMAT( * ROTATION SPEED IN RPM = , E12.5, * BETA= , E20.9,
1* ILIM = , E12.5)

356 FORMAT( * INPUT PARAMETERS --- PASS = , E12.4, * COND = , E12.4, *R0 =
1* , E12.4, * SET = , E12.4)

357 FORMAT ( * THE POTENTIAL MEASURE ) BY A REFERENCE ELECTRODE AT POSTN

388 FORMAT( * CURRENT DENSITY ON THE ACTIVE PORTION, LAPLACE = , F12.6,
1 KINETIC = , E12.6 )

319 FORMAT( * POTENTIAL DISTRIBUTED NORMALIZED TO THE PRIMARY DISTRIBUTION E11, 1.5)

310 FORMAT( * IRON CONCENTRATION (MOLE/LITRE) = , E12.5, * THE EXPONENT T
1 = , E12.5)

311 FORMAT ( * OPEN CIRCUIT POTENTIAL = , E12.5)

312 FORMAT( * THE NUMBER OF MESH POINTS = , I4, * THE NUMBER OF B COEFFI
1CIENTS = , I4)

313 FORMAT ( * THE EXCHANGE CURRENT DENSITY AT THE PRIMARY CONCENTRATION CFE =
1* , E12.5)

DIMENSION ACQOF(20,40), M2N(20), OHMOG(10)

DIMENSION GMH(10), OHME(10)

DIMENSION OHR(10)

READ 103, NMAX, IH, IM $ IMP1 = IM + 1

READ 1/8, (X(I), W(I)), I = IMP1, IM

DO 3 I=1, IM $ IF(I.LT.IMP1) GO TO 1 $ X(I)=0.5+0.5*X(I) $ GO TO 3

1 IR=IM+1 $ X(I)=0.5-0.5*X(IR) $ W(I)=W(IR)

3 CONTINUE

CALL COEF(6,40, ACQOF)

PI = 3.14159

AA = 1.0 $ A2 = 2.0 -AA

FR= 38, 92317859 $ CCLRF = 4.17 $ AC = 2.0 -AA

OMEGA = 7.50E2

T = 1.06

EX = 1.00E+7

BETA = 0.04033258

ILIM = BETA*SQRT(OMEGA)
NMXP = NMAX + 1
DO 2 K = 2,NMAX
2 B(K) = 0.0
B(INMXP) = 0.0
202 READ 104, CFE $ IF( CFE.EQ. 6.19) STOP
READ 105, PASS, COND, RG, SET
U = -0.7076 + ALOG(SQRT(CFE)*CCLR)/FRT
EX1 = EX/CFE*(EXP(FRT/U)**(AA+AC))
EXCHG = EX*EXP(AA*FRT/U)
AJ = EXCHG*(AA + AC)*FRT/COND*RO
PRINT 302
PRINT 303, AA, AC, EX, EX1
PRINT 304, EXCHG
PRINT 305, OMEGA, BETA, ILIM
PRINT 310, CFE, T
PRINT 311, U
PRINT 312, IM, NMAX
PRINT 106, CFE, EX, U
DO 21 I = 1, IM
CRD(I) = 0.30
XX = SQRT(1.0 - K(I)**2)
DO 20 NN = 1, NMAX
   $ M = NN - 1
21 R(NN,I) = P(2*N, XX) $ DO 4 NN = 1, NMAX $ N = NN - 1 $ P0(NN) = P(2*N, 0.0)
4 PM(NN) = -0.6366197723/P6(NN)**2
AJN = AJ
DO 99 II = 1, 10
JJJ = -II + 1
FRAC = (FLOAT(JJJ))/10.0
AJ = AJN*FRAC
RP = FRAC*RO
PRINT 101
PRINT 105, AJN, RP
C INITIAL GUESS FOR B(I) WITH T = 1.0
B(I) = PI*RP/4.0/COND
CALL SRCONV(NMXP)
V = B(7)
PRINT 306, PASS, COND, RO, SET FACL = 2.0/PI*FASS*RO/COND
DO 60 I = 1, IM
OMH(I) = FACL*ELINT2((RP/RO*K(I))**2) -FACL*RP/RO*ELINT2(X(I)**2) DO 60 N = 1, NMAX
60 OMH(I) = OMH(I) + R(N, I)*3(N)
PRINT 210, (OMH(I), I = 1, IM)
TOTIK = 0.00
DO 70 I = 1, IV
SUM = 0.00
DO 72 M = 1, NMAX
72 SUM = SUM + B(M)*R(M, I)*PM(M)
CUR(I) = -COND/RP/(SQRT(1.0 - X(I)**2))*SUM
7C TOTIK = TOTIK + CRD(I)**X(I)*W(I)*PI*(RP**2)
ACTCDK = TOTIK/PI/RP**2
PRINT 301
PRINT 212, (CUR(I), CRD(I), I = 1, IM, 10)
ACTCR = -2.0*COND*RP*B(1)**M(1)/RO**2
PASSCR = PI*(10**2 - RP**2)*PASS
ACTCO = ACTCR*(RP**2)/(RP**2)
SUM = ACTCR + PASSCR
PRINT 305, ACTCR, PASS, SUM
PRINT 308, ACTCO, ACTDCK
FRAC1 = (1.0 - FRAC)*10.0
JJ = INT(FRAC1 + 0.50)
DO 151 L = 1, JJ
RR = FLOAT(10-JJ + L)/FLOAT(10-JJ)
\[ \lambda I = \sqrt{RR^2 - 1,0} \]
CALL DISK(XI,M2N,ACOEF,NMAX)
SUM = 0.00 $ 00 150 M = 1,NMAX
150 SUM = B(M)*P(Z*H-Z,O)*M2N(M) + SUM
OMH0(L) = SJM
PRINT 210,0,OMH0(L),RR
OMH1(L) = FAC1*RR*ELINT2(1.0/RR)**2) -(1.0-(1.0/RR)**2)*ELINT1(1.0/RR)**2)
PRINT 210,OMH1(L),RR
OMH2(L) = OMH0(L) - OMH1(L) *FAC1*ELINT2(FRAC**2)
PRINT 210,OMH2(L),RR
151 CONTINUE

C THIS SECTION OF THE PROGRAM CALCULATES THE POTENTIAL OF A REFERENCE ELECTRODE AT VARIOUS LOCATIONS.

C LOCATIONS
Z = 1.0 $ RR = 0.30
ETA = SQRT((SQRT(1.0 + (Z/R)**2) + 4.0*(Z/R)**2)
1 -((RR/R)**2 - 1.0 + (Z/R)**2))/2.0
\[ \lambda I = Z/R/ETA \]
CALL DISK(XI,M2N,ACOEF,NMAX)
PHI = 0.00
DO 73 I = 1,NMAX
73 PHI = PHI + B(I)*M2N(I)*P(Z*H-Z,O)/ETA
DIFF = V - PHI
PRINT 307,RZ,PHI,DIFF
DO 74 I = 1,IM,10
74 PRRS(I) = OMH0(I)*B(I)*COND/4.0*PI
PRRS(I) = OMH0(I)*B(I)*COND*PI
PRINT 3.8,PRESS(I), I = 1,IM,10
99 CONTINUE
GO TO 202
END
FUNCTION ELINT1(XK)


FUNCTION ELINT2(XK)

THIS ROUTINE SOLVES COMPLETE ELLIPTIC INTEGRALS OF THE SECOND KIND BY USING CHEBYSHEV APPROXIMATIONS. THE MAXIMAL ERROR IS 2.18E-13.

DIMENSION A(8), B(8)
DATA(A(I), I=1,8) / 1.38629436111989E+00, 9.65736020516771E-02,
1.0899633861795E-02, 1.52518321622534E-02, 1.25565693543211E-02,
2.18659568596791E-02, 1.092381688623E-02, 1.4673491549611E-03 / 
DATA(B(I), I=1,8) / 55, 1.24999998458539E-04, 
17.6311405853296E-02, 4.8737915945218E-02, 3.5721844307327E-02,
22.0985767736790E-02, 5.8107796871996E-03, 3.4280571922974E-04 / 
IF (XK .NE. 1.00) GO TO 2
PRINT 1,0,XK
RETURN
2 CONTINUE
X= 1.0 - XK
SUM1= A(8)
SUM2= B(8)
DO1 I=1,7
J= 8-I
SUM1= X*SUM1+ A(J)
SUM2= X*SUM2+ B(J)
1 CONTINUE
ELINT1=SUM1-A.0G(X)*SUM2
RETURN
END

FUNCTION ELINT2(XK)

THIS ROUTINE SOLVES COMPLETE ELLIPTIC INTEGRALS OF THE SECOND KIND BY USING CHEBYSHEV APPROXIMATIONS. THE MAXIMAL ERROR IS 2.18E-13.

DIMENSION A(8), B(8)
DATA(A(I), I=1,8) / 1.38629436111989E+00, 9.65736020516771E-02,
1.0899633861795E-02, 1.52518321622534E-02, 1.25565693543211E-02,
2.18659568596791E-02, 1.092381688623E-02, 1.4673491549611E-03 / 
DATA(B(I), I=1,8) / 55, 1.24999998458539E-04, 
17.6311405853296E-02, 4.8737915945218E-02, 3.5721844307327E-02,
22.0985767736790E-02, 5.8107796871996E-03, 3.4280571922974E-04 / 
IF (XK .NE. 1.00) GO TO 2
ELINT2= 1.00
RETURN
2 CONTINUE
X= 1.00 - XK
SUM1= A(8)
SUM2= B(8)
DO1 I=1,7
J= 8-I
SUM1= X*SUM1+ A(J)
SUM2= X*SUM2+ B(J)
1 CONTINUE
ELINT2=SUM1-A.0G(X)*SUM2
RETURN
END
SUBROUTINE DF/N
COMMON/R,E,M,R,E,M,EX,RO,RP,COND,SET,AA,PASS,CFE,BETA,OMEGA
COMMON/Y,L,Q,0,FOLD(21)
COMMON/RED/CR/96),T,IM
DIMENSION CR/96)
REAL ILIM
DIMENSION X(96),M(96),Q(21,21),D(21),R(21,95),PM(20)
FRT = 38.9317859 / CCLRF = 4.7 & AC = 2.0 -AA
U = 4.70764 + ALOQ(SQRT(CFE) + CCLRF)/FRT
EX1 = EX/CFE*(EXP(FRT)*((AA+AC)
ILIM = BETA*SQRT(OMEGA)
NLOOP = 50
PI = 3.14159
NMAX = N-1
SUM = 0.00
DO K = 1,NMAX & FOLD(1) = D(1) & SUM1 = SUM1 + D(1)*P(2*K-2,0.0)
DO J = 1,NMAX
3 Q(I,K) = 0,00
DO I = 1,IM
SUM = 0.00 & DO K = 1,NMAX
2 SUM = SUM + D(K)*R(K,I)
ETAS = (N) - SUM
Q1 = CFE*EXL/LIM*EXP(-AC*FRT*ETAS)
IF(Q1.LT.1.2E-11 .AND. T .LT. 0.25) GO TO 8
Q2 = EX/ILIM*EXP(AC*ETAS)
C THIS LOOP IS FOR SMALL VALUES OF CI. F+Q1=I/(1-F)*Q2)**T
CI = 0.00 & P1 = 1.00-C1
DO JJ = 1,NLOOP
IF(C1.GE.1.0) GO TO 11
Q4 = Q2*(1.0-C1)**T
DF = (Q4-Q1-C1)/(1.0 +T*Q4/(1.0-C1))
CI = CI + DF & P1 = P1 -DF
IF(ABS(DF)/LT. 0.0) DF = -J.5*ABS(C1)
IF(ABS(DF)/LT. 1.0E-8*ABS(C1)) GO TO 6
CONTINUE
9 CONTINUE
C THIS LOOP IS FOR LARGE VALUES OF CL, USING THE FORM(F+Q1)**T/(1-F)*Q2
8 IF(Q1.LT.1.2E-12) GO TO 10
CI = 1.0 & P1 = 1.00-C1 & GO TO 5
10 CI = 1.0 & P1 = 1.00-C1
Q2 = (EX/ILIM*EXP(AC*FRT*ETAS)**(1.0/T)
DO JJ = 1,NLOOP
Q3 = CI +Q1 & Q4 = Q3**(1.0/T)
DF = (P1*Q2-Q4)/(Q4/Q3 +2)
IF(DF.GT.0.0) DF = P1*0.5
CI = CI + DF & P1 = P1-DF
IF(ABS(DF)/LT. 1.0E-8) GO TO 6
4 CONTINUE
IF(P1.LT.0.5) CRD(J) = (1.0-P1)*ILIM
6 CRD(J) = CI*ILIM
Q1DE = FRT*(AA*(C1+Q1)+B*Q1)*(1.0-C1)/(1.0-C1)*(C1+Q1)**T
DO J = 1,NMAX
7 FOLD(I,J) = FOLD(I,J) +FLOAT(4*J-3)/PM(J)*R/COND*R(J,1)*X1+W(I)*0.5
1*CRD(J)
DO 1 M = 1,NMAX
DO J = 1,NMAX
1 Q(M,J) = Q(M,J) + FLOAT(4*M-3)/PM(M)*R/COND*R(M,1)*X1+W(I)*0.5
1*ILIM
DO 5 M = 1,NMAX
Q(M,N) = -Q(M,1) & Q(M,M) = 1.00 + Q(M,M)
5 Q(N,N) = -P(2*M-2,0.00)
RETURN $ END
PROGRAM SECLIN (INPUT, OUTPUT)

