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Effects of Nonuniform Potential and Current Distributions in Electrochemical Systems

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Effects of Nonuniform Potential and Current Distributions in Electrochemical Systems

Alan C. West

Abstract

We examine the effects that nonuniform current and potential distributions have on electrochemical systems. Chapter 1 provides definitions used by researchers studying these phenomena. In chapter 2, we discuss boundary integral techniques, which are powerful numerical methods used in such studies. In chapters 3 and 4, an asymptotic solution is developed that shows explicitly how the extreme characteristics of a primary current distribution are approached when the ohmic resistance of the cell becomes large compared to the resistance of the faradaic reaction. It is shown how these results can be used to complement and verify more common numerical analyses. Chapters 5 and 6 show how to determine exchange current densities and transfer coefficients when the reaction rate along the electrode is nonuniform. The results can be used to design experiments that provide for a more straightforward interpretation of data. The ohmic resistance and current distribution for a recessed disk electrode are given in chapter 7. Chapter 8 discusses briefly experimental work intended to elucidate whether the dissolution kinetics of ferrous-sulfate films must be included in mathematical descriptions of the complicated dynamic behavior of iron dissolution in sulfuric acid.
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CHAPTER 1
Introduction

This chapter defines terms that are used by researchers studying how reaction rates, electrochemical potentials, and surface concentrations are distributed along an electrode.

The best known parameter used in characterizing current distributions is the Wagner number. Its importance was established by Hoar and Agar [1] and was clarified by Wagner in 1951 [2]. In general, the Wagner number does not characterize completely the current and potential distributions in the solution. In 1966, Newman [3] showed for the rotating disk electrode which parameters are important for the various limiting cases and for the general problem. With his 1966 paper, the study of the distribution of current density on planar electrodes becomes a well-defined science. The study of current distributions in porous electrodes is also understood [4].

Wagner Number

The Wagner number represents the ratio of the kinetic to ohmic resistances to the flow of current. As the Wagner number approaches zero, the current approaches a "primary current distribution." When the kinetic resistance dominates, the distribution of current density is uniform. Since the Wagner number is defined by different variables for different reaction regimes, Newman does not explicitly use it.
Mass-Transfer Controlled Current Distributions

An important limiting case is the mass-transfer controlled (limiting) current distribution. In the absence of migration, the limiting current density is determined by procedures that are common in the heat and mass-transfer literature [5,6,7]. Newman showed [8] that, for boundary-layer flows, migration at the limiting current does not affect the distribution of current but does change its magnitude.

Primary Current Distributions

In the absence of concentration variations, Laplace's equation determines the current distribution. When the kinetic resistance of the interfacial reaction is zero compared to the ohmic resistance, the current distribution is known as primary. This case is important because it may be desirable to compare different cell designs to minimize the ohmic resistance. The ohmic potential drop increases with the size of an electrochemical system; therefore the primary current distribution is approached as a system is scaled-up. The primary current distribution is also approximately valid, for example, for short times after a step change in the electrode potential.

Secondary Current Distributions

In practical situations, the kinetics of a reaction are important. When an interfacial resistance is included but mass-transfer effects are neglected, the current distribution is known as secondary. To study the effects of finite kinetics, it is instructive to
study the two limiting cases of the Butler-Volmer equation, known as linear and Tafel kinetics. The behavior of a system, for a given Wagner number, depends on which reaction regime is applicable. A dimensionless exchange current density is the important parameter for linear kinetics, and a dimensionless average current density is important in characterizing the distribution for Tafel kinetics.

For linear kinetics, analogous boundary conditions are found in heat-transfer problems, and experience obtained from these studies can provide insight into the behavior of current distributions. For Tafel kinetics, analogous boundary conditions do not exist, and it is necessary to develop intuition specifically for this important limiting case. For example, Smyrl and Newman [9] show that, under certain well-defined conditions, the current density at the edge of an electrode is proportional to the square of the average current density.

Tertiary Current Distributions

Below the limiting current, when both ohmic potential drop and convective diffusion are important, the problem is complicated. Newman discussed this class of problems [10]. Complete characterization of a tertiary current distribution can require many parameters.

Porous Electrodes

Newman and Tiedemann [4] reviewed the solution procedure for the determination of current distributions in porous electrodes. The same limiting cases discussed above are important. Intuition developed from studying planar electrodes aids in understanding the
current distribution in porous electrodes.

Summary

Significant progress in studying current distributions requires useful numerical procedures. Chapter 2 discusses a numerical method that we have used for studying primary and secondary current distributions. Chapters 3 through 7 present results that are obtained with this method. It is hoped that these results are directly useful to the reader. If not, they elucidate behavior that is helpful in understanding phenomena observed in other current distribution studies.

Chapter 8 discusses experimental observations of the Fe/H₂SO₄ system. The complicated behavior that is observed for this system is, in part, a result of nonuniform potential and current distributions. This is a passivating system, which makes it quite sensitive to the potential distribution along the electrode.

To allow for leisurely reading, the chapters have been largely written so that they can be read independently. Particularly, the details of the numerical method given in chapter 2 are unnecessary for the rest of the thesis.

References


Laplace's equation often arises in mathematical descriptions of electrochemical systems. This chapter discusses the use of boundary integral methods for solving it. For a more general discussion of numerical methods used in current distribution problems, see references [1], [2], [3], and [4]. Greenberg [5] and Ramkrishna and Amundson [6] gave details pertaining to the application of boundary integral techniques to other linear operators.

Boundary-elements have become increasingly popular since the mid-1970's [7], [8], [9]. Also becoming popular are the finite-element methods. Comparisons of these methods are found in papers by Hume et al. [10] and by Dukovic and Tobias [11]. Most of the advantages and disadvantages of boundary integral techniques apply regardless of how the equations are formulated or solved.

Boundary-element methods require fewer nodes, at which the finite-difference approximations to the equations are solved, than finite-element methods. However, the resulting equations form a dense matrix (as opposed to a banded matrix). Therefore, computation time is not greatly reduced, even though the number of unknowns can be considerably less.

Contrary to many techniques [7], [8], [9], the solution procedure that we discuss does not pose the problem as one to be solved by the method of weighted residuals. The method permits any type of
basis function\(^\dagger\) and allows for the form of the basis function to vary with position. This is particularly important for primary current distributions.


The technique of Cahan et al. discretizes the boundary conditions and solves for the potential near, but not on, the boundary. In this manner, the method avoids evaluating the singularities that arise in equations (5), (12), and (14). We prefer handling directly these singularities because errors that arise from their procedure are avoided. This becomes particularly important in the calculation of primary current distributions.

**Green's Theorem**

Boundary integral methods are based on the second form of Green's theorem (see [15], for example),

\[
\int_V \left( g \nabla^2 \phi - \phi \nabla^2 g \right) dV = \int_{\partial V} n \cdot \left( g \nabla \phi - \phi \nabla g \right) dA. \tag{1}
\]

\(^\dagger\) *Basis functions* is a term borrowed from traditional finite and boundary-element methods. It describes the manner in which a function is interpolated between nodes.
If $\Phi$ satisfies Laplace's equation, equation (1) becomes

$$-\int_V \Phi \nabla^2 \Phi \ dV = \int \nabla \cdot \left( \frac{\Phi \nabla \Phi}{\Phi} \right) dA. \quad (2)$$

A clever choice of $g$ greatly facilitates the determination of the potential. Specifically, $g$ is chosen to satisfy

$$\nabla^2 g = \delta(x-x_q,y-y_q,z-z_q), \quad (3)$$

where $\delta$ is the three-dimensional Dirac delta function, $x$, $y$, and $z$ are the Cartesian coordinates, and $x_q,y_q,z_q$ specifies a point. One Green's function $g$ that satisfies equation (3) is $g = \frac{1}{\xi_3}$, where

$$\xi_3 = \left[ (x-x_q)^2 + (y-y_q)^2 + (z-z_q)^2 \right]^{\frac{1}{2}}. \quad (4)$$

Physically, $g$ can be thought of as the potential at $x_q,y_q,z_q$ due to a point source of current at $x,y,z$.

Substituting $g$ into equation (2) gives

$$-\alpha_3 \Phi(x_q,y_q,z_q) = \int \nabla \cdot \left( \frac{1}{\xi_3} \nabla \Phi - \Phi \frac{1}{\xi_3} \right) dA, \quad (5)$$

where $\alpha_3$ is $4\pi$ for a point, $x_q,y_q,z_q$, in the domain of the problem, $2\pi$ for a point on a smooth boundary, and zero for a point outside the domain. In general,

$$\alpha_3 = \lim_{R_o \to 0} \frac{A_S}{R_o^2}, \quad (6)$$

where $A_S$ is the surface area of the portion of a sphere around $x_q,y_q,z_q$ which falls within the domain of the problem [7]. Figure 1 shows the two-dimensional analog to $\alpha_3$. Equation (5) shows that the solution for $\Phi$ is reduced to a problem on the boundary of the domain.
Figure 1. Schematic showing the coefficient given in equation (6) for two-dimensional geometries. $A_s$ is the surface area of the portion of the sphere that falls within the domain of the problem, and $C_s$ is the arc length of the portion of a circle that falls within the domain.
Once the potential and current density are known everywhere on the boundary, the potential can be found anywhere in the domain.

Since equation (3) is linear, solutions for $g$ can be superposed. Specifically, if $g_h$ satisfies Laplace's equation, $\frac{1}{\xi_3} + g_h$ satisfies equation (3). Choosing $g_h$ so that $n \cdot \nabla (\frac{1}{\xi_3} + g_h) = 0$ everywhere along the boundary of the domain can reduce greatly the numerical computation necessary for a solution since equation (5) becomes

$$ -\alpha_3 \Phi(x_q, y_q, z_q) = \int_{\partial V} n \cdot \left( \frac{1}{\xi_3} + g_h \right) \Phi dA. $$

(7)

This approach is taken, for example, by Alkire and Mirarefi [16] and has been used extensively by mathematical physicists [17]. A good discussion of these methods is given by Greenberg [5].

Many electrochemical cells are approximated as two dimensional or axisymmetric. The next two sections give boundary integral equations that are more conveniently used for these cases.

**Two-Dimensional Geometries**

If the geometry of interest contains no $z$ dependence, equation (2) can be written as

$$ - \left( \int_A \Phi^2 g \, dx \, dy \right) \Delta z - \left( \int_{\partial A} n \cdot \left[ g \nabla \Phi - \phi \nabla g \right] dl \right) \Delta z, $$

(8)

where $dl$ is a differential line element. If $g$ is now chosen to satisfy
\[
\frac{\partial^2 G}{\partial x^2} + \frac{\partial^2 G}{\partial y^2} = \delta(x-x_q, y-y_q), \tag{9}
\]
then equation (8) reduces to

\[
\alpha_2 \Phi(x_q, y_q) = \int_{\partial A} \left[ \Phi \frac{\partial G}{\partial n} - G \frac{\partial \Phi}{\partial n} \right] dl, \tag{10}
\]
where \(\partial/\partial n\) implies the component of the gradient that is normal to the boundary. \(\alpha_2\) is \(2\pi\) for a point inside the domain, zero for a point outside the domain, and \(\pi\) for a point on a smooth boundary.

Figure 1 shows \(\alpha_2\) for a point where the slope of the line drawn tangent to the boundary is discontinuous.