C PROGRAM FOR SECONDARY CURRENT DISTRIBUTION TO A DISK ELECTRODE WITH
C BUTLER-VOLMER KINETICS
C MASS TRANSFER LIMITATIONS ARE INCLUDED IN THE KINETIC EXPRESSION
C THE OVERPOTENTIAL IS DEFINED WITH RESPECT TO A SATURATED CALOMEL ELECTRODE
C THE EXPONENT T IS THE EXPONENT ON THE FACTOR (1 - I/ILIM)
DIMENSION X(96), PH(96), R(20, 96), P0(20), PM(20), A(20, 20), CJR(96)
1.
DIMENSION ACOEF(20, 40), N2N(20)
DIMENSION PHIZ(96), SURF(96)
DIMENSION CRD(96)
COMMON A, B
COMMON/RED/ X, W, R, PH, EX, R0, COND, AA, V, CFE, BETA, OMEGA
COMMON/RED/CRD,T,IM
REAL ILIM, RZERO
REAL M2N
101 FORMAT (1H1, 3X, *J*)
103 FORMAT (4I4)
104 FORMAT (6E10.4)
105 FORMAT (5F12.6)
106 FORMAT (8E14.5)
118 FORMAT (2X,F13.16, 16, 2X, F19.15)
1.5, * POTENTIAL = *, E12.5)
110 FORMAT (* THE POTENTIAL DIFFERENCE MEASURED BY A REFERENCE ELECTRODE
AT THE POSITION GIVEN ABOVE IS *, E12.5)
111 FORMAT (* INPUT PARAMETERS ARE J = *, E12.5, * CONDUCTIVITY = *, E12
1.5, * RZERO = *, E12.5)
112 FORMAT (* AVERAGE CURRENT ON THE DISK = *, E12.5)
113 FORMAT (* THE POTENTIAL, V = *, E12.5, * RADIAL POSITION OF REFERENCE
ELECTR., RR = *, E12.5, * DISTANCE FROM DISK, Z = *, E12.5)
114 FORMAT (* TOTAL CURRENT ON THE DISK, LAPLACE = *, E12.5, * KINETIC = *
1E12.5)
115 FORMAT (20X, * ADDITIONAL PARAMETERS / * ROTATION SPEED IN RPM = 1*
= *, E12.5, * IRON CONCENTRATION (MOLE/LITRE) = *, E12.5)
1E12.5)
118 FORMAT (* THE LOCAL CURRENT DENSITY IS GIVEN FOR VALUES OF THE DEF/NED
OVERPOTENTIAL*/ * CURRENT DENSITY*/, E12*/ * OVERPOTENTIAL*)
119 FORMAT (4X, E12.5, 10X, E12.5)
120 FORMAT (* THE NUMBER OF ITERATIONS NEEDED TO CALCULATE THE LOCAL
CURRENT DENSITY = *, I4)
121 FORMAT (* THE NUMBER OF MESH POINTS = *, I4, * THE NUMBER OF B COEF = *
1I4)
122 FORMAT (* THE EXCHANGE CURRENT DENSITY AT THE CONCENTRATION CFE = *
1E12.5)
123 FORMAT (* THE NUMBER OF ITERATIONS NEEDED TO GET B(I) = *, I4)
210 FORMAT (F12.5)

C THE ARRAY OVER IS AA=FR*ETAS + LN((X/ILIM)
DATA (OVER(I), I = 1,20) / 31.820+.4, 1.00, 6.100, 3.500, 0.0, 3.050,
1.100, -2.0, -3.000, -4.000, -5.000, -6.000, -7.000, -9.000, -1.00, -1.20, -1.50,
2.20, -2.0, -3.000, -4.000 / READ 103, NMAX, IH, IM $ IM1 = I + 1
READ 103, (XI(I), W(I), I=IM1, IM)
DO 3 IM = 1, IM $ IF(I-LT.IM1) GO TO 1 $ X(I)=0.5+0.5*X(I) & GO TO 2
1 IR=IM-I+1 $ XI=0.5-0.5*XI(IR) & W(I)=W(IR)
2 XX=SQRT(1.0-XX) $ DO 4 NN=1, NMAX & NN=NN-1 $ PHI(NN) = P(2*N, 0.5)
3 R(NN,2)=P(2*N, XX) $ DO 4 NN=1, NMAX & NN=NN-1 $ PHI(NN)=P(2*N, 0.5)
100 ETA1(I) = 0.60*SET
101 CD(I) = EXP(EXP(AA*FFT*ETA1(I))-EXP(-AC*FFT*ETA1(I)))
102 Q(I,M) = Q(I,M) + 0.5*M(I)*X(I)*R(M,I)*CD(I)
103 S(M) = FLOAT(4*M-3)/PM(M)*RP/COND*Q(I,M)
104 I = 1,1M
105 SUM = 0.00
106 M = 1,NMAX
107 DO 108 M = 1,NMAX
108 SUM1 = SUM + B(M)*P(2*NN,0,0)
109 SUM = SUM + B(M)*R(M,I)
1010 ARG = RP/R0*X(I)
1011 OHM(I) = SUM + FAC1*ELINT2(ARG)**2 - FAC1*RP/R0*ELINT2(X(I)**2)
1012 V = SUM1 + FAC1*ELINT2((FP/R0)**2) - FAC1*RP/R0*ELINT2(X(I) + SET
1 + U
1013 PRINT 210, (B(M), M = 1,NMAX)
1014 PRINT 300
1015 PRINT 210, (OHM(I), M = 1,1M)
1016 PRINT 210, V
1017 IF (ABS(V-VOLD)/V) LT 1.00 E-6 GO TO 99
1018 VOLD = V
1019 KK = KK + 1
1020 IF (KK GT 25) DAMP = 0.05
1021 DO 106 I = 1,1M
1022 ETA1(I) = (V-OHM(I)-U)*CAMP + ETA1(I)*(1.0-DAMP)
1023 DO 107
1024 CONTINUE
1025 DO 36 I = 1,1M
1026 SUM = 0.00
1027 M = 1,NMAX
1028 DO 35 M = 1,1M
1029 ARG = RP/R0*X(I)
1030 CUR(I) = -COND/RP/SORT*1.0 -X(I)**2)*SUM
1031 C2 = CALCULATION OF CURRENT DIRECTION FROM CLARIZATION EQUATION
1032 CUR(I) = CALCULATION OF CURRENT FROM LAPLACE'S EQUATION
1033 PRINT 305
1034 DO 40 I = 1,1M
1035 ARG = RP/R0*X(I)
1036 PRINT 210, ETA1(I), ARG
1037 ACTCR = -2.0*COND/RP*9(1)*PH(1)/R0**2
1038 PASSCR = PI*(P0**2 - RP**2)*PASS
1039 SUM = ACTCR + PASSCR
1040 CURL = (ACTCR + PASSCR)*PI*R0**2
1041 DO 33 I = 1,1M
1042 ARG = RP/R0*X(I)
1043 PRINT 210, ETA1(I), ARG
1044 CD11 = EXP(EXP(AA*FFT*(V-OHM(I)-U))-EXP(-AC*FFT*(V-OHM(I)-U)))
1045 PRINT 105, A1
1046 PRINT 306, PASS,COND,R0,SET
1047 PRINT 302, RP,R0
1048 PRINT 301
1049 PRINT 212, (CUR(I), CD(I), I = 1,1M)
1050 PRINT 303
1051 PRINT 210, CURL
1052 PRINT 304, ACTCR, PASSCR, SUM
1053 FRAC1 = (1.0 - FRAC)*10.0
1054 JJ = INT(FRAC1 + 0.5)
1055 DO 151 L = 1,JJ
1056 RR = FLCAT(10-JJ)/FLCAT(10-JJ)
CALL DISK(RR,M2N,ACOE,F,E)
DO 150 M = 1,NMAX
  SUM = B(M)*P(2*M-2,0.0)*M2N(M) + SUM
150 SUM = SUM
PRINT 210,OHMC(L),RR
OHML(L) = FAC*R*(ELINT2((1.0/RR)**2) - (1.0 - (1.0/RR)**2)*ELINT1((11.0/RR)**2))
PRINT 210,OHM1(L),RR
OM2(L) = OHMO(L) - OHM1(L) + FAC*ELINT2(FPAC**2)
PRINT 210,OHM2(L),RR
CONTINUE
199 CONTINUE
GO TO 202
END
FUNCTION P(N,X)
C CALCULATION OF LEGENDRE POLYNOMIALS
P1 = 1.0
P2 = X
IF (N = 1) 1,2,3
1 P = P1
RETURN
2 P = P2
RETURN
3 NM1 = N - 1
DO 4 NU = 1,NM1
  X = X*FLOAT(Z*NU+1)/FLOAT(NU+1)
  P = X*FLOAT(Z*NU+1)*P2 - FLOAT(NU)*P1/FLOAT(NU+1)
  P1 = P2
  P2 = P
4 RETURN
END
FUNCTION ELINT1(XK)
C THIS PROGRAM CALCULATES ELLIPTIC INTEGRALS BY THE CONVENTION AND NOTATION OF "ABRAMCITZ AND STEGUN"
100 FORMAT (* THE ARGUMENT IS EQUAL TO ONE *, F12.5)
DIMENSION A(8), B(8)
DATA ( A(I), I=1,8 ) / 1.38629436111989E+00, 9.65736020516771E-02,
  1.36909633861795E-02, 1.52618320622534E-02, 1.25565693543211E-02,
  1.6869568967517E-02, 1.9942818686623E-02, 1.4704915496101E-03 /
DATA ( B(I), I=1,8 ) / 5.1, 1.24999998585305E-01,
  1.0311410553296E-02, 4.87379519465219E-02, 3.57218443007327E-02,
  2.29857677336790E-02, 5.81807961371996E-03, 3.4280571922974E-04 /
IF ( XK .NE. 1.00 ) GO TO 2
PRINT 100,XK
RETURN
2 CONTINUE
  X = 1.0 - XK
  SUM1 = A(8)
  SUM2 = B(8)
  DO 1 I=1,7
  J = I-1
  SUM1 = X*SUM1 + A(J)
  SUM2 = X*SUM2 + B(J)
1 CONTINUE
  ELINT1 = SUM1 - ALOG(X)*SUM2
RETURN
END
FUNCTION ELINT2(XK)
THIS ROUTINE SOLVES COMPLETE ELLIPTIC INTEGRALS OF THE SECOND KIND BY USING CHEBYSHEV APPROXIMATIONS. THE MAXIMAL ERROR IS 2.1E-13.

THIS PROGRAM CALCULATES ELLIPTIC INTEGRALS BY THE CONVENTION AND NOTATION OF "ABRAMCITZ AND STEGUN".

DATA (A(I)), I=1,8)
1.0, 4.43147193467733E-01, 1.56847700239786E-02, 2.18194814669639E-02, 1.55618474745296E-03 / DATA (B(I)), I=1,8) / 4.0, 2.49999998446655E-01, 5.84950297066166E-02, 4.09074821593164E-02, 2.35091602564984E-02 / IF (XK.NE.1.00) GO TO 2

ELINT2 = 1.00
RETURN

2 CONTINUE
X=1.00-XK
SUM1=A(8)
SUM2=B(8)
DO I=1,7
J=8-I
SUM1=X*SUM1+ A(J)
SUM2=X*SUM2+ B(J)
CONTINUE
ELINT2=SUM1-ALOG(X)*SUM2
RETURN
END

SUBROUTINE COEF(NMAX,KMAX,AM) DIMENSION A(20,40)
A(1,1) = 1.9/3.170796326796486192 $ DO 1 K = 2,NMAX $ DO 1 N = 1,NMAX

1 A(N,K) = 0.00 $ DO 3 N = 2,NMAX $ QN = N -1
A(N,1) = 4.0*QN**2*A(N-1,1)/(4.0*QN +1.0)/(4.0*QN -1.0)
DO 3 KK = 2,KMAX $ OK = KK -1 $ SUM = 0.00 $ PFAC = 1.00
SIGNP = -1.0 $ DO 2 LP = 1,KK $ P = LP - 1 $ SIGN = -SIGNP
FACM = 1.0 $ IF(LP*GT.1) PFAC = PFAC*(2.0*P + 1.0)*2.0*P
SIGN = SIGNP $ DO 2 MM = LP,KK $ QM = MM-1
IF(MM*GT.LP) FACM = FACM*2.0*(QM-P)*(2.0*QM-2.6*P+1.0)
SUM = SUM + A(N,KK-M+1)*SIGN*4.0*(OK-QM+QM+0.5)*(OK-QM+QN)/PFAC
1 IFACM
SIGN = -SIGN
3 A(N,KK) = -SUM/4.0/QK/(2.0*QN +QK +0.5) $ RETURN $ END

SUBROUTINE DISK(R,PE,A2,NM) DIMENSION PE(20), A2(N=20,40), YM(60)
CALCULATES HY(2), THE LEGENDRE FUNCTION OF IMAGINARY ARGUMENT

Y = PI/2. -ATAN(XI), WHERE XI = SORT(R**2,-1.0)
Y = ASIN(1.0/R) $ YM(1) = Y $ Y2=YY $ MAX= YM+3.8 $ DO 1 M=1,MAX
1 YM(M+1) = YM(M)*Y2 $ DO 3 N = 1,NM $ PE(N)=0.0 $ DO 2 M = 1,40
ADD = A2(N,M)*YM(N+1) $ PE(N) = PE(N) +ADD
2 IF(ABS(ADD).LT.1.0E-7)ABS(PE(N))) $ GC TO 3
3 CONTINUE $ RETURN $ END
APPENDIX C