The two-dimensional Green's function \(g\) is \(g = \ln \xi_2\), where

\[
\xi_2 = \left[ (x-x_q)^2 + (y-y_q)^2 \right]^\frac{1}{2}. \tag{11}
\]
\(g\) is the potential at \(x_q, y_q\) due to a line source of current that is perpendicular to the \(xy\) plane and passes through the point \(x, y\). Substituting \(g\) into equation (10) gives

\[
\alpha_2 \Phi(x_q, y_q) = \int_{\partial A} \left[ \frac{\Phi}{\xi_2} \frac{\partial \xi_2}{\partial n} - \ln \xi_2 \frac{\partial \Phi}{\partial n} \right] dl. \tag{12}
\]

Axisymmetric Geometries

For axisymmetric geometries, equation (5) can be written as

\[
-\alpha_3 \Phi(r_q, z_q) = \int_{\partial V} \left[ \frac{1}{\xi_3} \nabla \Phi - \Phi \nabla \frac{1}{\xi_3} \right] r d\theta dl, \tag{13}
\]
where \(r, \theta, z\) are the cylindrical coordinates, \(r_q, z_q\) specifies a location, and \(r d\theta dl\) is the differential surface area.
Since by assumption the problem is axisymmetric, the \( \theta \) dependence of equation (13) can be eliminated to give

\[ -a_3 \Phi(r_q, z_q) - \int_A \left[ g \frac{\partial \Phi}{\partial n} - \Phi \frac{\partial g}{\partial n} \right] r dl, \]  

(14)

where we now set

\[ g = \frac{4K(m)}{\left[ (r+r_q)^2 + (z-z_q)^2 \right]^\frac{1}{2}}. \]  

(15)

\( g \) can be thought of as the potential at \( r_q, z_q \) due to a ring of point sources of current at \( r, z \). \( K(m) \) is the complete elliptic integral of the first kind,

\[ K(m) = \frac{\pi}{2} \int_0^{\pi/2} \frac{d\theta}{(1 - m \sin^2 \theta)^\frac{1}{2}}, \]  

(16)

and the modulus \( m \) is given by

\[ m = \frac{4rr_q}{(r+r_q)^2 + (z-z_q)^2}. \]  

(17)

Approximate forms of \( K(m) \) are given in Abramowitz and Stegun [18]. After integration over \( \theta \), \( dl \) signifies the length element for the path enclosing the region in the \( r, z \) half plane and \( n \) signifies a direction normal to this path. Where the path coincides with the \( z \)-axis, the integrand of equation (14) is zero.

Wrobel and Brebbia gave [19]

\[ \frac{\partial g}{\partial n} = \left\{ K(m) + \frac{r^2 - r_q^2 - (z-z_q)^2}{(r-r_q)^2 + (z-z_q)^2} E(m) \right\} e_r \]  

(18)
\[
\frac{4E(m)(z-q_z)}{\left[ \left( r+rq \right)^2 + \left( z+q_z \right)^2 \right]^{1/4} \left[ \left( r-rq \right)^2 + \left( z-q_z \right)^2 \right]} \cdot e_z
\]

where \( e_r \) and \( e_z \) are the unit vectors in the \( r \) and \( z \) directions, and

\( E(m) \) is the complete elliptic integral of the second kind,

\[
E(m) = \frac{\pi}{2} \int_0^{\pi/2} (1 - m \sin^2 \theta)^{-1/4} d\theta. \tag{19}
\]

Approximations of \( E(m) \) are also given in Abramowitz and Stegun [18].

**Interpolation Methods**

The numerical solution of differential (or integral) equations requires finite-difference approximations. It, therefore, is important to interpolate accurately between nodes. In modern texts concerned with boundary-element or finite-element methods some discussion of interpolation methods is found under the discussion of basis functions [20]. Popular (local) basis functions are known as quadratic or linear. These terms indicate the order of the interpolating polynomial. For example, a linear basis function varies linearly between two successive nodes. Quadratic basis functions, then, fit a quadratic equation between three successive nodes.

\[ \begin{align*}
\frac{dK(m)}{dm} &= -\frac{K(m)}{2m} + \frac{E(m)}{2m(1-m)} \\
\frac{dE(m)}{dm} &= \frac{1}{2m} \left[ E(m) - K(m) \right].
\end{align*} \tag{19}
\]

† Useful relations for deriving these and similar equations are:
Many textbooks give few details on interpolating functions that vary in a strongly nonlinear manner. For example, one might try to interpolate the primary current density near the edge of a disk electrode, where [21]

$$\frac{i(r)}{i_{avg}} = \frac{0.5}{(1 - r^2/r_o^2)^{0.5}}. \quad (20)$$

It is proper to interpolate the primary current density on a disk by assuming that it varies linearly with respect to $(1 - r^2/r_o^2)^{0.5}$. Of course, for problems to be solved numerically, the exact functional relation is not known a priori. Asymptotic solutions, though, predict the manner in which the current density varies, and can be used to avoid numerical errors (such as an artificial wiggle in the current distribution near the edge of an electrode) that commonly occur in the solution of primary current distributions. The interpolation procedures that we use assume a linear variation in the appropriately stretched coordinates between two successive nodes.

Away from insulator/electrode interfaces, variations in current density and potential are sufficiently mild that special interpolation procedures are unnecessary, although they may still improve accuracy and computational efficiency. Near an electrode edge, variations may be large. For primary current distributions, the current density is infinite at the edge of the electrode if the interior angle of intersection between the insulator and electrode is obtuse [22].
In reality, kinetic resistances become important, and the current density at the edge remains finite. If the kinetic resistances are included, it, therefore, is less important to know a priori how the current density varies. Nevertheless, asymptotic equations are useful for understanding and verifying results.

Smyrl and Newman [23] described current distributions for large, finite ohmic resistances for a coplanar electrode and insulator. Previously, Nişancioglu and Newman [24] showed the behavior for large ohmic resistances for linear kinetics on a disk electrode. Chapter 3 generalizes these results.

Integration Procedures

For two-dimensional geometries, when the potential or current density is interpolated linearly with respect to Cartesian coordinates, the integrals (between two successive nodes) resulting from equation (12) can be evaluated analytically.

The integrals appearing in the axisymmetric equations must be solved numerically. Standard integration methods are used for well-behaved functions. Functions containing singularities are handled by the subtraction and addition of a similarly behaved singularity or by changing the variable of integration. Edwards [25] discussed these procedures. For primary distributions, accurate solutions require knowledge of the asymptotic behavior of the current distribution.

In addition to the numerical difficulties that arise because of singularities in the current distribution, the axisymmetric Green's
function is singular as \( r,z \rightarrow q_r, q_z \) since [18]

\[
\lim_{m \to 1} K(m) = \frac{1}{2} \ln \left( \frac{16}{1 - m} \right).
\]  

This logarithmic singularity is integrated numerically by the addition and subtraction of a similarly behaved singularity.

When knowledge of the correct asymptotic behavior is used, interpolation and integration methods can yield highly accurate solutions. For the calculation of the primary current distribution on a disk electrode, the integration techniques can give solutions accurate to within a relative error of \( 10^{-8} \).

As a concrete example of these methods, it is instructive to look at the integral equations written for the disk geometry. The potential distribution on the disk electrode and insulating plane is given by [3]

\[
\Phi(r_q) = \frac{2}{\pi \kappa} \int_0^{r_o} \frac{i_n(r)K(m)r}{r + r_q} \, dr,
\]  

where \( r_o \) is the radius of the disk electrode. For a primary current distribution, the potential \( \Phi_o \) is specified on the electrode, and the current density, if it were unknown, can be described by

\[
i_n(r_q) = -\frac{2\kappa}{\pi} \int_{r_o}^{\infty} \frac{(\Phi(r) - \Phi_o)E(m)r}{(r-r_q)^2(r+r_q)} \, dr.
\]  

For secondary current distributions, equation (23) is unnecessary since a kinetic rate equation relates \( \Phi_o(r_q) \) and \( i_n(r_q) \).

Equation (22) contains examples of integrable singularities. For primary distributions, equation (5) of chapter 3 suggests that
which suggests changing the variable of integration to
\[ x = (r-o-r)^\frac{1}{2}. \]
After substituting for the exact form of \( i_n \), as given
by equation (20), equation (22) becomes

\[
\Phi(r_q) = \frac{2r_i \text{avg}}{\pi \kappa} \int_0^{\sqrt{r_o}} \frac{K(m)(r-o-x^2)dx}{(2r_o-x^2)^{1/2}(r_q+r-o-x^2)},
\]

which eliminates the singularity caused by the current density.

\( K(m) \), though, still presents a problem because it contains a
logarithmic singularity when \( r \rightarrow r_q \). To handle this singularity, if
\( r_q = r_o \), the integral could be written as

\[
\Phi(r_o) = \frac{2r_i \text{avg}}{\pi \kappa} \int_0^{\sqrt{r_o}} \left( \frac{(r_o-x^2)K(m)}{(2r_o-x^2)^{3/2} + \frac{2r_o \ln(x)}{(2r_o)^{3/2}}} \right) dx
\]

\[
- \frac{\sqrt{2r_i} \text{avg}}{\pi \kappa} \left( \sqrt{r_o} \ln(\sqrt{r_o}) - r_o \right).
\]

Logarithmic singularities can also be handled by a special Gaussian
quadrature procedure [26].

To handle some of the singularities that arise in these prob-
lems, Brebbia [27] suggests a device in which the evaluation of the
integrals near some of the singular points is avoided. His trick
recognizes that a system with constant potential everywhere has no
current flowing. Therefore, equation (14), for example, becomes

\[
\alpha_3 = \int \frac{\partial g}{\partial n} rdl.
\]

In his method, this integral is split into the regions between node
points, and the region containing the singularity is evaluated by difference so that the above equation is satisfied. This does not seem like a good idea because all of the numerical errors arising through the evaluation of the other elements of the integral are incorporated into the term that is the largest contributor. His idea, though, is useful because equation (26) provides a test on the accuracy of the integration procedures. Another approach that can test the accuracy of a solution is to evaluate equation (5), (12), or (14) at points outside the domain, where \( \alpha_3 = 0 \).

**Solution Method**

As was stated earlier, equation (12) or equation (14), when written for each node on the boundary, results in a "dense" matrix. This matrix equation is often solved by Gaussian elimination, but can also be solved by the method of successive substitutions. Edwards [25] discussed these two approaches. She concluded that the method of successive substitutions works well if a good initial guess is provided and a reasonable damping factor is used. The savings in computation time can be substantial for a large matrix. The disadvantage is that it is often more difficult to make the method of successive substitutions converge.

Despite her reported problems, we used this method. We also found that convergence depends on the value of the damping factor. With a proper choice and a good initial guess, the method of successive substitutions requires fewer calculations than a Gaussian-elimination procedure. For example, substantial savings can be
obtained if the results from a run with fewer node points is used as the initial guess.

To make the method of successive substitutions an attractive alternative to a Gaussian-elimination/Newton-Raphson procedure, an efficient algorithm to determine the optimum damping factor must be developed. This was not pursued since computer costs continue to decrease, and thus, for many applications, speed can be sacrificed for robustness.

**Summary**

A rigid method is not presented in this chapter. In fact, we purposely avoid the formalism of other methods in favor of tailoring the procedure to the particular problem. By using asymptotic solutions to guide the development of a method, greater accuracy, lower computation costs, and greater physical insight are possible. Using asymptotic results with more formal methods is possible, although this may require sacrificing generality, which is a major advantage to such procedures.

**List of Symbols**

- \( A \) indicates integration over the boundary, \( \text{cm}^2 \)
- \( A_s \) surface area shown in figure 1, \( \text{cm}^2 \)
- \( C_s \) arc shown in figure 1, cm
- \( E(m) \) complete elliptic integral of the second kind
\( \mathbf{e}_r, \mathbf{e}_z \)

unit normal vectors

\( g \)

Green's function, \( \text{cm}^{-1} \)

\( i_n \)

normal component of the current density, \( \text{A/cm}^2 \)

\( l \)

variable of integration in two dimensions, \( \text{cm} \)

\( K(m) \)

complete elliptic integral of the first kind

\( r \)

radial position coordinate, \( \text{cm} \)

\( r_o \)

radius of the disk, \( \text{cm} \)

\( R_o \)

radius shown in figure 1, \( \text{cm} \)

\( V \)

indicates integration over the entire domain, \( \text{cm}^3 \)

\( x, y, z \)

Cartesian coordinates, \( \text{cm} \)

\( \alpha_2, \alpha_3 \)

coefficients shown in figure 1

\( \beta \)

interior angle of intersection between electrode and insulator, radians

\( \delta \)

Dirac delta function

\( \xi \)

variable of integration in cylindrical coordinates, \( \text{cm} \)

\( \theta \)

cylindrical coordinate, radians

\( \kappa \)

solution conductivity, \( \text{S/cm} \)

\( \xi_2 \)

distance for two-dimensional geometries, \( \text{cm} \)

\( \xi_3 \)

distance for three-dimensional geometries, \( \text{cm} \)

\( \pi \)

3.141592654

\( \phi \)

potential of the solution, \( \text{V} \)

**Subscripts**

\( \text{avg} \)

average

\( \text{edge} \)

electrode/insulator interface

\( q \)

coordinate at which the potential is being solved
References


CHAPTER 3
Current Distribution near an Electrode Edge
as a Primary Distribution is Approached

It is well known [1] that the primary current density is infinite at an edge of an electrode if the angle of intersection between the electrode and insulator is obtuse. Also, the primary current density at the edge is zero for an acute angle. In all practical cases, the kinetics of the interfacial reaction enters, and these extreme values do not occur.