PROGRAM FOR CHARACTERISTICS OF THE DROPPING MERCURY ELECTRODE BELOW THE LIMITING CURRENT

A Newton-Raphson procedure is used to calculate the ohmic potential and the concentration at each time step.
PROGRAM HGROUP(INPUT,OUTPUT,PUNCH)
DIMENSION PHI(101),THETA(101),E(2,2),O(2)
DIMENSION TIII(101),DI(101),CRAV(101),SLOPE(101),DCRAV(101),OCUR(101)
DIMENSION A(99),B(99)
DIMENSION COLIB(75),TALIB(75),CROLIB(75),VILIB(75),ACROLIB(75)
DIMENSION DMATAU(101)
COMMON B,E
COMMON/BLUE/E1,E2,E11,E22,DC101,AC,C101,DCR101
COMMON/XTRA/NLIB,A,EAC,J,COLIA,TALIB
201 FORMAT(8E15.6)
202 FORMAT(1H5X,-F/TPHI-,8X,-C/CINF-,11X,'I',11X,'I/IL',112X,'TIME',112X,'AVERAGE I-',112X,'PROFILE OF THE OPEN CIRCUIT CELL POTENTIAL AND THE SURFACE COVERED WITH POTENTIAL',104 FORMAT(1H5X,E12.4),105 FORMAT('NORMA(IZEQ FOTENTIAl',EZD.81,106, FCRMATC10X,' SUMMARY OF CALCULATIONS',10X,-CURRENT',13X,'TIME',19X,-CONCE~TRATIO~·,11X,'SLOPE',10X.'AVERAGE I'.10X,'IAVG/ILEKOVIC',25X,'IINST/ILEKOVIC',107 FORMAT(6E19.&,E18.&1,108 FCRMATC - CHANGE IN MESH SIZE',/109 FORMATCI0X,' SIMPLIFIED RULE - AVERAGE CUR~E',13X,'TIME',110 FORMATCI0X.' SIMPLIFIED TRAPEZIAL RULE CL-JJ+21 POINTS',E15.81,111 FORMATCI0X,' UNCORRECTED TRAPEZIAL RULE - J' POINTS',E15.81,112 FORMATCI0X,' SUMMARY OF PARAMETERS USED',113 FORMATCI0X,' CONCENTRATION (MOLE/CM 3) =',E15.81,114 FORMATCI0X,' DIFFUSION COEFFICIENT (CM**2/SEC) =',E15.81,115 FORMATCI0X,' GAM (CM/SEC**1/3) =',E15.81,116 FORMATCI0X,' EXCITA(C/A**2) =',E15.81,117 FORMATCI0X,' SUMMARY OF THE STOICHIOMETRIC COEFFICIENTS ARE TAKEN AS 1. THE NUMBER OF ELECTRONS TRANSFERRED IS TAKEN AS 2.
REAL ILIM,IAVG,JDNUM,SPECAL,KONUM
C S~T PARAMETERS
C A ZERO VALUE FOR SPECIAL INDICATES THE SPECIAL LCCP FOR THE INITIAL
C VALUE OF PHI IS SKIPPED.
PI = 3.1415926535 F = 96487.0 $ FRT = 38.9231759
GAM = 0.20
AA = 0.50 $ AC = 0.50 $ Z = 1.0
TSEC = 1.0
CONDI = FRT/1.0E2
DIF = 1.0E-5
EXCO = 1.0E4
CINF = 1.202590421F-4
EXCD = 1.0E-10
E6 = -3.8779
A2 = 3.5723*F*GAM**2*CINF*SORT(OIF)*(4.0*PI/3.0)**(2.0/3.0)*GAM**2
A3 = 4.0*PI/3.0*GAM**3*E5
A4 = 4.0*(AA+AC)*F*GAM**2*CINF*SORT(7.0*PI*OIF/3.0)
A5 = AC*FRT/COND*GAM
C 3eta is the scan rate in millivolts/sec
BETA = 100.0
IF(BETA.NE.0.0) ALFA = TSEC*BETA*1.0E-3
NN = 100
L = NN + 1 $ N = 2
BAC(1) = 1.0 $ L2 = L-2 $ OO 6 I = 1,L2 $ A1 = FLOAT(I)
A(I) = 2.0*SQRT(A1) -SQRT(A1-1.0) -SQRT(A1 + 1.0)
BAC(I + 1) = SQRT(A1 + 1) -SQRT(A1)
6 CONTINUE
C E3 =SQRT(DI0/D5)/THETAS, e* = THETAME(0), E5 = 1/THETAS
E2 =EXCO*(7.0/3.0)*GAM**2*(1.0/7.0)*FRT/COND
E3 = 1.0 $ E4 = 0.0 $ E5 = 1.0
NDUM = SQRT(7.0*OIF/3.0/PHI**2*FRT*GAM/COND*CINF*AC
JONUH = EXCO*GAM*AC*FRT/COND
JONUH = JONUH**2*JONUH
DELCO = 0.02
C NUMERICAL TECHNIQUE
C DIVID IS THE FRACTIONAL VALUE OF THE FIRST TWO ORDERS OF MAGNITUDE
C OF TIME (TAUF) IN NN MESH INTERVALS
DIVID = 1.0E-29 $ JJJ = 30
TAUF = 3.0/7.0*GAM**4*TSEC**(7.0/3.0)
C INITIAL GUESSES
THETA(1) = 1.0
PHI(1) = 0.0
PRINT 113,CINF,DIF,AA,AC,Z,COND,GAM,EXCO,TSEC,BETA,ALFA,NK,DIVID,
1JJJ,DELCO,E3,E4,E5,NDUM,JONUH,KDNUM
DO 4 LL = 1,2
READ 115,E
E = -AC*VS $ PRINT 105,E
AD1 = 0.0 $ C2 = 0.0 $ SAVE = 0.0
MLIB = 3 $ DELCO = 0.02 $ CHECK = 1.0 -DELCO
TAUBLIB(1) = 1.0FICAT(NN)*TAUF*DIVID*COLIB(1) =1.0 $ TAUBLIB(1) = 0.0
TILIB(1) = 0.0 $ TILIB(2) = (7.0/3.0/GAM**4*TAUBLIB(2)**(3.0/7.0)
CRDLIB(1) = 0.0 $ CRDLIB(1) = 0.0
AD1 = 0.0
E1 = -COND*SQRT(P1/DIF)/FRT/F*(3.0/7.0/GAM**3)**(3.0/7.0)/CINF/3.
1*14.5/9.28141044
TAUF = CDIVID*TAUF
H = TAUF1/FLOAT(AN)
D(1) = PHI(1) $ D(2) = THETA(1)
D(1) = VS
IF((EXP(E)/EXP(-AA/AC*E)) .GT. 40.0) SPECA = 1
IFIRST = 0
Q2 = 0.10*VS
IF(SPECA .EQ. 0) GO TO 17
Q1 = 4LOG(JONUH*TAUBLIB(2)**(1.0/3.0))
15 CONTINUE
IFIRST = IFIRST + 1
Q3 = ABS(E) + Q1 -ALOG(AES(Q2))
IF(AESABS(Q3)-ABS(Q2)) .LT. 1.0E-5) GO TO 16
IF IFIRST .GT. 25 STOP
Q2 = Q3
GO TO 15
*4 CONTINUE
Q3 = 2.0*Q3
D(1) = SIGN(Q3,VS)
17 CONTINUE
PRINT 117,IFIRST,D(1)
CRAV(11) = 0.0
ADD = 0.0
DO 2 J = 1,JJJ
JJ = 2  $ IF(JJ .NE. 1) JJ = 12
JJPL1 = JJ + 1
JJPL2 = JJ + 2
DO 1 M = JJ,L
TAU = TAUFL*FLOAT(M-1)/FLCAT(NN)
DMTAU(M) = TAU/TAUF
IF(M .EQ. 3) E1 = E1*1.0/14.0*59281404472.0
T = (7.0*TAU/3.0/GAM**4)**(3.0/7.0)
VS = -FRT*(ALFA*FLOAT(LL-1) + BETA*1.0E-3*T)
T(LI) = T
ILIM = 4*T**(1.0/6.0)
IAVG = A2*T**(1.0/6.0)
TBLUE = TAU**(1.0/7.0)
CALL SRCOV(N,M)
PHI(M) = 0(1)
THETA(M) = 0(2)
IF(JJ.EQ.1 .AND. M .EQ.2) COLIB(2) = THETA(2)
CUR = 4.0*PI*COND*PHI(M)*(7.0/3.0*TAU*GAM**3)**(1.0/7.0)/FRT
CRO(M) = CUR/(4.0*PI*GAM**2*TI(M)**(2.0/3.0))
DOR(M) = CUR/IAVG
IF(JJ.EQ.1 .AND. M .EQ.2) CRO(2) = CRO(2)
C INTEGRATION TO OBTAIN AVERAGE CURRENT FOR DROP AT TIME TAU
AD = TAU**6*PHI(M)*H*0.50
ADD = ADD + AD
CRAV(M) = (ADD*A3 + ADD1)/T
AVCRD(M) = CRAV(M)/(4.0*PI*GAM**2*TI(M)**(2.0/3.0))
IF(JJ.EQ.1 .AND. M .EQ.2) AVCRD(2) = AVCRD(2)
OCRAV(M) = CRAV(M)/IAVG
IF(M.EQ.L) SAVE = SAVE + ADD*A3
ADD = ADD + AD
D(1) = PHI(M) & D(2) = THETA(M)
1 CONTINUE
IF(JJ.LT. 28) GO TO 14
DO 13 K = JJPL2,L,10
Q1 = ALOG10(-CRO(K)*AS*TI(K)**(1./3.))
Q2 = ALOG10(-AVCRD(K)*AS*TI(K)**(1./3.))
Q3 = ALOG10(NONUM**(-6.)*TI(K))
Q4 = ALOG10(JONUM**3*TI(K))
PUNCH 116,Q1,Q2,THETA(K),Q3,Q4,E,EXCD
13 CONTINUE
14 CONTINUE
AD1 = (ADD-AD)*A3 + AD1
ADD = TAUFL**6*PHI(L)*0.50*10.0*H
PRINT 110,CRAV(L)
PRINT 106
SLOPE(16) = 0.0
DO 5 J1 = 16,L,13
D1(J1) = 4.0*PI*COND*PHI(J1)*GAM*TI(J1)**(1.0/3.0)/FRT
IF(J1 .NE. 16) SLOPE(J1) = (ALOG(SIGNS(DI(J1,1),1)) - ALOG(SIGNS(DI(J1-13),
1.1)))/ALOG(TI(J1)) - ALOG(TI(J1-13))
PRINT 107,D1(J1),TI(J1),THETA(J1),SLOPE(J1),CRAV(J1),OCRAV(J1),
I0CUR(J1)
5 CONTINUE
H1 = 10.0*H & JJM1 = JJ-1 + 10
BDD = 0.0
IF(JJ .NE. 2) BDD = (TAUFL*FLOAT(JJ-2)/FLCAT(NN))**6*A3*0.5*PHI(JJ
1-1)*H1
DO 7 M = JJM1,NN,10
TAU = TAUFL*FLOAT(M-1)/FLCAT(NN)
BC = A3*TAU**6*PHI(M)*H1
7 SDO = BDD + BDD
BDD = BDD + 0.5*A3*PHI(L)*TAUFL**6*H1
BIAVG = (BOD + BCI)/T
BOD = B0C + B01
PRINT 114,BIAVG
CRAVL() = SAVE/T
PRINT 112,CRAVL()
C1 = 0.0 $ IF (JJ*NE.*2) C1 = (TAUFI*FLOAT(JJ-2)/FLOAT(NN))**E6*PHI(JJJ-1)
10 C1 = C1 + (TAUFI*FLOAT(H-1)/FLOAT(NN))**E6*PHI(H-1)**4.0 + (TAUFI*FLOAT(H-2)/FLOAT(NN))**E6*PHI(H-1)**4.0
C1 = C1 + (TAUFI/FLOAT(NN))**E6*(4.0*FLOAT(NN-1)**E6*PHI(NN) + 1)**A3*I/H/3.0
C2 = C1 + C2
CIAVG = C2/T
PRINT 109,CIAVG
C FOR EACH ORDER OF MAGNITUDE POINTS ARE SELECTED FOR PERMANENT
C STORAGE IN AN AUXILIARY ARRAY.
DO 8 M = 2,10
IF(J.EQ.1.AND. M .EQ.2) GO TO 8
IF(THEITA(M) .GT. CHECK) GO TO 8
C0L13(NLIB) = THEITA(M) $ TAULI9(NLIB) = TAUFI*FLOAT(M-1)/FLOAT(NN)
C0RDL13(NLIB) = CRD(M)
TILIB(NLIB) = (7./3.)*GAM4*TAULI9(NLIB)**(3./7.)
ACRD18(NLIB) = AVCRD(M)
NLIB = NLIB + 1 $ CHECK = CHECK - DELCO
8 CONTINUE
C0L13(NLIB) = THEITA(11) $ TAULI9(NLIB) = TAUFI*10.0/FLOAT(NN)
TILIB(NLIB) = (7./3.)*GAM4*TAULI9(NLIB)**(3./7.)
C0RDL13(NLIB) = CRD(11) $ ACRD18(NLIB) = AVCRD(11)
IF ( J .EQ. JJJ ) GO TO 2
PRINT 108
TAUFI = TAUFI*10.0 $ M = M*10.*0 $ DO 9 K = 2,11
THEITA(K) = THEITA1 +10*(K-1) $ PHI(K) = PHI(1 +10*(K-1))
C0RDL18(K) = CRD11 + 10*(K-1) $ AVCRD(K) = AVCRD(1 + 10*(K-1))
9 CONTINUE
IF ( T.GE. 30.0 ) GO TO 11
2 CONTINUE
PRINT 105,E
DO 12 K = 2,NLIB
Q1 = ALOG10(-CORDL18(K)-5*TILIB(K)**(1./3.))
Q2 = ALOG10(-ACRD13(K)-5*TILIB(K)**(1./3.))
Q3 = ALOG10(N0DUM**(-5)*TILIB(K))
Q4 = ALOG10(J0DUM**3*TILIB(K))
PUNCH 116,Q1,Q2,C0L13(K),Q3,Q4,E,EXCD
12 CONTINUE
Q1 = ALOG10(-CORDL18(K)-5*TSEC**(1.0/3.))
Q2 = ALOG10(-ACRD13(K)-5*TSEC**(1.0/3.))
Q3 = ALOG10(N0DUM**(-5)*TSEC)
Q4 = ALOG10(J0DUM**3*TSEC)
PUNCH 116,Q1,Q2,THEITA(L),Q3,Q4,E,EXCD
PRINT 103
DO 3 M = 2,4,5
UJZFO = ALOG(THEITA(L)/(E3*(1.0-THEITA(L)) + E4))/FR/(AA+AC)
ETAS = (VS -PHI(M))/FR-UJZFO
7 PRINT 104,UJZFO,ETAS
PRINT 202
PRINT 201,PHI(L),THEITA(L),CUR,DCUR(L),T,CRAVL(L)
4 CONTINUE
11 CONTINUE
END
SUBROUTINE SRCNV(N,L)
COMMON B,C
COMMON/YELL/C,A,FOLD
DIMENSION B(2,2),D(2),FOLD(2),A(2),C(2,2),SIGN(2),ERR(2)
C CARE SHOULD BE TAKEN SO THAT THE VARIABLES DO NOT EQUAL ZERO AT CONVERGENCE
FORMAT(* NO CONVERGENCE*,I4,* ITERATIONS*,/ ,8E15.8)
101 FORMAT(8E15.8)
JMAX = 30
DO 1 J = 1,N
1 A(J) = 0(J)
CALL DRVFCL(L)
8 IF(JCOUNT .GT. JMAX) GO TO 11
FAC = 1.00
JCOUNT = JCOUNT + 1
SUMERR = 0.0
DO 2 M = 1,N
SIGN(M) = 1.0 IF ( FOLC(M) .LT. 0.0) SIGN(M) = -1.0
SUMERR = SUMERR + FOLC(M)**2
Q(M) = -FOLC(M)
DO 2 J = 1,N
B(M,J) = C(M,J)
CALL MATINV(N,1,NLIB,DETERM)
DO 4 M = 1,N
A(M) = A(M) + FAC*D(M)
IF(A(M) .EQ. 0.0) ERR(M) =ABS(Q(M)/A(M))
IF(A(M) .EQ. 0.00) ERR(M) = 0.0
CONTINUE
DO 5 M = 1,N
5 IF( ERR(M) .LT. 1.00E-7) GO TO 9
CALL DRVFCL(L) & SUM = 0.0 & FACOLD = FAC
FLIP = 0.0
DO 3 M = 1,N & FLIP = FLIP + SIGN(M)*FOLD(M)
SUM = SUM + FOLD(M)**2
IF( SUM .LT. 0.05*SUMERR) GO TO 8
IF( FLIP .LT. 0.0) GO TO 8
IF( SUM .LT. SUMERR) GO TO 8
IF( SUM .LT. SUMERR .AND. FAC .LT. 0.99999) GO TO 8
FAC = 2.0/((SUM*SUMERR) + 1.0 + FAC**2)) & FACOLD = FAC
DO 7 M = 1,N
A(M) = A(M) + (FAC-FACOLD)*D(M)
 CONTINUE
GO TO 6
7 CONTINUE
9 DO 10 K = 1,N
10 D(K) = A(K)
RETURN
11 CONTINUE
PRINT 100,JMAX, (A(K),K = 1,N)
RETURN & END
SUBROUTINE DRVFCL(L)
DIMENSION F(2),OF(2,2),X(2),Y(101),A(99),B(100)
DIMENSION COLIB(75),TAULIB(75)
COMMON/BLUE/01,Q2,H.T,CNF,FRT,VS,Y,AA,AC,Q3,C4,Q5
COMMON/YELL/OF,X,F
COMMON/XTRA/NLIB,A,B,J,CLIB,TALIB
C SET UP THE DERIVATIVES AND FUNCTIONAL
SUMAC = 0.0
IF(J .EQ. 1) GO TO 4
TAU = T**7
DO 1 K = 2,NLIB
SUMAC = (COLIB(K-1) - COLIB(K))/(SQRT(TAU-TAULIB(K-1)) + SQRT(TAU - 1TAULIB(K-1))) + SUMAC
1 CONTINUE
4 CONTINUE
L1 = L-1 J1 = 3
IF(J.EQ.1) J1 = 2
IF(ABS(X(1)) .GT. ABS(VS)) X(1) = 0.50*VS
DF(1,1) = 1.0 - Q2*T*(AA*(Q3*(1.0 - X(2)) + Q4)*EXP(AA*(VS - X(1)))+ X(2)*
1AC*EXP(-AC*(VS - X(1))))
DF(1,2) = -Q2*T*(Q3*EXP(AA*(VS - X(1)))+ EXP(-AC*(VS - X(1))))
DF(2,1) = -Q1/T**3*SQRT(H)
DF(2,2) = -1.0
F(1) = X(1) + Q2*T*(Q3*(1.0 - X(2)) + Q4)*EXP(AA*(VS - X(1)))-X(2)*
1EXP(-AC*(VS - X(1)))
SUM = 0.0
IF(L.EQ.2) GO TO 3
DO 2 I = J1, L1
2 SUM = SUM + Y(I)*A(L-I)
CONTINUE
F(2) = -X(1)*Q1*SQRT(H)/T**3 - X(2) + SUM + Y(J1-1)*B(L-J1+1) +
1SQRT(H)*SUMAC
RETURN
APPENDIX D

PROGRAM FOR MASS TRANSFER TO ROTATING DISKS AND ROTATING RINGS
IN LAMINAR, TRANSITION, AND FULLY DEVELOPED TURBULENT FLOW

In program MTTURB the Thomas method is used to obtain results from equation 4-17.
PROGRAM MTTURB( INPUT, OUTPUT, PUNCH )
DIMENSION A( 499 ), B( 499 ), C( 500 ), D( 499 ), G( 499 ), ETA( 499 ), GAM( 499 )
DIMENSION RAT( 25 )
COMMON DBETAT, YDSK

100 FORMAT( 10E13.6 )
101 FORMAT( 3E10.3 )
102 FORMAT( * JMAX = *, I4; IXMAX = *, I4; IS = *, I4; DX = *, E10.3; RZ = *, E10.3 )
103 FORMAT( 10X; * RATIO = *, 5X; E15.5 )
104 FORMAT( 3F15.8 )

REAL LOCNU, K, NULAM, K1

COMMON ETA, 'DSK, 100 FORMAT( I13, 6E13.6 )
101 FORMAT( 3I10, 3E2E10, 3 )
102 FORMAT( JMAX = *, I4; IXMAX = *, I4; IS = *, I4; DX = *, E10.3; RZ = *, E10.3 )
103 FORMAT( 10X; RATIO = *, 5X; E15.5 )
104 FORMAT( 3F15.8 )


C AVERAGE NUMBER IS THE AVERAGE AND LOCAL NUSSELT NUMBERS WITH A
C SCHMIDT NUMBER TO THE -1/3 POWER IN THEM.
KMIX = 20
NUPR = 0
R1 = SQRT( 2.0E5 ) & RT2 = SQRT( 3.0E5 )
A1 = 0.986285 & A2 = 0.0137152 & EXD = 0 & E10 = 4.5 & B2D = 9
1 READ 101, JMAX, IXMAX, IS, DX, RZ
C PIERINI'S DATA ARE FOR SCHMIDT NUMBERS OF 1716, 1668, 1711.
C THESE CORRESPOND TO RING DIMENSIONS 0.9925, 0.9779, 0.9221 RESPECTIVELY.
SC = 1900.0
EXR1 = 3.0
EXR2 = 3.5
IXMAX = 80
ISET = 19
Q1 = 0.0, Q2 = 0.0, Q3 = 0.0, Q4 = 0.0, Q5 = 0.0
KK = 1
F = 0.0
IF( JMAX.EQ. 0 ) STOP
DFR = 0.0
GAM3 = 1.0/1.11985
PRINT 102, JMAX, IXMAX, IS, DX, RZ
C LIN, MOULTON, AND PUTNAM USE A VALUE OF K = 3.28E-4.
C WASAN, TIEN, AND WILKE USE A VALUE OF K = 4.4E-4.
K = 3.28E-4
K1 = 19.3
NULAM = 0.0
ADT = 0.0
SUM = 0.0
OFFST = 0.0
AD = 0.0
LOCNU = 0.0
EXI = 3.0/2.0
H = 2.25/FLOAT( JMAX )
JMP1 = JMAX + 1
C( JMP1 ) = 1.0
C( J ) = 0.0
DO 2 J = 2, JMAX
G( J ) = 0.0
2 CONTINUE
Y = 0.0
RX = RZ
DO I = 1, IXMAX
NUPR = NUPR + 1
BID = 4.5
SUMD = SUM $ SUMTO = SUM
FAC = 1.0
IF( T .EQ. 2 ) & AND. RZ .EQ. 0.0 ) FAC = 0.50
YD = Y & IF( I.GT. 1 ) RX = EXP( DX*FLOAT( I-1 ) ) + ( OFFST + RZ )
IF( KK .GT. KMIX ) GO TO 11
IF( RX .LT. RZ ) RX = EXP( RZ*FLOAT( KK ) ) .OR. RZ .EQ. 0.0 ) GO TO 11
PRINT 103, RAT( KK )
RX = RX/RAT(KK)  &  KK = KK + 1

11 CONTINUE
IF(I.EQ.ISET) OFFSET = DX*FLOAT(I-IS)
IF (I.EQ.ISET) DX = DX/5.0
IF (RX.GE.RT1 + ANG * RX /LE. RT2) F = (RX/RT1)/(RT2-RT1)
IF (RX.GT. RT2) F = 1.0

Y = X(RZ+RX) & R1 = RX**EX
IF(I.NE.1) GBETA = SQRT(0.BETA)
G1 = Y*Y
IF (I.EQ.1) GO TO 6 & G1 = 1.0 & R1 = 1.0

4 CONTINUE
DD = 1.0
DO 5 J = 2,JMAX
XI = FLOAT(J-1)*H
C DD IS THE VARIABLE THAT EXPRESSES THE FORM FOR THE LOCY DIFFUSIVITY.
C IF DD IS 1.0 THE K*YPLUS**3 FORM IS USED. K*YPLUS**4 IS EXPRESSED WHEN
C DD = 1.0 + ------

C IF(NUPR.EQ.2) YPLUS = XI*(Y/K)**(1.0/3.0)/SORT(RX)
C IF(RX.NE.0.0) DD = 1.0 + K1*XI/SORT(RX)*(Y/YK/SC)**(1.0/3.0)
C G(J) = G(J) + 5.0*XI*(Y*YC)**(0.5**2)*G(J)/G1*FAC
C A(J) = 1.0 + *XI**2*F/R1*DD + 0.5*XI**2*(1.0*Y*F/R1*DD)**H/2.0
C B(J) = -2.0*XI*Y**3*F/R1*DD - 9.0*XI*(Y*Y0)**H**2/G1*FAC
C D(J) = (1.0 + Y*XI**3*F/R1*DD) + 3.0*XI**2*(1.0*Y*F/R1*DD)**H/2.0
C IF(NUPR.EQ.2) DPL1 = 1.0 *K*YPLUS**3*(1.0 + K1*YPLUS)
C IF(NUPR.EQ.2) DPLV3 = 2.9/16-F*3*YPLUS**3 + 1.0
C IF(NUPR.EQ.2) PRINT 104,DPL1,DPLV3,YPLUS
5 CONTINUE
G(JMAX) = G(JMAX) -0.6*(JMAX)*C(JMP1)
BETA(2) = B(2) & GAM(2) = G(2)/B(2)
DO 6 J = 3,JMAX
BETA(J) = B(J-1)*D(J-1)/BETA(J-1)
GAM(J) = (G(J-1)/A(J-1)*GAM(J-1))/BETA(J)

6 CONTINUE
C(JMAX) = GAM(JMAX)
DO 7 J = 3,JMAX & JJ = JMAX - J + 2
C(JJ) = GAM(JJ-1)*C(JJ+1)/BETA(JJ)
7 CONTINUE
C(JMAX) = GAM(JMAX)
DO 8 J = 3, JMAX & JJ = JMAX - J + 2
C(JJ) = GAM(JJ-1)*C(JJ+1)/BETA(JJ)
8 CONTINUE

IF(RX.NE.RZ) NULAW = -0.62048*F X**2/(RX**3-RZ**3)**(1.0/3.0)
CP = (2.9*C(2)-1.5*C(1)-0.5*C(3))/H
CPI = C(2)*H
IF(RX.NE.0.0) CPTURB = -0.8269933431*(Y/P1)**(1.0/3.0)
SUM = CPI*Y**(2.0/3.0)/9.0/K
SUMT = SUM*CPI/P
IF(I.EQ.2) AD = 1.5*SUM
IF(I.EQ.2) ADT = CPTURB*AD/CPI
C 1.05*Q4*0.41
DO 3 J = 2,JMAX
XI = FLOAT(J-1)*H
G(J) = -A(J)*C(J-1) - B(J-1)*C(J) - D(J)*C(J+1)
1-9.0*XI*(Y*Y0)**H**2/G1*FAC*C(J)
3 CONTINUE
C DFR REPRESENTS A FIT OF THE DETAILED RESULTS OF THIS MODEL. DFR IS THE
C CONCENTRATION DERIVATIVE AT THE SURFACE. IT WAS NECESSARY TO FIT DISK
C RESULTS FOR TRANSITION AND TURBULENT FLOW, THEN ONE NEEDED TO KNOW HOW
C THE DERIVATIVE VARIED WITH PING DIMENSIONS FOR A GIVEN ROTATION SPEED.
XD = ALOG10(RX**2) - 5.315
YCEPT = 2.415
IF ( ALOG10(RX**2) .GT. 5.3 ) AND. ALOG10(RX**2) .LT. 5.55) 910 = 4.5
IF ( ALOG10(RX**2) .GT. 5.3 ) AND. ALOG10(RX**2) .LT. 5.55)
1YCEPT = 2.417
ONULC = ALOGI((A10*EXP(B1C*SXD*XD) + A20*EXP(C20*E0*XD))**(1./EYD))
1 + YCEPT + ALOG10(GAM43)
1 - YX = EXR1 + (RX-FT1)/(1.0E3-RT1)*EXR2
XR = (RX/RX)**EXR
IF(YX >= 0.0) 91P = ONULC + ALOG10((XDSK/K)**(1./3.0)/Q1/DBETA)
IF(ALOG10(RX**2) .GT. 5.315) DFR = 1.0**91RI/SORT(1.0-XR)/GAM43
IF(ALOG10(RX**2) .LE. 5.315) DFR =1.0/GAM43
12 CONTINUE
IF(I(2) .EQ. 9,10)
10 CONTINUE
AD = (SUM-SUMO)*ALOG(Y/YC)/ALOG(SUM/SUMO) + AD
ADT = (SUMT-SUMTO)*ALOG(Y/Y0)/ALOG(SUMT/SUMTO) + ADT
1 AVHERU = 2.0**K**1.3*(RX-2**2)**2*AD
TURLMT = 2.0**K**1.0*ADT
IF(I(2,.N.E.1) LOCNU = CPI*R1*OBETA*(K/Y)**(1.0/3.0)
Q1 = ALOG10(LCNU/NULAM)
Q2 = ALOG10(CPI*GAM43) \& Q3 = ALOG10(AVHERU/(6.2048***(RX**3-RZ**3)
1***(1.0/3.0)))**(RZ**2-RH**2)/RY)
Q4 = ALOG10(AVENU) \& Q5 = 2.0*ALOG10(RX)
PRINT 100,Y,RDX,OFF,Q2,CP,CI,CFTR9,AVHERU,LCCLN,TURLMT,OF,5,4,3,101
8 CONTINUE
GO TO 1
END
FUNCTION XR(RR,RX)
C RR IS THE SQUARE ROOT OF THE PEYNOILON'S NUMBER FOR THE STEP CHANGE IN
C SURFACE CONCENTRATION. RX IS THE SQUARE ROOT OF REYNOLDS NUMBER FOR
C THE SPECIFIC POSITION IN QUESTION.
COMMON DBETA,XDSK
REAL RX
IF(RZ-NE. RX) GO TO 11
X = 0.0
RETURN
11 CONTINUE
K = 3.28E-4
A = SQRT10.5(1.23E2)
RT1 = SQRT11.9E5 \& RT2 = SQRT(1.0E5)
IF(RX-RT2) 1,1,6
1 IF(RX-RT1) 2,2,3
2 X = 3.0*K*A**(FX**3-FZ**3)
OBETA = A**2*FX
XDSK = 3.0*K*A**RZ**3
RETURN
3 X = 3.472E1*K**(RZ**2.559-RT1**2.559) + 3.0*K*A*RT1**3
OBETA = 9.7*7E1*FX**(-1.186)
XDSK = X
3 IF(RZ-RT1) 4,4,5
4 X = X-3.0*K*A*RZ**3
RETURN
5 X = X-3.0*K*A*RT1**3-3.472E1*K*(RZ**2.559-RT1**2.559)
RETURN
6 X =3.0*K*A*RT1**3 + 3.472E1*K**(RT2**2.559-RT1**2.559) + 2.622*K**2
RX**3-3.5*PT2**3.3)
OBETA = 8.55E-3*R**1**1.6
XDSK = X
IF(RZ-RT1) 7,7,9
7 X = X-3.0*K*A*RZ**3
RETURN
8 IF(RZ-RT2) 9,9,10
9 X = X-3.0*K*A*RT1**3 - 3.472E1*K*(RZ**2.559-RT1**2.559)
10 X = X - 3.0*K*A*RT1**3.9 - 3.472E1*K*(RT2**2.559 - RT1**2.559) - 2.522*K
1*(RZ**3.3 - RT2**3.3)