This chapter demonstrates how the potential and current approach a primary distribution as the kinetic resistance becomes negligible (compared to the ohmic resistance). The analysis is valid in the edge region of an electrode and insulator, is a function of the angle, $\beta$, shown in figure 1, and is independent of the geometric details of the rest of the electrochemical cell. Results from this abstract geometry can be used to verify numerical investigations of actual geometries. Additionally, an a priori estimate of the behavior in an edge region can aid in the development of more efficient and more accurate numerical procedures.

Nişancioğlu and Newman [2] solved this problem for linear kinetics in the edge region of a disk electrode. Smyrl and Newman [3] extended the results for the linear kinetics case and gave results for Tafel kinetics. Their results are valid when $\beta = \pi$.

In both of these papers, it was recognized that, for high ohmic resistances, the current distribution could be described adequately
Figure 1. Primary current distribution in the *edge region* of an electrode and insulator.
by the primary distribution away from the edge region but showed large deviations from this distribution near the edge. Stated another way, the resistance of the faradaic reaction is important only in the edge region. They realized that this suggests that the problem is treated properly by a singular-perturbation analysis.

**Primary Current Distribution**

The primary current distribution in the edge region shown in figure 1 can be determined by Laplace’s equation in cylindrical coordinates, which reduces to

$$\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \Phi}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 \Phi}{\partial \theta^2} = 0. \quad (1)$$

The boundary conditions are

$$\frac{\partial \Phi}{\partial \theta} = 0 \text{ at } \theta = \beta, \quad (2)$$

and

$$\Phi = 0 \text{ at } \theta = 0. \quad (3)$$

The solution (for small r) to equations (1) through (3) is

$$\Phi^P = -\frac{2\beta}{\pi \kappa} P_o r^{\pi/2\beta} \sin \left( \frac{\pi \theta}{2\beta} \right), \quad (4)$$

where $P_o$ relates to the magnitude of the primary current distribution:

$$i^P(r) = -\frac{\kappa}{r} \frac{\partial \Phi^P}{\partial \theta} = P_o r^{(\pi/2\beta-1)}. \quad (5)$$

It is necessary to introduce $P_o$ because equations (1) through (3) do not completely specify the solution, and the magnitude of the
current can be changed by changing the cell potential. The placement of the counterelectrode and the geometric details of the working electrode in the region away from the corner region are not given. To do so would eliminate the possibility of a general analysis. In a region sufficiently close to the corner, the distribution of current density behaves in a manner independent of these details. In general, the details of the geometry away from the edge region are incorporated into $P_o$, which is determined through comparisons of equation (4) with the primary current distribution valid for the entire geometry. Smyrl and Newman [3] showed that $P_o = \frac{i_{avg}}{r_o/8}$ for the rotating disk electrode. They also gave $P_o$ for the flow-channel geometry.

**Linear Kinetics**

For linear kinetics, the boundary condition along the working electrode becomes

$$- \frac{\kappa}{r} \frac{\partial \phi}{\partial \theta} = \frac{(\alpha_a + \alpha_c)F_i}{RT} \frac{\phi_o}{(V - \phi_o)}, \quad (6)$$

where $V$ is the potential of the electrode and $\phi_o$ is the potential of the solution adjacent to the electrode. For large values of the exchange current density, the current is given adequately by equation (5) for large (but not too large) values of $r$. Near the corner, though, kinetics is important, and the current deviates from the primary distribution. To emphasize this corner region, a stretched radial distance should be defined by
\[ \overline{r} = r S_L = r \frac{(\alpha_a + \alpha_c) F i_o}{R T \kappa}, \] (7)

and a stretched potential by

\[ \overline{\phi} = (\Phi - V) \frac{\kappa S_L \pi/2 \beta}{P_o}. \] (8)

The problem, in terms of these variables, is given by

\[ \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \overline{\phi}}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 \overline{\phi}}{\partial \theta^2} = 0, \] (9)

with the boundary conditions,

\[ \frac{\partial \overline{\phi}}{\partial \theta} = 0 \text{ at } \theta = \beta \] (10)

and

\[ \frac{1}{r} \frac{\partial \overline{\phi}}{\partial \theta} = \overline{\phi}_o \text{ at } \theta = 0. \] (11)

Finally, for large \( \overline{r} \) (but small \( r \)) \( \overline{\phi} \) must satisfy the condition that

\[ \overline{\phi} \rightarrow - \frac{2 \beta}{\pi} \frac{\pi \pi/2 \beta}{\sin \left( \frac{\pi \theta}{2 \beta} \right)} \text{ as } \overline{r} \rightarrow \infty . \] (12)

(\( \overline{r} \rightarrow \infty \) because \( S_L \) becomes large.)

It should be noted that \( V \) has effectively been set equal to zero in the matching condition given by equation (12). This is justified for obtuse angles because the primary current density (see equation (5)) decreases for large \( \overline{r} \). Acute angles require the treatment outlined in the appendix.

Details of the numerical solution for \( \overline{\phi} \) are given below. It should be recognized that the equations are free of parameters and that \( \overline{\phi} \) is therefore independent of the stretching parameter \( S_L \).
An important result of this section is that, for high exchange current densities, the current density in the corner region is given by

$$i(r) = \frac{-[(a+a_c)FI_o]}{RT\kappa} \left(1-\frac{\pi}{2\beta}\right) \frac{1}{\Phi_o}.$$  \hspace{1cm} (13)

That the current density at the edge of the electrode approaches infinity as a power of a parameter involving the exchange current density should not be too surprising since previous experience [4] suggests that such a parameter dictates the distribution of current for linear kinetics.

**Tafel Kinetics**

For anodic Tafel kinetics, the boundary condition along the electrode is

$$-\kappa \frac{\partial \Phi}{r \partial \theta} = i_o \exp \left[ \frac{aF}{RT} (V - \Phi_o) \right]. \hspace{1cm} (14)$$

The exchange current density is no longer a key variable in determining the distribution of current. Previous experience suggests that a dimensionless average current density is the important parameter. Since a characteristic length is missing from this problem, no such parameter can be defined. $P_o$, though, is analogous in that it specifies the magnitude of the current, and it may be expected to be important for Tafel kinetics.

If $P_o$ is large—so that the ohmic resistance is large and the analysis is valid—the current distribution far from the edge is
given adequately by the primary distribution. To investigate the region where the primary distribution does not apply, the potential should be stretched as

$$\bar{\phi} = \frac{\alpha F}{RT} (\Phi - V) - \ln(S_T) + \ln \left( \frac{\alpha F_i}{RT} \right),$$  \hspace{1cm} (15)$$

and the radial distance by

$$\bar{r} = rS_T = r \left( \frac{\alpha FP}{RT} \right)^{2\beta/\pi}.$$  \hspace{1cm} (16)$$

In terms of these variables, equations (9) and (10) apply, and the boundary condition along the electrode becomes

$$\frac{1}{r} \frac{\partial \bar{\phi}}{\partial \theta} = -\exp(-\bar{\phi}) \text{ at } \theta = 0.$$  \hspace{1cm} (17)$$

For large $\bar{r}$, $\bar{\phi}$ must approach the asymptotic solution suggested by Smyrl and Newman [3]:

$$\bar{\phi} \rightarrow -\frac{2\beta}{\pi} r^\pi/2 \beta \sin \left( \frac{\pi \theta}{2\beta} \right) + \left( \frac{\pi}{2\beta} - 1 \right) \ln(r) \text{ as } \bar{r} \rightarrow \infty.$$  \hspace{1cm} (18)$$

The numerical procedure used to solve for $\bar{\phi}$ is discussed in the next section. For large values of $P_o$, the current in the edge region is given by

$$\frac{i(r)}{P_o} = \left( \frac{\alpha FP}{RT} \right)^{(2\beta/\pi-1)} \exp(-\bar{\phi}).$$  \hspace{1cm} (19)$$

Again, the parameter that is important for specifying the current

---

† A complication which could arise in the analysis is that Tafel kinetics may no longer apply at distances at which the primary distribution is approached. The possibility of entering a linear kinetics regime before the primary distribution is approached was not investigated.
density in the edge region is consistent with previous experience.

Numerical Analysis

Since, in two dimensions, currents can not flow to infinity without an infinite potential drop, it is necessary to calculate deviations from the primary potential distribution. A new potential, $\psi$, is defined as

$$
\psi = \overline{\phi} - \overline{\psi}_P ,
$$

(20)

where $\overline{\psi}_P$ is given by equation (12). To facilitate the solution for $\psi$, the geometry of figure 1 can be mapped conformally so that the insulator and electrode are coplanar. The coordinates of this new geometry are related to the original coordinates through

$$
x = \frac{\pi}{\beta} \tan \theta \quad \text{and} \quad \theta = \frac{\pi}{\beta} .
$$

(21)

In terms of these new variables, the problem can be stated as

$$
\frac{1}{x} \frac{\partial}{\partial x} \left( x \frac{\partial \psi}{\partial x} \right) + \frac{1}{x^2} \left( \frac{\partial^2 \psi}{\partial \theta^2} \right) = 0 ,
$$

(22)

with the boundary conditions:

$$
\frac{\partial \psi}{\partial \theta} = 0 \quad \text{at} \quad \theta = \pi
$$

(23)

and

$$
\frac{1}{x} \frac{\partial \psi}{\partial \theta} - \beta \left( f(\psi_o) x^{(\beta/\pi - 1)} + x^{-1/2} \right) \quad \text{at} \quad \theta = 0 .
$$

(24)

For linear kinetics, $f(\psi_o) = \psi_o$, and for Tafel kinetics, $f(\psi_o) = - \exp(- \psi_o)$. 
The boundary integral equation describing the potential of the solution adjacent to the electrode is

$$\psi_0(x_q) = \frac{\beta}{2\pi^2} \int_0^\infty \ln(x-x_q)^2 \left[ f(\psi_0) x^{(\beta/\pi-1)} + x^{-1/2} \right] dx.$$  (25)

For linear kinetics and $\beta \leq \pi/2$, the integrand does not approach zero quickly enough for the integral to converge. The appendix demonstrates the modification to the solution procedure necessary to obtain convergence.

A finite-difference approximation to equation (25) was solved with an iterative procedure. An upper limit of integration, $x_{\text{max}}$, was chosen to set a finite domain of integration. The contribution of the integral for $x > x_{\text{max}}$ was assumed to be negligible, which is consistent with requiring that the primary current distribution be approached at $x_{\text{max}}$.

The accuracy of this procedure was verified by increasing $x_{\text{max}}$ until the value of the current at the corner changed by some small amount. A procedure of node-point doubling was also used. The results for the case of $\beta = \pi$ were compared with the results from references (2) and (3). Finally, an integral constraint can be used to check the accuracy of the answer. This arises from the asymptotic behavior expressed in equations (12) and (18) and takes the form, for linear kinetics (obtuse angles),

$$0 = \int_0^\infty \left[ \psi_0 x^{(\beta/\pi-1)} + x^{-1/2} \right] dx,$$  (26)

and, for Tafel kinetics,
The reported values are estimated to be accurate within 0.5 percent.