RETURN $ END

399 80 3 0.25 0.0
399 80 3 0.25 100.0
399 80 3 0.25 150.0
399 80 3 0.25 200.0
399 80 3 0.25 250.0
399 80 3 0.25 300.0
399 80 3 0.25 350.0
399 80 3 0.25 400.0
399 80 3 0.25 447.21359
399 80 3 0.25 500.0
399 80 3 0.25 547.72255
399 80 3 0.25 600.0
399 80 3 0.25 700.0
399 80 3 0.25 800.0
399 80 3 0.25 900.0
399 80 3 0.25 1000.0
APPENDIX E

PROGRAM FOR CORROSION OF IRON

The program FECOR calculates the current, potential, and concentration distributions across a disk using a method of successive approximation.
PROGRAM FECOR(INPLT,OUTPLT,PUNCH)
DIMENSION B(6),O(6),BOLD(6),DCOL(6),ERR(6),S(101),T(101),Z(101)
F(101),C1(101),C2(101),C01(101),C02(101),RDF(101),PO(6),
IAC(101),101),RPR(101),RPR(101),X(101),W(101)
F6(101),C3(101),PR(101),ERD(6)
COPCPN FROD,LPAX
REAL K,NJ1,NJ2
REAL ILAMP2
INTEGER OPTN
100 FORMAT(20I4)
101 FORMAT(2X,F19.16)
102 FORMAT(20X,*SUMMARY OF THE PARAMETERS*,/*DIFFUSION COEFFICIENTS
1CM**2/SEC)*,FX* FL = **E15.4,*O2 = **E15.4,* CH = **E15.4,
2* DENSITY(G/CM**3) = **E12.4,*VISCOSITY(CP**2/SEC) = **E12.4,
3* CONDUCTIVITY((GMHCM)**-*1) = **E12.4,* REFERENCE CONCENTRATIONS
4 MOLE/CM**3)*,FX* FL = **E12.4,* O2 = **E12.4,* CH = **E12.4,*
5 CONCENTRATIONS AT INFINITY(MOL/CM**3)*,FX* FL = **E12.4,* O2 = **E12.4,* CH = **E12.4,*
6* REFERENCE EXCHANGE CURRENT DENSITY(A/CM**2)*,FX* EXCH(1) = **E15.4,
7* EXCH(2) = **E15.4,* ZERO(1CM)* = **E12.4,*
8* THE NUMBER OF EVENLY SPACE POINTS = **I4)
103 FCSTM(9E14.7)
104 FCSTM(2X,* IRON CURRENT = AMP**E15.8,* OXYGEN CURRENT = AMP**E15.8)
1.8,* TOTAL CURRENT = AMP**E15.8)
105 FORMAT(2X,* THE POTENTIAL DISTRIBUTION*)
106 FORMAT(2X,* THE IRON CURRENT DENSITY DISTRIBUTION*)
107 FORMAT(2X,* THE OXYGEN CURRENT DENSITY DISTRIBUTION*)
108 FORMAT(2X,* IRON CONCENTRATIONS- MOLE/LITRE*)
109 FORMAT(2X,* OXYGEN CONCENTRATIONS- MOLE/LITRE*)
110 FORMAT(2X,* E COEFFICIENTS*)
111 FORMAT(2X,* D COEFFICIENTS*)
112 FORMAT(2X,* R NCLOS NUMBER AT THE EDGE OF THE DISK IS **E14.7)
113 FORMAT(2X,* HYDROXYL CONCENTRATION- MOLE/LITRE*)
C SETTING UP THE CONSTANTS AND THE DIMENSIONAL PARAMETERS
READ 100,LMAX,NMAX,IP-IM
NJ1 = 2*0 $ NJ2 = 4*0 $ RHO = 1*0
EX1 = 1.0/3.0 $ EX2 = 2.0* EX1
TOL = 1.0E-3
GAM=3 = 0.83298
PI = 3.1415916 $ F1 = 96487.0 $ FRT = 38.92317859
K = 2.91186E-3 $ A = SORT(0.91023262)
RT1 = SORT(1.0E5) $ RT2 = SORT(3.0E5)
C1(1) = 0.0 $ C2(1) = 0.0
BAC(1,1) = 0.0
CCLREF = 4.17
VM = -0.2676 $ ALCP(CCLREF)/FFT
AA1 = 1.0 $ AC1 = 1.0
AA2 = 1.0 $ AC2 = 1.0
C THE DENSITY OF THE SOLVENT IS TAKEN AS 1.0 AND IS INCLUDED IN THE
C APPROPRIATE CONSTANTS.
UFE = 0.4*W $ L02 = 1.229
SET = -0.4576
PASS = 1.0E-7
EXCH1 = 1.0928494E-5 $ CFKEF = 4.0
EXCH2 = 7.487E-2 $ CO2EF = 1.0E-4
DFF = 0.739E-5 $ CO2 = 1.3E-5 $ OOH = 5.260E-5
DAMP = 0.50 $ DAMPD = 0.50
C CONCENTRATIONS ARE IN MOLES/LITRE
CFKIF = 0.0 $ CO2IF = 1.0E-4 $ COIMF = 1.0E-7
CCHMIF = 1.0E-7
C A 3.5 PERCENT SEA WATER SOLUTION HAS THE SAME CONDUCTIVITY AS
C A NACl SOLUTION OF 0.152 MOLAR. SEE CRC FOR VALUES.

VIS = 0.01
C STATEMENTS THROUGH 4 ARE FOR THE LEGENDRE POLYNOMIALS X,W ARRAYS
IHPI = IH + 1
READ 101, (X(I), W(I), I = IHPI, IH)
DO 3 I = IH, IM $ IF(I .LT. IHPI) GO TO 1 $ X(I) = 0.5 + 0.5*Y(I)
GO TO 2
1 IF = IH-I+1 $ X(I) = 0.5-0.5*W(I) $ W(I) = W(IR)
2 X = SORT(1.0 - X(I)**2) $ DO 3 NN = 1, NMXX $ N = NN-1
3 R(NN+I) = P(2*N+X,1) $ DO 4 NN = 1, NMXX $ P0(NN) = P(2*N,0,0)
4 CONTINUE
PRINT 103, (X(I), W(I), I = 1, IM)
C THE POINT OF PASSIVATION IS CHOOSEN BY SPECIFYING THE SPECIFIC MESH
C POINT AT WHICH IT IS TO OCCUR.
C THE RADIAL COORDINATE, RP, IS THEN CALCULATED

ROT = 122.30
R0 = 6.35
NRO = 2
DO 24 JR = 1, NRO
READ 103, (COND, RHC, VIS, COND, COREF, CO2REF, COHREF, CFEIF, 1)
1002, C02IF, COHIF, AA1, AA2, AC1, AC2, NJ1, NJ2, EXCH1, EXCH2, RC, ROT, LMAX
Q1 = EXP((AA1**FRT*(VM+UFE))**EXCH1/CFEREFF**A1/2.0)
Q2 = EXP((AA1 + AA1)**FRT*(VM+UFE))
Q3 = EXCH2*EXP(-AA2**FRT*(VM+U02))**CO2REF*(1.0-AC2/4.0)/COHREF**1.0
Q4 = EXP((AA2 + AC2)*(VM+U02)**FRT)
Q6 = SQRT(ROT/VIS)**((1.0/6.0)*K**EX1*Q2**EX2)**1.0E-3
Q7 = Q6*(0.02QF)**EX2
Q8 = COHIF + 4.0*(0.02QF)**EX2**CO2IF
Q9 = DFE**EX2**SAVZ**AA2**GAM43**AA2/3.0**EX1**SQRT(ROT/VIS)**((1.0/6.0)*1.0E-3
ILAM02 = 4.0**F1**CO2IF**AA2/3.0**EX1**GAM43**SQRT(ROT)*0.02**EX2/
1VIS**((1.0/6.0)**1.0E-3
PRINT 103, ILAM02
RZRO = R0**SQRT(ROT/VIS)
REEG5 = R205**2
PRINT 113, REEG5
M = 1.0/(FLOAT(LMAX)-1.0)
DO 20 I = 1, LMXX
S(I) = (FLOAT(I) -1.0)**4*EX1
DUM = RZRO**S(I)
20 CONTINUE
C THE ROW INDEX REPRESENTS THE UPPER LIMIT OF THE INTEGRAL. THE COLUMN
C INDEX IS A SPECIFIC POINT WHERE THE STEP CHANGE IN CONCENTRATION OCCURS.
DO 6 LL = 2, LMAX
SAV2 = GG1, LL)
DRL(1) = SAV2
DO 6 I = 2, LL
SAV1 = GG1, LL)
IF (LL EQ.I) BAC1, LL) = -1.0/EX2**SAV2**S(I)(LL) -Z(1LL) -Z(LL-I)**EX2
BAX = SAV1**Z(1LL) -Z(I)**EX2
BZ = SAV2**Z(1LL) -Z(I)**EX2
SAV2 = SAV1
IF (LL .NE. I) B3AC1, LL) = (BAX-BAZ)/ALOG(BAX/BAZ)*ALOG((Z(1LL) -Z(I)
1)/Z(1LL) -Z(I-1))
IF (LL .NE. 2 AND I .NE. 2) AAC1, LL, I) = BAC1, LL, I-1) -BAC1, LL, I)
6 CONTINUE
ICOUNT = 0
IF (F) = 1
IMIN = G I IMAX = 0
OPTN = 0
23 CONTINUE
DO 17 N = 1,NMAX
B(N) = 0.0 $ D(N) = 0.0
BOLD(N) = B(N) $ DOLD(N) = D(N)
17 CONTINUE
26 CONTINUE
ICOUNT = ICOUNT + 1
IF(ITER.EQ.100) GO TO 24
IF(ITER.EQ.1) LP = LMAX
IF(ITER.EQ.2) LP = 2
IF(LP.LE.1) LP = 2
RP = ((FLOAT(LP)-1.0)/(FLOAT(LMAX)-1.0))**EX1*R0
C SETTING UP THE ARRAY OF EVENLY SPACED POINTS AND LEGENDRE POLYNOMIALS
DO 5 I = 1,LMAX
T(I) = SII*R0/RP
DO 5 LL = 1,NMAX
M1 = SQRT(1.0 -((FLOAT(I)-1.0)**EX2)
IF(I .GT. LP) H2 = SQRT(1.0 -((FLOAT(I)-1.0)**EX2*(R0/RP)**2)
RP(LL,I) = P(2*LL-2,M1)
IF(I.GE. LP) H2 = 0.0
IF(I.LE. LP) RR(RL,I) = P(2*LL-2,H2)
5 CONTINUE
IF(ITER .LE. 90) GO TO 27
PRINT 100,LP,MINMAX
PRINT 110
PRINT 102,(B(N), N = 1,NMAX)
PRINT 111
PRINT 103,(D(N), N = 1,NMAX)
PRINT 103,(ERP(N), N = 1,MAX)
27 CONTINUE
C MI IS THE DISTANCE IN (R/R0)**3
C M2 IS THE DISTANCE IN (R/RP)**3
DO 7 I = 1,LMAX
M1 = (FLOAT(I) -1.0)**H
ETA = SQRT(1.0 -M1**EX2)
IF(I .GT. LP) XIP = SQRT(M1**EX2*(R0/RP)**2 -1.0)
IF(I.EQ. LP) IRP = I
SUM = 0.0
C B(N) ARE FOR THE IRON REACTION ON THE DISK RP
C D(N) ARE FOR THE OXYGEN REACTION ON THE DISK R0
DO 8 N = 1,NMAX
SUM = RP(N,I)*D(N) + SUM
8 CONTINUE
IF(I.GT. LP) GO TO 10
DO 9 N = 1,NMAX
SUM = SUM + RFR(N,I)*3(N)
9 CONTINUE
F(I) = SUM
GO TO 12
10 CONTINUE
DO 11 N = 1,NMAX
SUM = SUM + 3(N)*FO(N)*FLNM(2*K-2,XIP)
11 CONTINUE
F(I) = SUM
12 CONTINUE
7 CONTINUE
V = F(IP) + SET
DO 15 L = 1,LMAX
ETA = (V+F(L))*FRT
DUMR = F20*R*S(L)
IF(DUMR.LE. RT1) XL = A*DUMR
IF(DUHR > GT, RT1 > AN0, DLMR > LI, RT2) XL = SRT(0,7478E1*DUHR**21,11 18E1)
IF(DUHR > GT, RT2) XL = SRT(0,55E-3*DUHR**2, E)
SUM1 = 0.0 % SUM2 = 0.0
IF(L.LT.3) GO TO 14
LM1 = L-1
DO 13 J = 2,LM1
SUM1 = SUM1 + AAC(L,J)*C1(J)
SUM2 = SUM2 + AAC(L,J)*C2(J)
13 CONTINUE
14 CONTINUE
IF(L.NE.1) SUM1 = SUM1-C1(1)*BAC(L,2) + FZ(L)/Z(L)**EX1*(C1(1)-
1CEIF)
IF(L.NE.1) SUM2 = SUM2 -C2(1)*BAC(L,2) + CRV(L)/Z(L)**EX1*(C2(1)-
1CO2IF)
IF(L.EQ.1) C1(1) = (CEIF+Q1*EXP(AA1*ETA)/2,0/F1/09)/(1,0+Q1*02/
1O9/2,0/F1*EXP(-AC1*ETA))
IF(L.EQ.1) C2(1) = (CC2IF*Q9*(C02/DFE)**EX2 + (C01+IF/4,0 + (D02/D0H)
1**EX2*C02IF)
2 *Q3/F1*EXP(AA2*ETA))/O9*(D02/D0H)**EX2 +G3/F1*(DC2/D0H)
3**EX2*EXP(AA2*ETA) + Q3*G4/4,0/F1*EXP(-AC2*ETA))
IF(L.EQ.1 1) SUM1 = (Q1/2,0/F1*EXP(AA1*ETA) - Q6*XL
1*SUM1/(Q1**2/2,0/F1*EXP(-AC1*ETA) + Q6*XL*BAC(L,L))
IF(L.GT. IRP) C1(L) = (PASS/2,0/F1/XL/06-SUM2)/BAC(L,L)
IF(L.NE.1) C2(L) = (Q3/4,0/F1*Q9*EXP(AA2*ETA)-Q7*XL*SUM2)/(Q3/4,
1/F1*(4,0*D02/D0H)**EX2*EXP(AA2*ETA) +Q4*EXP(-AC2*ETA)) +Q7*XL*BAC
1(L,L))
C3(L) = CCG1F + 4,0*(CC2IF -C2(L))**EX2
IF(L.LE. IRP) CR(l,L) = C1**(EXP(AA1*ETA)-C1(L)**G2*EXP(-AC1*ETA))
IF(L.GT. IRP) CR(l,L) = PASS
CRD2(L) = Q3*(C3(L)**EXP(AA2*ETA) -Q4*C2(L)**EXP(-AC2*ETA))
15 CONTINUE
TCO1 = 0.0 % TCO2 = 0.8
DO 16 I = 1,IM
LI = X(I)**3/8 + 1
LIR = (LI**RP/80)**3/8 + 1
IF(LIR .LT. 10) CRD1(LIR) = CRD1(LIR) + (CRD1(LIR+1)-CRD1(LIR)+
1*Q2(LIR)**2/(LI**2-10)**2)**2)
C02(I) = C02(I) +Q2D2(LI)**2*CRD2(LI) +Q3**2*SLI**2)/(SLL
I+1)**2-S(LI)**2)
TC01 = TCO1 + PI**RP**2*X(I)**W(I)*C01(I)
TC02 = TCO2 + PI**F0**2*X(I)**W(I)*C02(I)
16 CONTINUE
TCR = TCO1 + TCO2
DO 25 N = 1,NMAX
BOLD(N) = (B(N)**(1,0-DAPFB)*BOLD(N))/DAPFB
DOLD(N) = (D(N)**(1,0-DAPPD)*DOLD(N))/DAPPD
B(N) = 0.0 % D(N) = 0.8
DO 18 I = 1,IM
B(N) = B(N) +P0(N)**2*PI**RP/2,0/COND*FLCAT(4*N-3)**0,5*X(I)**W(I)*
1*(C02(I) +PASS)**R(N,I))
D(N) = D(N) +P0(N)**2*PI**RP/2,0/COND*FLCAT(4*N-3)**0,5*X(I)**W(I)*
1*(C02(I) +PASS)**R(N,I))
18 CONTINUE
25 CONTINUE
DC 19 N = 1,NMAX
ERR(N) = ABS(B(N) -BOLD(N))/B(N))
ERD(N) = ABS(D(N) -DOLD(N))/D(N))
IF(ERD(N) > LT, TCL .AND. CPTN,E0,3) GO TO 24
IF(ERD(N) > GT, TCL .OR. ERD(N) > GT, TCL) GO TO 21
19 CONTINUE
ICOUNT = 0
ITER = ITR + 1
PRINT 106, ITER
PRINT 106, LP, INN, LMAX
PRINT 112, OPTN
PRINT 103, V
PRINT 108
PRINT 103, (C1(L), L = 1, LMAX)
PRINT 109
PRINT 103, (C2(L), L = 1, LMAX)
PRINT 106
PRINT 114
PRINT 103, (C3(L), L = 1, LMAX)
PRINT 103, (C01(L), L = 1, LMAX)
PRINT 107
PRINT 103, (C02(L), L = 1, LMAX)
PRINT 105
PRINT 103, (F(L), L = 1, LMAX)
PRINT 104, TC01, TC02, TCR
PRINT 103, (C01(I), I = 1, IM)
PRINT 103, (C02(I), I = 1, IM)
IF (ITER .EQ. 1) INN = LMAX
IF (ITER .EQ. 2) CURMAX = TCR
IF (ITER .EQ. 3) IMIN = 2
IF (ITER .EQ. 3) CURMIN = TCF
IF (ITER .EQ. 2) TCRSV1 = TCR
IF (ITER .EQ. 3) TCRSV2 = TCR
IF (ITER .EQ. 2) GO TO 23
IF (TCRSL + 0.0 .AND. TCRSV2 + LT. 0.0) OPTN = 0
IF (TCRSL + 0.0 .AND. TCRSV2 + LT. 0.0) OPTN = 1
IF (TCRSL + 0.0) GO TC 24
IF (OPTN .NE. 0) GO TO 24
IF (TCRSL + 0.0) IMAX = LP
IF (TCRSL + 0.0) CURMAX = TCR
IF (TCRSL + 0.0) IMIN = LP
IF (TCRSL + 0.0) CURMIN = TCR
LP = IMIN + (IMAX - IMIN) * (-CURMIN / (-CURMIN + CURMAX))
IF (LP .LT. IMAX .AND. LP .LT. IMAX) GO TO 26
IF (IMAX .EQ. IMIN + 1) GO TO 24
IF (LP .EQ. IMIN) LP = LP + 1
IF (LP .EQ. IMAX) LP = LP - 1
GO TO 26
21 CONTINUE
DC 22 N = 1, NMAX
B(N) = (1.0 - DAMPE) * BOLD(N) + DAMP * B(N)
D(N) = (1.0 - DAMPD) * DOLD(N) + DAMPD * D(N)
22 CONTINUE
GO TO 26
24 CONTINUE
END
FUNCTION FUNMIN(XI)
XI2 = XI**2 $ ADD = 1.0 $ SUM = 1.0
PI2 = 1.5707963267948
IF (ABS(XI) + LT. 1.0) GO TC 7 $ DO 1 K = 1, N
ADD = ADD * FLOAT(2*K+N-1)**2/FLOAT(K) / (FLOAT(K+N)+0.15)**2
SUM = SUM + ADD
1 IF (ABS(A) + LT. 1.0E-9*ABS(SUM)) GO TO 2
FUNM = SUM/XI**2*(1.0/N)*PI2 $ IF (N . EQ. 0) RETURN
DC 3 NN = 1, N
3 FUNM = FUNM*FLOAT(NN)/FLOAT(2*N+1) $ N2 = N/2
IF (N . NE. 2*N2) GO TO 5 $ DO 4 NN = 1, N
4 FUNM = FUNM*FLOAT(NN)/FLOAT(2*N+1) $ RETURN
FUNCTION F3M(Z1, Z2)
C Z1 IS THE SQUARE ROOT OF THE REYNOLDS NUMBER FOR THE STEP CHANGE IN
C SURFACE CONCENTRATION. Z2 IS THE SQUARE ROOT OF REYNOLDS NUMBER FOR
C THE SPECIFIC POSITION IN QUESTION.
REAL K
IF(Z1.NE. Z2) GO TO 11
XX = 0.0
RETURN
11 CONTINUE
K = 2.9116E-3  A = SQRT(0.51023262)
RT1 = SQRT(1.5E5)  RT2 = SQRT(3.0E5)
IF(ZX-RT2) 1,1,6
1 IF(ZX-RT1) 2,2,3
2 XX = 3.0*K*A*(FX**3-PZ**3)
DBETA = A**2*FX
XDSK = 3.0*K*A*RX**3
RETURN
3 XX = 3.47E1*K*(RX**2.559-RT1**2.559)+ 3.0*K*A*RT1**3
DBETA = 9.747E1*RX**(1.186)
XDSK = XX
IF(ZX-RT1) 4,4,5
4 XX = XX-3.0*K*A*XZ**3
RETURN
5 XX = XX-3.0*K*A*RT1**3-3.47E1*K*(Z1**2.559-RT1**2.559)
RETURN
6 XX = 3.0*K*A*RT1**3+3.47E1*K*(RT2**2.559-RT1**2.559)+.2522K*(
1RX**3.3-RT2**3.3)
DBETA = 9.59E-3*RX**1.6
XDSK = XX
IF(ZX-RT1) 7,7,8
7 XX = XX-3.0*K*A*RX**3
RETURN
8 IF(ZX-RT2) 9,9,10
9 XX = XX-3.0*K*A*RT1**3-3.47E1*K*(Z1**2.559-RT1**2.559)
RETURN
10 XX = XX-3.0*K*A*RT1**3+3.47E1*K*(RT2**2.559-RT1**2.559)-.2522K*
1*(Z1**3.3-RT2**3.3)
RETURN
END
FUNCTION GSIZ(L)
C I REPRESENTS THE POINT AT WHICH THE STEP CHANGE IN CONCENTRATION OCCURS.
C S, L IS THE PARTICULAR FRESH POINT AT WHICH THE DERIVATIVE IS EVALUATED.
C THIS FUNCTION CALCULATES THE DERIVATIVES BY FITTING THE RESULTS
C FROM PROGRAM METRUB. THIS PROGRAM IS CHEAP TO RUN.
COMMON RZD0, LMAX
REAL K
100 FORMAT(5E15.3)
EX1 = 3.0/2.0  EX2 = 1.0/3.0
EXR1 = 3.0  EXR2 = -3.5  EXAM4 = 1.0/1.11985
A1D = 0.986288  A2E = 0.017152  EXD = 10.5  EXC = 4.5  EG2D = 0.9
RZ = RZD*(IFLOAT(11-1.0)/(IFLOAT(LMAX-1.0)**EX2