Results and Discussion

Results for linear kinetics are shown in figures 2 and 3. These figures, along with equation (13), give a good estimate of the current density in the corner region only for large values of \((a + \alpha_c)F / RT\). Figure 4 shows results for Tafel kinetics. It can be used with equation (19) to predict current distributions near corner regions for high values of \(a FP / RT\).

Our experience has shown (and this analysis suggests) that numerical difficulties can arise when ohmic resistances begin to dominate. In other words, the results of this chapter become applicable when other numerical analyses begin to become suspect. A practical use, then, of these results could be as a tool for the verification of other results. One test which could be made for linear kinetics is to determine whether

\[
\frac{i_{\text{edge}}}{P_o} = A_L(\beta) \left(\frac{(a + \alpha_c)F}{RT}\right)^{(1-\pi/2\beta)}
\]

(28)
as the right side of the equation goes to infinity. The test for Tafel kinetics is whether

\[
\frac{i_{\text{edge}}}{P_o} = A_T(\beta) \left(\frac{a FP}{RT}\right)^{(2\beta/\pi - 1)}
\]

(29)
as the right side of the equation goes to infinity. Smyrl and Newman [3] have demonstrated such tests for the case of \(\beta = \pi\). The
Figure 2. Current distribution for linear kinetics (obtuse angles).
Figure 3. Current distribution for linear kinetics (acute angles).
Figure 4. Current distribution for Tafel kinetics.
coefficients, $A_L(\beta)$ and $A_T(\beta)$, are shown in figure 5. The appendix shows that the value of $A_L$ is 6.0 for an angle of $\beta = \pi/8$.

By solving the primary current distribution for an actual cell, it is possible to relate $P_o$ to measureable electrochemical and geometric variables. It might, though, not be desired to take the time to determine the exact relation between $P_o$ and these other variables. As a quick check, one might recall that $P_o$ is proportional to $i_{avg}$ and determine whether the proper relationship, suggested by equation (28) or (29), is followed.

The analysis can also be used to establish the proper mesh-spacing for an accurate and efficient finite-difference procedure. For linear kinetics, the region where the primary distribution does not apply is of the order \( \left( \frac{a + \alpha}{a} \right) F_i \). For Tafel kinetics, the region where the kinetic resistance is important is of the order \( \left( \frac{a F_p}{a} \right)^{-2\beta / \pi} \).

Conclusions

A singular-perturbation analysis has shown explicitly the manner in which the current density near an electrode edge approaches extreme values as the primary current distribution is approached. The results are consistent with previous analyses of a coplanar electrode and insulator and also with the special case of $\beta = \pi/2$. 
Figure 5. Dimensionless coefficient which specifies the value of the stretched current density at the edge. See equations (28) and (29).
Appendix

For linear kinetics, the solution to equations (9) through (12) might be approximated by

$$\bar{\phi} = \sum_{i=0}^{\infty} A_i r^n_i \cos(n_i(\beta - \theta)), \quad (A.1)$$

where $n_i$ and $A_i$ are determined through the boundary conditions and the matching condition. This series diverges except for certain angles, $\beta$, where it terminates. Three angles which terminate are $\beta = \pi/2$, $\beta = \pi/4$, and $\beta = \pi/8$. For these angles, the potential of the solution adjacent to the electrode edge is given by

$$\bar{\phi}_o = -1 \ (\beta = \pi/2), \quad (A.2)$$

$$\bar{\phi}_o = -1 - r \ (\beta = \pi/4), \quad (A.3)$$

and

$$\bar{\phi}_o = -6 - 14.4852r - 7.2464r^2 - r^3 \ (\beta = \pi/8). \quad (A.4)$$

As $r \to \infty$, the difference between the actual stretched current and the stretched primary current (in terms of $x$) is of the order given by

$$\psi_o x^{(\beta/\pi-1)} + x^{-1/2} \alpha x^{-(1/2+\beta/\pi)}. \quad (A.5)$$

For angles $\beta$ less than $\pi/2$, the integral equation (25) is unbounded since the first neglected term is of order greater than $x^{-1}$.

Stated another way, for linear kinetics and acute angles, the first neglected term in the matching condition is sufficiently large.
along the electrode surface that the integral does not converge. For
\( \pi/4 < \beta \leq \pi/2 \), equations (30) and (34) suggest that an equation which
calculates the deviations of the current density from the first two
terms of the series will converge. A potential defined in this
manner is

\[
\psi' = \phi + \frac{2\beta}{\pi} \frac{\pi/2\beta}{r} \cos \left( \frac{\pi}{2\beta} (\beta - \theta) \right) - A_1 r^{(\pi/2\beta-1)} \cos \left( \frac{\pi}{2\beta} - 1 \right) (\beta - \theta) .
\]

(A.6)

\( A_1 \) is determined by applying the matching and boundary conditions:

\[
A_1 = \frac{-1}{\sin (\beta)} .
\]

(A.7)

The integral equation which gives \( \psi' \) is

\[
\psi'_o = \frac{\beta}{2} \int_0^\infty \ln(x-x_0)^2 \left[ \psi'_o(x/\pi-1) - A'_x(-1/2-\beta/\pi) \right] dx ,
\]

(A.8)

where

\[
A' = \left[ \frac{\pi}{2\beta} - 1 \right] \frac{-1}{\tan (\beta)} .
\]

(A.9)

The matching condition used numerically for \( \psi'_o \) is given by the next
term of the series:

\[
\psi'_o \rightarrow A_2 r^{(\pi/2\beta-2)} \cos \left( \frac{\pi}{2} - 2\beta \right) \text{ as } \bar{r} \rightarrow \infty .
\]

(A.10)

For example, for \( \beta = 3\pi/8 \), the potential at the electrode sur-
face is

\[
\bar{\phi}_o = -\bar{r}^{-1/3} - 0.13807 \bar{r}^{-2/3} + ... .
\]

(A.11)

For \( \beta \leq \pi/4 \), additional terms need to be subtracted from \( \psi' \). The
number of additional terms is given by equation (30), the solution for \( \phi \) as \( r \to \infty \).

To obtain results for \( \beta \leq \pi/2 \), this appendix is necessary. It can also be used with obtuse angles because it shows how asymptotic corrections can be used to relax the assumption that the integrand in equation (25) is zero for \( x > x_{\text{max}} \). This reduces the value of \( x_{\text{max}} \) needed to obtain accurate results.

Appendix B of Smyrl and Newman [3] can be used to show that, for Tafel kinetics, the difference between the current density and the primary current density is sufficiently small that the integral equation (25) converges for acute, as well as obtuse, angles.

List of Symbols

\[ A_L, A_T \quad \text{dimensionless coefficients given in figure 5} \]
\[ F \quad \text{Faraday’s constant, } 96487 \text{ C/equiv} \]
\[ i \quad \text{current density, } A/cm^2 \]
\[ i_{\text{avg}} \quad \text{average current density, } A/cm^2 \]
\[ i_{\text{edge}} \quad \text{current density at the electrode/insulator edge, } A/cm^2 \]
\[ i_0 \quad \text{exchange current density, } A/cm^2 \]
\[ P_0 \quad \text{parameter defined in equation (5), } A/cm^{(1+\pi/2\beta)} \]
\[ R \quad \text{universal gas constant, } 8.3143 \text{ J/mol-K} \]
\[ r \quad \text{radial distance variable, cm} \]
\[ \bar{r} \quad \text{stretched, dimensionless radial distance variable, defined by equation (7) or (16)} \]
\( S_L \) stretching variable for linear kinetics, cm\(^{-1}\)

\( S_T \) stretching variable for Tafel kinetics, cm\(^{-1}\)

\( T \) absolute temperature, K

\( x, x_q \) dimensionless position in transformed coordinate system

\( V \) electrode potential, V

\( \alpha_a, \alpha_c \) transfer coefficients

\( \beta \) angle defined in figure 1, radians

\( \theta \) angular coordinate in cylindrical coordinates

\( \Theta \) angular coordinate of transformed geometry

\( \pi \) 3.141592654

\( \kappa \) specific conductivity, ohm\(^{-1}\)cm\(^{-1}\)

\( \phi \) potential, V

\( \phi^p \) primary potential, V

\( \bar{\phi} \) stretched, dimensionless potential

\( \psi \) dimensionless potential defined by equation (20)

\( \psi' \) dimensionless potential defined by equation (35)

References


CHAPTER 4
A Criterion to Verify Current Distribution Calculations

This chapter provides a practical demonstration and partial verification of the abstract results of chapter 3. Specifically, it shows how the results provide a criterion by which the validity of current distribution calculations can be tested. The geometry used to demonstrate the procedure is a slotted-electrode cell for which the primary current distribution was given by Orazem and Newman [1]. Previously, Smyrl and Newman [2] applied similar results to the rotating disk and flow channel cells.

A summary of the results of chapter 3 is given below: To generalize the treatment, a parameter $P_o$ is used. It sets the magnitude of the current density for small distances from the edge:

$$i^P = P_o r^{(\pi/2\beta - 1)}$$  \hspace{1cm} (1)

The angle $\beta$ and the radial coordinate $r$ are shown in figure 1 of chapter 3. $P_o$ is determined by the cell potential and the details of the entire geometry. It is obtained by comparing the primary current distribution of the cell with equation (1), the asymptotic form valid near the edge.

For large polarization parameters, chapter 3 shows:

1. that the current density deviates appreciably from the primary current density where
\[ r = \left( \frac{(\alpha + \alpha_c) F I_o}{\frac{\alpha_c}{RTk}} \right)^{-1} \]  

(2)

for linear kinetics, and

\[ r = \left( \frac{\alpha F P C}{\frac{\alpha_c}{RTk}} \right)^{-2\beta/\pi} \]  

(3)

for Tafel kinetics.

2. that the current density near an electrode edge behaves as

\[ \frac{i_{\text{edge}}}{i_{\text{avg}}} \propto \left( \frac{(\alpha + \alpha_c) F I_o}{\frac{\alpha_c}{RTk}} \right)^{(1 - \pi/2\beta)} \]  

(4)

for linear kinetics, and

\[ \frac{i_{\text{edge}}}{i_{\text{avg}}} \propto \left( \frac{\alpha F P C}{\frac{\alpha_c}{RTk}} \right)^{(2\beta/\pi - 1)} \]  

(5)

for Tafel kinetics.

3. detailed distributions in the edge region for various angles, \( \beta \).

**Numerical Analysis**

The primary current distribution of the slotted-electrode cell shown in figure 1 was determined by a technique that utilizes two numerical, Schwarz-Christoffel transformations. Conformal mapping techniques such as this one are often used for the determination of primary current distributions. When coupled with other numerical procedures, problems with more complicated boundary conditions can be analyzed.

Orazem and Newman [2] gave the transformation relating the coordinates of figure 1a and figure 1c. Since this is a conformal
Figure 1. Schematic diagram of the slotted-electrode cell. Figure 1a shows the cell in the original coordinate system. To facilitate solution of Laplace's equation it is mapped conformally to the coordinate system of figure 1c, with the coordinate system shown in figure 1b as an intermediate coordinate system. See reference [1] for details.
mapping, Laplace's equation maintains the same form. Insulator boundary conditions also remain the same. Along the counterelectrode, the kinetics are assumed to be infinitely fast, and the constant potential boundary condition is unchanged. At the working electrode, the boundary condition becomes

$$\frac{\partial \Phi}{\partial x_i} = f(\Phi_o) \gamma(x),$$  \hfill (6)

where

$$f(\Phi_o) = -\frac{(\alpha + \alpha_c) \Phi_i}{RT \kappa} (V - \Phi_o)$$ \hfill (7)

for linear kinetics, and

$$f(\Phi_o) = -\frac{i_0}{\kappa} \exp \left[ \frac{\alpha F}{RT} (V - \Phi_o) \right]$$ \hfill (8)

for anodic, Tafel kinetics.