5 FUNM = FUNM*PI2 1 IF(N2.EQ.0) RETURN 5 DC 6 NN = 1*N2
6 FUNM = FUNM*FLOAT(NN) + 0.50)/FLOAT(NN) 1 RETURN
7 A2 = 0.0  N2 = N/2 1 IF(2*N2.EQ.N) GO TO 9 8 A1 = -PI2
IF(N.EQ.1) GO TO 11 1 DO 9 NN = 3*K+2
8 A1 = A1/(1.0-1.0/FLOAT(NN))**2 1 GO TO 11
9 A1 = -1.0/PI2 1 IF(N.EQ.0) GO TO 11 1 DO 10 NN = 2*N2
10 A1 = A1/(1.0-1.0/FLOAT(NN))**2
11 A1 = A1*XI 1 FUNM = A2 + A1 1 DO 12 K = 2,500,2
A2 = A2**2*FLOAT(K-N-2)*FLOAT(K-N-1)/FLOAT(K-K)
A1 = -A1*XI*2*FLOAT(K-N-1)*FLOAT(K-K+K)
A2 = A2**2*FLOAT(K-K+K)
12 IF(ABS(ACD)+LT.1.E-9*ABS(FUNM)) RETURN 1 RETURN 1 END
RX = FZRC*((FLOAT(L)-1.0)/(FLCAT(LMAX)-1.0))**EX2
RT1 = SORT(1.5E5) $ RT2 = SORT(3.0E5)
RTT1 = SORT(2.0E5)
IF(RX-RT1) > 0.0 E5
6 GG = 1.0/GAM43
RETURN
7 CONTINUE
R1 = RX**EX1
C THIS PORTION OF THE PROGRAM CALCULATES XDISK* X WHEN RZ = 0.
K = 2.9116E-3 $ A = SQRT(10.5102362)
1 IF(RX-RT2) > 1.1

2 XDSK = 3.0*K*A*RX**3
DBETA = A**2*FX
GO TO 5
3 XDSK = 3.0*K*A*RX**3 + 3.472E1*K*(RX**2,559-RT1**2,559)
DBETA = 9.747E1*RX**10.1186
GO TO 5
4 XDSK = 3.0*K*A*RX**3 + 3.472E1*K*(RT2**2,559-RT1**2,559) + 0.2522
1*K*(RX**3.3-RT2**3.3)
DBETA = 8.55E-3*RX**1.6
5 CONTINUE
DBETA = SQRT(DBETA)
XD = ALOG10(RX**2)-5.315
YCEPT = 2.415
1 IF ALOG10(RX**2) > 5.3 AND, ALOG10(0.3)-LT. 5.55) B1DF=4.58
2 IF ALOG10(RX**2) > 5.3 AND, ALOG10(0.3)-LT. 5.55)
DBETA = 2.417
DNULC = ALOG10(X10*EXP(B1C*EXP*X0)+A20*EXP(B20*EXP*X0))**10.0/EXD1)
1 XFD + YCEPT + ALOG10(GAM43)
EXR = EXR1 + (RX-RTT1)/(1.0E3-RTT1)*EXR2
XR = (RZ/RX)**EXR
IF(XDOSK.NC. 0.0) BiF = DNULC + ALOG10((XDKS/K)**(1.0/3.1)+P1/DBETA)
IF(ALOG10(RX**2) > 5.315) GG = 1.0**81F*SQRT(1.0-P1)/GAM43
IF(ALOG10(RX**2) > 5.315) GG = 1.0/GAM43
IF(L .EQ. MAX) AND, I .EQ. 2) PRINT 100,RX,GG
RETURN $ END
FUNCTION GG(II,I) AX
C THIS SUBROUTINE CALCULATES THE DERIVATIVES AS IS DONE IN PROGRAM
C MATFUE. THIS FUNCTION IS EXPENSIVE TO RUN.
DIMENSION A(199),B(199),C(200),D(199),G(199),BETA(199),GAM(199)
COMMON RZRO,LMAX
COMMON/RES/DBETA
RT1 = SORT(2.0E5) $ RT2 = SORT(3.0E5)
GAM43 = 0.89298
RTT1 = SORT(1.5E5)
JMAX = 199
EX1 = 3.0/2.0 $ T = 2.25/FLCAT(JMAX)
EX2 = 1.0/3.0
RCHECK = RZRO*((FLOAT(I MAX)-1.0)/(FLCAT(LMAX)-1.0))**EX2
1 IF(RCHECK-RTT1)> 9.9,1
1 CONTINUE
F = 0.0
IF(JMAX .EQ. 0) STOP
C LIN.,MOULTON, AND PUTNAP USE A VALUE OF K = 3.28E-4.
C WASAN, TIAN, AND WILKE USE A VALUE OF K = 4.4E-4.
JMP1 = JMAX + 1
C(JMP1) = 1.0 $ C(O) = 0.0
DO 2 J = 2,JMAX
G(J) = 0.0 $ C(J) = 0.0
2 CONTINUE
Y = 0.0
RZ = RZRO*((FLOAT(I)-1.0)/(FLOAT(LMAX)-1.0))**EX2
RX = RZ
DO 8 I = II, I*MAX
FAC = 1.0
IF(I.EQ.II+1) AND (FZ.EQ.0.0) FAC = 0.50
YO = Y
IF(I.GT.II) RX = RZRO*((FLOAT(I)-1.0)/(FLOAT(LMAX)-1.0))**EX2
IF(RX.GT.RT1) AND (RX.LE.RT2) F = (RX-RT1)/(RT2-RT1)
IF(RX.GT.RT2) F = 1.0
Y = XX(RZ,RX) $ R1 = RX**EX1
IF(I.NE.II) DBETA = SOR(T(DBETA))
G1 = Y-YO
IF(I.NE.II) GO TO 4 $ G1 = 1.0 $ R1 = 1.0
4 CONTINUE
DO = 1.0
DO 5 J = 2, JMAX
XI = FLOAT(J-1)*H
C DO IS THE VARIABLE THAT EXPRESS THE FORM FOR THE LODY DIFFUSIVITY.
C IF DO IS 1.0, THE KPLUS**3 FORM IS USED, KPLUS**4 IS EXPRESSED WHEN
C DO = 1.0
G(J) = G(J) -9.0*XI*(Y+Y)H**2*C(J)/G1*FAC
A(J) = 1.0 +3.0*XI**2*(1.0+Y*Y*/R1*DD)H/2.0
B(J) = 9.0*XI**3*F/R1*DD -5.0*XI*(Y+Y)*H**2/G1*FAC
D(J) = (1.0 +3.0*XI**2*(1.0+Y*Y*/R1*DD)H/2.0
5 CONTINUE
G(JMAX) = G(JMAX) -D(JMAX)*C(JMP1)
BETA(2) = B(2) $ GAM(2) = G(2)/B(2)
DO 6 J = 3, JMAX
BETA(J) = B(J) -A(J)*D(J-1)/BETA(J-1)
GAM(J) = (G(J) -A(J)*GAM(J-1))/BETA(J)
6 CONTINUE
C(JMAX) = GAM(JMAX)
DO 7 J = 3, JMAX $ JJ = JMAX -J + 2
C(JJ) = GAM(JJ) -D(JJ)*C(JJ+1)/BETA(JJ)
7 CONTINUE
CPI = C(2)/H
DO 3 J = 2, JMAX
XI = FLOAT(J-1)*H
G(J) = -A(J)*C(J-1) -9.0*XI**2*C(J)+D(J)*C(J+1)
1-9.0*XI*(Y+Y)H**2/G1*FAC*C(J)
3 CONTINUE
8 CONTINUE
GG = CPI
return
9 GG = 1.0/GAM43
RETURN
END
FUNCTION P(N,X)
P1 = 1.0
P2 = X
IF(N-1) 1.2, 3
1 P = P1
RETURN
2 P = P2
RETURN
3 NM1 = N-1
DO 4 NU = 1,NM1
P = (X*FLOAT(2*NU+1)*P2-FLOAT(NU)*P1)/FLOAT(NU+1)
P1 = P2
P2 = P
RETURN
END
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