\(\gamma(x)\) relates the normal derivatives along the working electrode in the two coordinate systems and is given by

$$\gamma(x_e) = \frac{\sqrt{t-a} \sqrt{t-a} \sqrt{t+a}}{\sqrt{t+b} \sqrt{c-t} \sqrt{d-t}}$$ \hfill (9)

where \(t\) is related to \(x\) through

$$x = \int_a^t \frac{j dt}{\sqrt{t-a} \sqrt{t-b} \sqrt{t+c} \sqrt{t+d}}$$ \hfill (10)

and the original coordinate \(z\) is related to \(t\) through

$$z = \int_0^t \frac{\sqrt{t-a} \sqrt{t+a} dt}{\sqrt{t-b} \sqrt{t-c} \sqrt{t+d}}$$ \hfill (11)

This problem was solved with a boundary-integral technique.
In this chapter, the geometric ratios used are $L/h = 0.5$, $\tau/g = 0.1$, and $h/G = 6.0$, where $L$, $h$, $\tau$, and $g$ are shown in figure 1. The polarization parameter for linear kinetics is

$$J = \frac{(\alpha + \alpha_C)FLi}{RT\kappa}$$

(12)

and for Tafel kinetics is

$$\delta = \frac{\alpha a FL|i_{avg}|}{RT\kappa}$$

(13)

The length $L$ used in defining $J$ and $\delta$ is chosen arbitrarily.

Applicability of the Perturbation Analysis

Singular perturbation analyses can be quite involved. Nevertheless, their results can be simple to use. In this chapter, a tool that checks the validity of numerical calculations is established. To use it effectively, one must be aware of the limited range of applicability of the perturbation analysis. Also, a physically significant length should be used in the definitions of the polarization parameters. Otherwise, the coefficients in the series may be very different from unity.

The first neglected term in a perturbation series determines the range of applicability. Because the term arises from the details of the entire cell (and not one specific detail like $\beta$), a general conclusion is difficult to make. To estimate its magnitude, it is useful to study in detail one particular geometry: the disk electrode. For this cell, the characteristic length $L$ in equations (12) and (13) should be replaced with $r_o$, the disk radius.
Linear Kinetics—For large $J$, the current density at the electrode edge is given by [3]

$$\frac{i_{\text{edge}}}{i_{\text{avg}}} = 0.62 \sqrt{J} + \epsilon(2) \frac{\ln J}{\sqrt{J}}, \quad (14)$$

where $\epsilon(2)$ is determined by solving for the second order correction to the primary potential distribution.

The condition for when the first term adequately predicts the current density is

$$\sqrt{J} \gg \frac{\epsilon(2)}{0.62} \frac{\ln J}{\sqrt{J}}. \quad (15)$$

Although a determination of $\epsilon(2)$ may not be worth the effort, its value should be near unity, and one can make a reasonable estimate of the range of applicability.

Figure 2 compares calculated values of the current density at the edge of the electrode with the first term of the asymptotic prediction. The predicted behavior is approached by values of $J$ consistent with the above inequality. Equation (14) also suggests an alternate, more sensitive way of plotting results. For example, a plot of $i_{\text{edge}} / \sqrt{J} i_{\text{avg}}$ vs. $\ln J$ could be used. For such plots, the ordinate intercept is predicted.

To comment generally about the magnitude of the next term, the relation of Nişancıoğlu and Newman [4] is useful:

$$\frac{1}{0} \int (1 - \Phi_o/V) r dr = O(\frac{\ln J}{J}) \quad (for \ high \ J). \quad (16)$$
Figure 2. The current density at the edge of a disk electrode for linear kinetics. The points are calculated values, and the dashed line is the asymptotic prediction.
An analogous term should give the order of the next term for other geometries, and it is expected to be of the same magnitude. If so, for large $J$ and $\beta > \pi/2$,

$$\frac{i_{\text{edge}}}{i_{\text{avg}}} = \varepsilon(1)J^{(1-\pi/2\beta)} + \varepsilon(2)\frac{\ln J}{J^{\pi/2\beta}}. \quad (17)$$

This implies that the analysis of chapter 3 applies when

$$J \gg \frac{\varepsilon(2)}{\varepsilon(1)} \ln J. \quad (18)$$

**Tafel Kinetics**—For Tafel kinetics on a disk electrode, Appendix A shows that the order of the next term in the perturbation expansion is unity with respect to $\delta$, thus implying that

$$\frac{i_{\text{edge}}}{i_{\text{avg}}} = 0.196 \delta + \varepsilon(2). \quad (19)$$

Figure 3 compares the first term with calculated results. In harmony with equation (19), the calculated values lie on a line parallel to the asymptotic prediction. The figure shows that the last data point (near $\delta = 90$) is inaccurate. For larger $\delta$ (not shown), errors are more noticeable. A more sensitive test of numerical calculations would be to plot $\frac{i_{\text{edge}}}{\delta i_{\text{avg}}}$ vs. $1/\delta$, with a predicted ordinate intercept of 0.196.

Appendix A suggests that the next term of a perturbation series will be of order unity for other cell geometries. Previous calculations [4] verify this for the channel geometry (again, $\beta = \pi$). In general, for $\beta > \pi/2$, the expected relationship is
Figure 3. The current density at the edge of a disk electrode for Tafel kinetics. The points are calculated values, and the dashed line is the asymptotic prediction.
\[ \frac{i_{\text{edge}}}{i_{\text{avg}}} = \varepsilon(1) \delta(2\beta/\pi - 1) + \varepsilon(2). \]  \hfill (20)

The third term in this series will be of order less than unity. For \( \delta(2\beta/\pi - 1) > 10 \) we can expect the numerical calculations to attain the correct slope but to be offset from a line through the origin by an amount \( \varepsilon(2) \).

Results and Discussion

For the slotted-electrode cell, the primary current distribution near the electrode edge is

\[ i_{\text{as}} = P_0 r^{-2/3}, \]  \hfill (21)

where \( r \) is the distance along the electrode measured from point A. \( P_0 \) is determined by comparing this asymptotic form with the current distribution as calculated by the method of Orazem and Newman (see figure 4):

\[ P_0 = 0.569 L^{2/3} i_{\text{avg}}. \]  \hfill (22)

For linear kinetics in the slotted-electrode cell, equation (28) of chapter 3 gives

\[ \frac{i_{\text{edge}}}{i_{\text{avg}}} \sim 1.5 J^{2/3} \]  \hfill (23)

as \( J \to \infty \). In figure 5 this relationship is compared to calculated values of \( i_{\text{edge}}/i_{\text{avg}} \). Good agreement exists for \( J^{2/3} \geq 4 \).

For Tafel kinetics, equation (29) of chapter 3 gives

\[ \frac{i_{\text{edge}}}{i_{\text{avg}}} \sim 0.426 \delta^2 \]  \hfill (24)
Figure 4. The primary current distribution of a slotted-electrode cell. The dashed line is the asymptotic approximation of the current distribution, given by equations (21) and (22).

\[ \frac{i_{edge}}{i_{avg}} \propto (\frac{r}{L})^{2/3} \]

\[ \mu_0 = 0.569 \, i_{avg} \, L^{2/3} \]
Figure 5. The current density at point $A$ of the slotted-electrode cell (figure 1) as it varies with the polarization parameter for linear kinetics. The points are calculated values, and the dashed line is the asymptotic behavior predicted by equation (23).
as $\delta \to \infty$. Figure 6 compares this relationship with calculated results. An empirical curve, with the predicted slope of 0.426, is fit through the calculated results. Its intercept is determined from the slope of the curve shown in figure 7.

Figure 7 provides a sensitive test of numerical calculations. If the next term in the series is of order unity with respect to $\delta$, the curve should be linear at high $\delta$ and have the ordinate intercept predicted by equation (24). This figure shows that the numerical calculations begin to fail near $\delta^2 = 30$. For larger $\delta$ (not shown), the numerical calculations are clearly in error. The deviation from the semi-empirical curve of figure 6 also suggests that the calculations begin to fail near $\delta^2 = 30$. Our experience suggests that it becomes difficult to obtain highly accurate solutions with traditional numerical procedures when $i_{edge}/i_{avg}$ is much greater than 10.

Figures such as 5, 6, and 7 are recommended as checks on numerical results, where, for large polarization parameters, numerical difficulties arise. To check data quickly, the proportionalities given by equations (3) and (5) can be tested. Deviations from a linear relationship indicate that results are inaccurate.

Few numerical difficulties are expected for small polarization parameters; therefore, a perturbation analysis describing the deviations from a uniform current distribution might not be as interesting. Nevertheless, Appendix B demonstrates by example how the deviations could be predicted. For other geometries, the same functional dependence on the polarized parameter is expected, but general
Figure 6. The current density at point $A$ of the slotted-electrode cell (see figure 1) as it varies with the polarization parameter for Tafel kinetics. The points are calculated values, the solid line is the asymptotic behavior predicted by equation (24), and the dashed line has the predicted slope but an empirical ordinate intercept.
Figure 7. An alternate, more sensitive way of plotting calculated results for Tafel kinetics in the slotted-electrode cell. The ordinate intercept is predicted by the perturbation analysis, and the slope of the line gives an estimate of the next term in the series.
predictions of the coefficients in the series is not possible.

Conclusions

Applications of the results of chapter 3 are demonstrated. The results, valid for asymptotically large polarization parameters, provide a test of numerical results. The predictions do not hold for small polarization parameters, partly because $i_{\text{edge}}/i_{\text{avg}} = 1$ for a zero polarization parameter. For Tafel kinetics and obtuse angles of intersection between the electrode and insulator, the next term in a perturbation series is expected to be of order unity. Calculated values of $i_{\text{edge}}/i_{\text{avg}}$ are expected, therefore, to fall on a line that is parallel to the predictions of chapter 3.

The importance of asymptotic analyses should not be underestimated. In addition to giving insight, they can provide checks on calculations. With the emergence of high-speed computers and sophisticated, packaged software, complicated numerical calculations are more prevalent, and simple tests of these results are necessary.

Appendix A
Tafel Kinetics on a Disk Electrode

The order of the next term in a perturbation series describing $i_{\text{edge}}/i_{\text{avg}}$ for Tafel kinetics on a rotating disk electrode is shown to be unity. It is also suggested that a term of order unity can be expected for other geometries. $O(\epsilon)$ means of order $\epsilon$, and $o(\epsilon)$ means of order lower than $\epsilon$. 
Following Smyrl and Newman [2], a potential $\phi$ is defined as

$$\phi = \frac{\pi}{4} \left[ 1 - \Phi/\Phi_o^\rho \right],$$

(A.1)

where $\Phi_o^\rho$ is the primary potential difference, for the same total current, between the disk electrode and a reference electrode placed at infinity. The stretched variables for the outer region (away from the edge of the electrode) are $\bar{\phi} = \phi$, $\bar{\eta} = \eta$, and $\bar{\xi} = \xi$, where $\xi$ and $\eta$ are the rotational elliptic coordinates. In the inner region, the appropriately stretched variables are

$$\bar{\phi} = \delta \phi - \ln \delta,$$

(A.2)

$$\bar{\xi} = \delta \xi,$$

(A.3)

and

$$\bar{\eta} = \delta \eta.$$  

(A.4)

The stretched potentials, $\bar{\phi}$ and $\bar{\Phi}$, can be expanded in terms of $\delta$:

$$\bar{\Phi} - \bar{\Phi}(0) + \bar{F}_1(\delta)\bar{\Phi}(1) + \ldots,$$

(A.5)

$$\bar{\phi} - \bar{\phi}(1) + \bar{F}_2(\delta)\bar{\phi}(2) + \ldots.$$  

(A.6)

Smyrl and Newman showed that $\bar{\Phi}(0) = \frac{1}{2} \tan^{-1} \xi$, and they determined numerically $\bar{\phi}(1)$.

In the inner region, terms of order $\delta^{-2}$ are neglected in Laplace's equation. Terms can also arise from the matching and boundary conditions. The insulator boundary condition does not introduce additional terms. Along the disk electrode, the boundary condition is
\[
\frac{E}{2} e^{\phi_o} = \frac{1}{\eta} \left( \frac{\partial \phi}{\partial \xi} \right)_{\xi=0}, \tag{A.7}
\]

where

\[
E = \frac{2i}{i_{\text{avg}}} \exp \left\{ \frac{\alpha F}{RT} (V - \Phi_o^P) \right\}. \tag{A.8}
\]

It is shown [2] that

\[
\ln E = 1 + \frac{1}{\delta} \ln \xi^{(1)} + \ldots, \tag{A.9}
\]

where \( \ln \xi^{(1)} \) is the second term in a perturbation expansion of \( \ln E \).

The boundary condition, therefore, can be rewritten as

\[
\frac{\partial \phi}{\partial \xi} \bigg|_{\xi=0} + i \bar{\xi}^{(2)} \frac{\partial \phi}{\partial \xi} \bigg|_{\xi=0} + o(\bar{\xi}^{(2)}) = 0,
\]

which is expanded further to yield

\[
\frac{\partial \phi}{\partial \xi} \bigg|_{\xi=0} + i \bar{\xi}^{(2)} \frac{\partial \phi}{\partial \xi} \bigg|_{\xi=0} + o(\bar{\xi}^{(2)}) = 0.
\]

Equating terms of the same order in \( \delta \) suggests that \( \bar{\xi}^{(2)} = \frac{1}{\delta} \). To decide conclusively necessitates inspecting the matching conditions, where higher order terms due to the outer solution can arise.
In the outer region, the exact form of Laplace's equation (in rotational elliptic coordinates) was solved, and thus no terms arise from the governing equation. Also, no terms arise from the boundary condition at infinity, on the insulator, or on the axis. The boundary condition along the electrode in the outer region can be expressed by

\[
\frac{1}{2} E e^{\delta \varphi_o} - \frac{1}{\eta} \frac{\partial \varphi_o}{\partial \xi} |_{\xi=0}.
\]  
(A.12)

Since \( \varphi_o^{(0)} = 0 \), this boundary condition is rewritten as

\[
\frac{e}{2} \left[ 1 + \frac{1}{\delta} \ln \xi^{(1)} + o(1/\delta) \right] \left[ 1 + \delta \tilde{I}_2(\delta) \varphi_o^{(2)} + \ldots \right] e^{\delta \tilde{I}_1(\delta) \varphi_o^{(1)}} = \frac{1}{\eta} \left\{ \frac{\partial \varphi^{(0)}}{\partial \xi} \bigg|_{\xi=0} + \tilde{I}_1(\delta) \frac{\partial \varphi^{(1)}}{\partial \xi} \bigg|_{\xi=0} + \ldots \right\}.
\]  
(A.13)

This suggests that \( \tilde{I}_1 = \frac{1}{\delta} \) and that

\[
\varphi_o^{(1)} = -1 - \ln(\eta),
\]  
(A.14)

which is expected from a straightforward attempt to correct the potential (from the primary potential) for finite electrode kinetics. Smyrl and Newman [2], with a different approach, implied the same results.

\( \varphi^{(1)} \) is described by Laplace's equation in rotational elliptic coordinates:

\[
(1 - \eta^2) \frac{\partial^2 \varphi^{(1)}}{\partial \eta^2} + (1 + \xi^2) \frac{\partial^2 \varphi^{(1)}}{\partial \xi^2} + 2\xi \frac{\partial \varphi^{(1)}}{\partial \xi} - 2\eta \frac{\partial \varphi^{(1)}}{\partial \eta} = 0.
\]  
(A.15)

The insulator boundary condition at \( \eta = 0 \) is unchanged, the boundary condition at the disk electrode is given by equation (A.14) and
\( \psi^{(1)} \rightarrow 0 \) as \( \xi^2 + \eta^2 \rightarrow \infty \). Furthermore, no current should flow to infinity since \( \delta \) specifies the total current, and this is supplied by the primary current term, \( \psi^{(0)} \).

From separation of variables, the solution is

\[
\psi^{(1)}(\eta, \xi) = \sum_{n=1}^{\infty} B_n P_{2n}(\eta) M_{2n}(\xi), \tag{A.16}
\]

where \( P_{2n} \) are the even Legendre polynomials, and \( M_{2n} \) are Legendre functions of imaginary argument [5]. The \( B_n \) are determined through the orthogonality condition (see, for example, reference [6]):

\[
B_n = -\frac{1}{(4n+1)} \int_{0}^{\infty} P_{2n}(\eta) \ln(\eta) \, d\eta. \tag{A.17}
\]

The asymptotic behavior (for small \( \xi, \eta \)) of \( \psi^{(1)} \) must be developed to provide the matching condition for the inner solution. If \( r = (\xi^2 + \eta^2)^{1/4} \) and \( \theta = \tan^{-1}(\eta/\xi) \), Laplace's equation becomes

\[
0 = \left( \frac{\partial^2 \psi^{(1)}}{\partial r^2} + \frac{1}{r} \frac{\partial \psi^{(1)}}{\partial r} + \frac{1}{r^2} \frac{\partial^2 \psi^{(1)}}{\partial \theta^2} \right) \left[ 1 + \frac{\xi^2}{2}(1 - 2\sin^2 \theta) \right] \tag{A.18}
\]

\[
+ \frac{r}{2 \sin \theta \cos \theta} \left[ \frac{1}{r} \frac{\partial \psi^{(1)}}{\partial \theta} - \frac{\partial^2 \psi^{(1)}}{\partial r \partial \theta} \right]
\]

\[
+ 2r(1 - 2\sin^2 \theta) \frac{\partial \psi^{(1)}}{\partial r} - 4 \sin \theta \cos \theta \frac{\partial \psi^{(1)}}{\partial \theta}. \]

Using a coordinate expansion technique and separation of variables, and applying the appropriate boundary conditions,

\[
\psi^{(1)} = -1 - \ln r + A_1^{(1)} r \cos \theta - r^2 \cos^2 \theta - \left( \frac{2}{7} A_1^{(1)} r^3 \cos \theta + A_2^{(1)} r^3 \cos(3\theta) + O(r^4) \right. \tag{A.19}
\]
which can be written in terms of $\xi$ and $\eta$ as

$$\phi^{(1)}(\eta \to 0, \xi \to 0) = -1 - \ln(\eta^2 + \xi^2) + A_1^{(1)} \xi - \xi^2 \quad (A.20)$$

$$\frac{2}{7} A_1^{(1)} \xi (\xi^2 + \eta^2) + A_2^{(1)} \xi (\xi^2 + \eta^2)^{3/2} \left(\frac{1}{\xi^2 + \eta^2}\right)^{1/2} + O((\eta^2 + \xi^2)^2).$$

$A_1^{(1)}$ and $A_2^{(1)}$ would be determined by comparing this asymptotic solution with the complete solution.

Finally, the matching condition is applied. This condition is expressed formally as

$$\frac{\ln \delta}{\delta} + \frac{1}{\delta} \phi(\eta^2 + \xi^2 \to \infty) = \phi(\eta \to 0, \xi \to 0). \quad (A.21)$$

Agreement must be observed for all orders in $\delta$ and also all orders in $(\xi^2 + \eta^2)^{\frac{1}{2}}$. Equation (B-8) of Smyrl and Newman can be rewritten in terms of $\xi$ and $\eta$ as

$$\phi(\eta^2 + \xi^2 \to \infty) = \frac{1}{2} \xi - \ln(\xi^2 + \eta^2) + \frac{1}{\delta} \frac{A_1^{(1)} \xi}{\xi^2 + \eta^2} \quad (A.22)$$

$$+ \frac{1}{\delta} \phi(\eta^2 + \xi^2 \to \infty) + o(1/\delta),$$

where $A_1^{(1)}$ is the same as Smyrl and Newman's $A_1$ and is estimated to be -3.1. Substituting for $E$ with equation (A.9) gives

$$\frac{\ln \delta}{\delta} + \frac{\phi(\eta^2 + \xi^2 \to \infty)}{\delta} = \frac{\xi}{2} - \frac{1}{\delta} \left(1 + \ln(\eta^2 + \xi^2)^{\frac{1}{2}}\right) \quad (A.23)$$
To specify completely the matching condition for \( \phi(2) \), it is necessary to investigate the outer region expansion:

\[
\Phi(\eta \to 0, \xi \to 0) = \frac{\xi}{2} - \frac{\xi^3}{6} + O(\xi^5) + \frac{1}{\delta} \left[ -1 - \ln(\xi^2 + \eta^2)^{1/2} \right].
\] (A.24)

The leading term of \( \phi(2) \) must match the highest unmatched term in \( \Phi \).

Although it might not be worth the effort of solving it, for completeness, the problem statement is given.

The governing equation remains

\[
\frac{\partial^2 \Phi(2)}{\partial \eta^2} + \frac{\partial^2 \Phi(2)}{\partial \xi^2} = 0.
\] (A.25)

The insulator boundary condition is

\[
\frac{\partial \Phi(2)}{\partial \eta} = 0 \text{ at } \eta = 0.
\] (A.26)

Along the working electrode, the boundary condition is

\[
\frac{\partial \Phi(2)}{\partial \eta} = \eta^{(1)} \left[ \ln \Phi^{(1)} + \phi_o^{(2)} \right] - \frac{1}{\eta} \frac{\partial \Phi(2)}{\partial \xi} \bigg|_{\xi=0},
\] (A.27)

where equation (A-18) of Smyrl and Newman gives

\[
\ln \Phi^{(1)} = \int_0^\infty \left( \frac{\phi_o^{(1)}}{\phi_o} + \ln \eta \right) d\eta.
\] (A.28)
Results of finite-difference calculations can be correlated by

$$\frac{E}{2} = \frac{4.3 + \delta}{4.3 + 0.73585},$$  \hspace{1cm} (A.29)

which is expanded to suggest that $\ln \xi^{(1)} = -1.544$. Finally, the matching condition is

$$\tilde{\phi}^{(2)}(\eta + \xi^2 \rightarrow \infty) = \frac{\xi^{(1)}}{\xi},$$ \hspace{1cm} (A.30)

and, in principle, $\tilde{\phi}^{(2)}$ can be obtained.

The next term for $i_{\text{edge}}/i_{\text{avg}}$ would be

$$\frac{i_{\text{edge}}}{i_{\text{avg}}} = e^{\frac{\phi_0^{(1)}(\eta=0)}{2}} \left[ \delta + \ln \xi^{(1)} + \tilde{\phi}_0^{(2)}(\eta=0) \right].$$ \hspace{1cm} (A.31)

Without further numerical work, the important result is that the next term in a perturbation series is of order unity.

A thorough treatment of the rotating disk geometry is presented. The $E$ parameter of Smyrl and Newman [3] is the key to obtaining the next term in a perturbation series. For other cell geometries, an analogous term arises, and it might be expected to behave similarly. For a coplanar electrode and insulator, a term of order unity seems likely. For other angles of intersection, the correct expansion for the primary current distribution near the edge may cause unforeseen terms to arise. This makes it difficult to draw a more general conclusion.
Appendix B
Current Distributions for Small Polarization Parameters

A perturbation analysis describing the deviations from a uniform current distribution is regular. Such an analysis is given here for linear and Tafel kinetics on a disk electrode.

Before proceeding, one should recall the integral equation relating the potential and current distributions on the disk [7]:

\[ \Phi_o(r) = \frac{2}{\pi} \int_0^r \frac{K(m)r}{r + r_q} dr \quad (B.1) \]

\( K(m) \) is the complete elliptic integral of the first kind [8], and

\[ m = \frac{2\sqrt{rr_q}}{r + r_q} \quad (B.2) \]

**Linear Kinetics**—For linear kinetics, the boundary condition along the disk electrode can be expressed as

\[ i_n = \frac{(\alpha + \alpha)F_i c_o(V - \Phi_o)}{RT} \quad (B.3) \]

We solve this problem as one with a set electrode potential. It is equally valid to specify the total current, as we prefer for Tafel kinetics.

For \( J = 0 \), the current distribution is uniform, and \( \Phi = 0 \); that is, the ohmic potential drop in the solution is negligible. This fact, along with equation (B.3), suggests that the potential is appropriately expanded as

\[ \frac{\Phi}{V} = J\Phi^{(1)} + J^2\Phi^{(2)} + \ldots \quad (B.4) \]
Substitution of equations (B.3) and (B.4) into equation (B.1) gives a formal solution for the potential, where terms of the same order in $J$ are equated:

$$
\phi^{(1)}_o(r_q) = \frac{2}{\pi} \int_0^1 \frac{K(m) r}{r + r_q} \, dr,
$$

and, for $n > 1$,

$$
\phi^{(n)}_o(r_q) = \frac{-2}{\pi} \int_0^1 \frac{\phi^{(n-1)}_o K(m) r}{r + r_q} \, dr.
$$

Nanis and Kesselman [9] show that

$$
\phi^{(1)}_o = \frac{2}{\pi} E(r^2/r_o^2),
$$

where $E(m)$ is the complete elliptic integral of the second kind.

These results give

$$
\frac{i}{i_{\text{avg}}} = 1 + J(\bar{\phi}^{(1)}_o - \phi^{(1)}_o) + J^2(\bar{\phi}^{(2)}_o - \phi^{(2)}_o) + O(J^3),
$$

where the $\bar{\phi}^{(n)}_o$ arise as corrections to the average current density,

$$
\bar{\phi}^{(n)}_o = 2 \int_0^1 \phi^{(n)}_o r \, dr.
$$

Nanis and Kesselman [9] showed that $\bar{\phi}^{(1)}_o = \frac{8}{3\pi}$.

---

Note that our argument for the elliptic integral is the square of Nanis and Kesselman’s argument. We use a definition of the elliptic integral chosen to be consistent with Abramowitz and Stegun [8].
**Tafel Kinetics**—For Tafel kinetics,

\[ i_n = i_0 \exp \left( \frac{aF}{RT}(V - \phi) \right). \quad (B.10) \]

For relatively uniform current distributions, Wagner [10] suggested that the Tafel kinetics boundary condition can be linearized:

\[ i_n = \frac{\alpha a^i}{\alpha a} \left[ \frac{RT}{\alpha a} - \phi \right]. \quad (B.11) \]

This suggests that the first correction to a uniform current distribution for Tafel kinetics will be identical to the first correction for linear kinetics (with a properly modified definition of \( J \)). Only for higher order corrections will differences appear.

We solve this problem by setting \( \delta \), the dimensionless average current density. As \( \delta \to 0 \), the current distribution is uniform, and \( \phi \) is zero (as a zeroth approximation). This fact, along with equation (B.10), suggests that the potential of the solution can be written as

\[ \frac{aF\phi}{RT} = \delta \phi (1) + \delta^2 \phi (2) + \ldots. \quad (B.12) \]

The electrode potential must also be expanded:

\[ \frac{aFV}{RT} + \ln \left( \frac{aF \phi_i}{RT} \right) = \ln \delta + \sum_{n=1}^{\infty} \delta^n \nu (n). \quad (B.13) \]

The \( \ln \delta \) term on the right side of equation (B.13) can be thought of as the zeroth order term, which is determined by requiring that the dimensionless current distribution be uniform with a magnitude specified by \( \delta \). Since this term satisfies the specified average current density, all of the higher order corrections to the potential
distribution \( \phi^{(2)} \), etc.) must have a zero average current density. This provides the condition to determine \( V^{(n)} \).

Following the same procedure used for linear kinetics gives

\[
\phi^{(1)}_o = \frac{2}{\pi} \int_0^1 \frac{K(m) r}{r + q} \, dr = \frac{2}{\pi} E(r^2/r_o^2), \quad (B.14)
\]

\[
\phi^{(2)}_o = \frac{2}{\pi} \int_0^1 \frac{K(m)(V^{(1)} - \phi^{(1)}_o)r}{r + q} \, dr, \quad (B.15)
\]

and

\[
\phi^{(3)}_o = \frac{2}{\pi} \int_0^1 \frac{K(m)[(V^{(2)} - \phi^{(2)}_o + \frac{1}{2}(V^{(1)} - \phi^{(1)}_o)^2]r}{r + q} \, dr, \quad (B.16)
\]

where

\[
V^{(1)} = 2 \int_0^1 \phi^{(1)}_o r \, dr = \frac{8}{3\pi}, \quad (B.17)
\]

and

\[
V^{(2)} = 2 \int_0^1 \phi^{(2)}_o r \, dr - \int_0^1 (V^{(1)} - \phi^{(1)}_o)^2 \, dr. \quad (B.18)
\]

These results give

\[
\frac{i_n}{i_{\text{avg}}} = 1 + \delta (V^{(1)} - \phi^{(1)}_o) + \delta^2 \left[ V^{(2)} - \phi^{(2)}_o + \frac{1}{2} (V^{(1)} - \phi^{(1)}_o)^2 \right] + O(\delta^3). \quad (B.19)
\]

Summary—These analyses demonstrate the correct procedure to calculate small deviations from a uniform current distribution. The terms in each series can be obtained by a numerical integration of
the previously determined, lower order current distribution. Since 
\(E(l) = 1\), the current density at the edge of the electrode for 
linear kinetics is

\[
\frac{i_{\text{edge}}}{i_{\text{avg}}} = 1 + \frac{2}{3\pi} J \quad \text{(small } J),
\]

and for Tafel kinetics is

\[
\frac{i_{\text{edge}}}{i_{\text{avg}}} = 1 + \frac{2}{3\pi} \delta \quad \text{(small } \delta). \tag{B.21}
\]

As expected [10], the first correction to a uniform distribution is 
the same for linear and Tafel kinetics. Figure 8 compares numerical 
results obtained from finite-difference calculations with these 
asymptotic predictions. The current density at the center of the disk 
is also compared with its asymptotic value. Since \(E(0) = \pi/2\),

\[
\frac{i_{\text{center}}}{i_{\text{avg}}} = 1 + (\frac{8}{3\pi} - 1)J \quad \text{(or } \delta). \tag{B.22}
\]

These analyses show how the current densities for linear and 
Tafel kinetics deviate from one another for larger values of the 
polarization parameter. For other cell geometries, the same linear 
dependence on \(J\) or \(\delta\) is expected.

**List of Symbols**

- \(A_{\text{coefficients arising in matching conditions (see }} \) \(n\)
  - \(A_{\text{equations (A.19-23))}}\)
- \(a, b, c, d\) parameters used in the conformal mapping procedures, 
  shown in figure 2, cm
Figure 8. Calculated and predicted current densities for linear and Tafel kinetics at the center and edge of a disk electrode for small polarization parameters. For linear kinetics, the current density depends on $J$, and, for Tafel kinetics, it depends on $\delta$. 
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>$B_n$</td>
<td>coefficients defined by equation (A.17)</td>
</tr>
<tr>
<td>$f_n$</td>
<td>stretching functions for the solution potential</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday's constant, 96487 C/equiv</td>
</tr>
<tr>
<td>$E$</td>
<td>parameter defined by equation (A.8)</td>
</tr>
<tr>
<td>$E(m)$</td>
<td>complete elliptic integral of the second kind</td>
</tr>
<tr>
<td>$i$</td>
<td>current density, A/cm$^2$</td>
</tr>
<tr>
<td>$i_o$</td>
<td>exchange current density, A/cm$^2$</td>
</tr>
<tr>
<td>$j$</td>
<td>$\sqrt{-1}$</td>
</tr>
<tr>
<td>$J$</td>
<td>dimensionless exchange current density</td>
</tr>
<tr>
<td>$K(m)$</td>
<td>complete elliptic integral of the first kind</td>
</tr>
<tr>
<td>$L,r,h,G$</td>
<td>lengths characterizing the slotted electrode, cm</td>
</tr>
<tr>
<td>$M_{2n}$</td>
<td>even Legendre functions of imaginary arguments</td>
</tr>
<tr>
<td>$P_o$</td>
<td>parameter defined by equation (1), A/cm$^{(1+\pi/2}\beta}$</td>
</tr>
<tr>
<td>$P_{2n}$</td>
<td>even Legendre polynomials</td>
</tr>
<tr>
<td>$r$</td>
<td>radial distance away from the electrode/insulator edge, cm</td>
</tr>
<tr>
<td>$r_o$</td>
<td>radius of the disk electrode, cm</td>
</tr>
<tr>
<td>$r_q$</td>
<td>radial position where the potential is being determined, cm</td>
</tr>
<tr>
<td>$R$</td>
<td>universal gas constant, 8.3143 J/mol-K</td>
</tr>
<tr>
<td>$S$</td>
<td>stretching variable, cm$^{-1}$</td>
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<td>$T$</td>
<td>absolute temperature, K</td>
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<td>$t,x,z$</td>
<td>complex coordinates</td>
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<td>$V$</td>
<td>electrode potential, V</td>
</tr>
<tr>
<td>$\alpha_a, \alpha_c$</td>
<td>transfer coefficients</td>
</tr>
<tr>
<td>$\beta$</td>
<td>interior angle between insulator and electrode, radians</td>
</tr>
</tbody>
</table>
\( \gamma(x) \) relates normal derivatives in original and transformed coordinate systems

\( \delta \) dimensionless average current density

\( \epsilon^{(n)} \) \( n^{th} \) coefficient in a perturbation series

\( \eta, \xi \) rotational elliptic coordinates

\( \kappa \) specific conductivity, \( \text{S} \cdot \text{m}^{-1} \)

\( \pi \) 3.141592654

\( \phi \) dimensionless solution potential

\( \Phi \) solution potential, V

\( \Phi_0 \) solution potential adjacent to the electrode, V

Subscripts

\( as \) asymptotic

\( avg \) average

\( center \) center of the disk electrode

\( edge \) electrode/insulator interface

\( i, r \) imaginary and real parts of a complex variable

Superscripts

\( p \) primary

\( - \) inner region variable

\( \sim \) outer region variable

References


CHAPTER 5
Corrections to Kinetic Measurements Taken on a Disk Electrode

Newman [1], [2] has suggested that a nonuniform ohmic potential drop to an electrode can lead to errors in the determination of kinetic parameters. A subsequent paper [3] showed that for linear kinetics the error in the measured exchange current density, $i_o$, can be as great as 300 percent, depending on the reference electrode placement and the dimensionless exchange current density, $J$, defined by Newman [4].

The present analysis considers the errors in kinetic parameters determined on the disk for the Tafel region in the absence of concentration variations. The apparent surface overpotential is taken to be that measured by a reference electrode of the same kind as the working electrode, with the ohmic-potential drop being determined by the interruption of the current. Since the reference electrode passes no current, it can be at equilibrium with the solution even though the working electrode is operating in the Tafel regime.

In the Tafel region, the exchange current density or $J$ is no longer an important parameter in determining the distribution of current density and potential in the solution. Instead, the relevant parameter is a dimensionless average current density, $\delta$, defined by

$$\delta = \frac{\alpha Fr i}{a o' avg}$$

(1)

This analysis presents the error in the measured exchange current density as a function of $\delta$ and three reference electrode placements.
Concentration variations are neglected in the analysis. Thus the ratio of the average current density to the limiting current density should be small. Since the expression for the limiting current density does not involve \( r_0 \) or \( \kappa \), which appear in \( \delta \), and does involve the rotation speed and the bulk concentration of the limiting reactant, which do not appear in \( \delta \), it is possible to neglect concentration variations in certain situations while still achieving moderately large values of \( \delta \). Figure 132-2 of reference 4, reproduced from reference 1, illustrates how the uniformity of current distribution is governed by the average current density, the exchange current density, and the limiting current density, as given by \( \delta, J, \) and a dimensionless mass-transfer rate, \( N \).

**Analysis**

The potential in solution, outside the double layer, in the absence of concentration variations, is given by Laplace's equation,

\[
\nabla^2 \phi = 0, \tag{2}
\]

with boundary conditions,

\[
\frac{\partial \phi}{\partial z} = 0 \text{ for } r > r_0 \text{ and } z = 0 \tag{3}
\]

\[ \phi = 0 \text{ as } r^2 + z^2 \to \infty \]

and

\[ i(r) = f(\eta_s) \text{ for } r < r_0 \text{ and } z = 0. \]

\( \eta_s \) is the local surface overpotential given by
where $V$ is the potential of the electrode and $\Phi(r,0)$ is the potential of the solution just outside the diffuse double layer measured with a reference electrode of the same kind as the working electrode. In the Tafel region, the boundary condition describing the electrode kinetics for anodic currents is

$$i(r) = i_0 \exp \left( \frac{a_{app} F \eta_s}{RT} \right).$$

Without the sectioning of an electrode, local current densities and overpotentials cannot be measured. Common practice, then, is to relate the average current density to the apparent surface overpotential, given by

$$\eta_{s,app} = V - \Phi(r,z) - \Phi(r,0) + \Phi(r,z).$$

$\Phi(r,z)$ is the potential of the reference electrode, and $\Phi(r,z) - \Phi(r,0)$ represents the potential change observed upon interruption of the current and corresponds to the ohmic drop associated with the primary distribution of the same average current density [5].

To interpret a polarization curve obtained with a disk electrode, equation (5) may be more appropriately written as

$$i_{avg} = i_{0,app} \exp \left( \frac{a_{app} F \eta_{s,app}}{RT} \right).$$

Two defined parameters, $i_{0,app}$ and $a_{app}$, are involved in this equation, and there are at least two possibilities for determining them from the experimental data. One is to take $a_{app} F/RT$ to be the
slope of the line tangent to the Tafel plot of the data and \( i_{o,app} \) to be an intercept obtained when this tangent line is extrapolated to \( \eta_{s,app} = 0 \). Then \( i_{o,app} \) and \( \alpha_{a,app} \) would be, in general, functions of \( \delta \), since the data will not yield exactly a straight line on a semi-logarithmic plot. Another approach is to assume that \( \alpha_a \) is known and that its value is used for \( \alpha_{a,app} \). A line of slope \( \alpha_a \frac{F}{RT} \) is extrapolated through the data to obtain \( i_{o,app} \). Again, the value obtained depends on the position along the Tafel plot through which the line is extrapolated.

Figure 1 shows a simulated Tafel plot of \( \psi \) vs. \( \ln(\delta) \) for three reference electrode placements. \( \psi \) is defined in the caption of figure 1 and is used in order to make the plot valid for any (low) value of the exchange current density. Thus, in the Tafel range a decrease in the value of \( i_o \) with no change in \( i_{avg} \) would leave unchanged the current density and potential distributions. The only change would be to increase the electrode potential \( V \), and hence \( \eta_s \) by an amount reflected in the definition of \( \psi \).

For values of \( \ln(\delta) < -1 \), \( \alpha_a = \alpha_{a,app} \). Additionally, for \( \ln(\delta) > 3 \) and for a reference electrode placed at the center of the disk or at infinity, \( \alpha_a = \alpha_{a,app} \). For a reference electrode placed adjacent to the edge of the disk, \( \alpha_{a,app} = \alpha_a / 2 \) as \( \delta \to \infty \). For values of \( \ln(\delta) > 4 \), \( \eta_{s,app} \) should be determined by the asymptotic solution shown with the dashed line. The deviation of the solid and dashed lines shows the difficulty in calculating potentials at the edge of the disk for high values of \( \delta \) [6]. Only for intermediate
Figure 1. Average current density vs. $\psi$, where

$$\psi = \eta_{s, \text{app}} + \frac{RT}{a_F} \ln \left( \frac{i_o a_F r_o}{RTa} \right)$$

$T = 298.15 \ K$

$\alpha_a = 0.5$
values of \( \delta \) will \( \alpha_a = \alpha_{a,\text{app}} \); therefore, it is reasonable to assume that one typically has a good estimate of \( \alpha_a \). The following analysis will develop the equations for the more general case but will emphasize the results for the case of \( \alpha_a = \alpha_{a,\text{app}} \).

To develop the relationships between the apparent parameters and the true parameters, it is convenient to introduce a new variable,

\[
A = \frac{\alpha_a F r_0 i_0}{RT} \exp \left( \frac{\alpha_a F V}{RT} \right).
\]

(8)

As is suggested in the appendix, \( A \) is a function only of \( \delta \). The relationship defined by equation (8) can be used to determine the disk potential necessary for a given average current. Originally, \( A \) was calculated by a boundary integral method. The method, as written, can not be used for high values of \( \delta \), since, as \( \delta \) becomes large, the problem of the secondary current distribution becomes singular. Smyr1 and Newman [6] give a parameter, \( E \), valid for all \( \delta \), which can be related to \( A \) through

\[
A = \frac{E}{2} \delta \exp \left( \frac{\pi \delta}{4} \right).
\]

(9)

\( E \) is shown in figure 2 and can be used to obtain \( A \) for any \( \delta \). It arises as a correction factor in an estimation of the potential of the disk electrode at high values of \( \delta \). The electrode potential \( V \) would be estimated by the sum of the ohmic potential drop to the center of the disk (estimated with the primary resistance) and the surface overpotential (estimated with \( i/i_{\text{avg}} = 0.5 \) at the center for a primary distribution):
Figure 2. $E$ vs. $\delta$ (Adopted from Smyrl and Newman [6]).
As $\delta \to \infty$, $E \to e$, the base of the natural logarithm.
\[
\frac{\alpha a F V}{RT} = \frac{\pi \delta}{4} + \ln \left(\frac{i_{\text{avg}}}{2i_0}\right) + \ln E . \tag{10}
\]

At low \( \delta \) the correction factor takes on the value \( E = 2 \). At high \( \delta \), Smyrl and Newman [6] found by means of a singular perturbation analysis that \( E \to e \).

The ratio of the actual exchange current density to the apparent exchange current density as a function of \( \delta \) can be found by combining equations (5), (7), and (8):

\[
\frac{i_o}{i_{o,\text{app}}} = \frac{A}{\delta} \exp \left( -\frac{\alpha a F V}{RT} \right) \exp \left( \frac{\alpha a,\text{app} F n_{s,\text{app}}}{RT} \right). \tag{11}
\]

The ohmic drop between a disk with a primary current distribution and a reference electrode at infinity is given by

\[
\Phi(r,z) - \Phi(r,0) = -\frac{\pi \delta RT}{4a F} . \tag{12}
\]

Therefore, for a reference electrode at infinity, equation (11) becomes

\[
\frac{i_o}{i_{o,\text{app}}} = \frac{A}{\delta} \exp \left( -\frac{\alpha a F V}{RT} \left( \frac{\alpha a,\text{app}}{\alpha a} - 1 \right) \right) \exp \left( -\frac{-\pi \delta a,\text{app}}{4a a} \right) . \tag{13}
\]

With the reference electrode placed adjacent to the surface,

\[
\frac{i_o}{i_{o,\text{app}}} = \frac{A}{\delta} \exp \left( -\frac{\alpha a F V}{RT} \left( \frac{\alpha a,\text{app}}{\alpha a} - 1 \right) \right) \exp \left( -\frac{\alpha a,\text{app} F}{RT} \Phi(r,0) \right) . \tag{14}
\]

The potential of the solution at the interface, \( \Phi(r,0) \), is given by Smyrl and Newman [6] and is shown in figure 3 as a function of \( \delta \) for \( r = 0 \) and \( r = r_o \).

When \( \alpha a = \alpha a,\text{app} \), equation (13) reduces to
Figure 3. Dimensionless potential at the center and edge of the disk.
and equation (14) reduces to

\[ \frac{i_o/\text{o, app}}{i_o} = \frac{E}{2}, \quad (15) \]

\[ \frac{i_o/\text{o, app}}{i_o} = \frac{E}{2} \exp \left( \frac{\pi \delta}{4} - \frac{\alpha_a F}{RT} \Phi(r, 0) \right). \quad (16) \]

Equations (15) and (16), the latter for \( r = 0 \) and \( r = r_0 \), are shown in figure 4. The results of Smyrl and Newman [6] imply that, as \( \delta \to \infty \), \( i_o/\text{o, app} \) goes to 0.5 for a reference electrode at the center of the disk, to infinity for a reference electrode at the edge of the disk, and to \( e/2 \) for a reference electrode at infinity, where \( e \) is the base of the natural logarithm.

Figure 1 shows that, for intermediate values of \( \delta \), \( \alpha_a \) may not equal \( \alpha_a, \text{app} \). In the rare case that experimental data exist only in this intermediate range, \( \alpha_a \), if determined by differentiation of exact data, would be given by

\[ \frac{\alpha_a}{\alpha_a, \text{app}} = 1 + \frac{\text{dln}E}{\text{dln} \delta} + \frac{\text{dln}g(\delta)}{\text{dln} \delta}, \quad (17) \]

where \( g(\delta) \) is one for a reference electrode at infinity and \( \exp(\pi \delta/4 - \alpha_a F \Phi(r, 0)/RT) \) for a reference electrode adjacent to the surface. The second term on the right side of equation (17) is shown in figure 5. The last term is shown in figure 6 for a reference electrode at the center of a disk and at the edge of a disk. The true value of \( \alpha_a \) can be determined from figure 7, where

\[ \delta, \text{ app} = \frac{\alpha_a, \text{app} F r_0 \text{i avg}}{RT \kappa} \quad (18) \]

For a reference electrode placed at infinity, the apparent transfer coefficient differs from the true value of the transfer coefficient.
Figure 4. Correction to the exchange current density for three reference electrode placements, assuming $\alpha_a = \alpha_{a,\text{app}}$. 
Figure 5. Correction term for the transfer coefficient, used in equation (17).
Figure 6. Correction term in equation (17) for a reference electrode at the edge and center of the disk.
Figure 7. Correction to the transfer coefficient for three reference electrode placements as a function of $\delta_{\text{app}}$. 
by less than four percent for any value of \( \delta \). For a reference electrode placed adjacent to the disk electrode, the maximum errors can be rather large. For any reference electrode placement other than at the edge of the disk, the errors become negligible for both low and high values of \( \delta \).

Once \( \alpha_d \) is known, two approaches are possible to determine the true value of the exchange current density. In the first approach, equation (13) or (14) could be used to obtain \( i_o \). These equations can be rewritten as

\[
\frac{i_o}{i_{o,app}} = \frac{E}{2} g(\delta) \left( \frac{\alpha_{d,app}}{\alpha_d} - 1 \right).
\]

The last term in equation (19) can be thought of as a correction to figure 4, where

\[
\chi = \exp \left( \frac{\alpha_d F V}{RT} - \frac{\pi \delta}{4} \right) g(\delta) = \frac{E}{2} \frac{i_{avg}}{i_o} g(\delta).
\]

Unfortunately, as is suggested by the last expression of equation (20), \( \chi \) can vary over many orders of magnitude.

Since \( \chi \) can be very different from one, the value of \( i_o \) obtained from equation (19) is very sensitive to the value of \( \alpha_{d,app} \) determined from experimental data. Any uncertainty in this value can cause even greater uncertainties in \( i_o \). The more accurate approach would be to extrapolate a line of slope \( \alpha_d F/RT \) that best fits the data to obtain a new \( i_{o,app} \), where \( \alpha_d \) was determined through figure 7. Then, equation (15) or (16) would be valid and figure 4 could be used to obtain \( i_o \).
The above analysis can also be applied to cathodic Tafel kinetics. The appropriate kinetic boundary condition becomes

\[ i(r) = -i_0 \exp \left( \frac{-\alpha F \eta}{RT} \right) \]

(21)

If one now takes

\[ A = \frac{\alpha Fr i_o}{RT} \exp \left( \frac{-\alpha F V}{RT} \right) \]

(22)

the results, equations (11), (13), and (14), will be identical if absolute values of \( \delta \) and \( \Phi(r,0) \) are used in the analysis. One would want to substitute cathodic transfer coefficients and apparent cathodic transfer coefficients everywhere.

**Discussion**

This analysis shows that \( i_o / i_{o,app} \) and \( \alpha / \alpha_{a,app} \) vary with the average current density. Therefore, a traditional plot of \( \eta_{s,app} \) vs. \( \ln(i_{avg}) \) should not be expected to fall on a straight line. Figure 1 shows the range of \( \delta \) over which significant variations in the slope can occur. When possible, experiments should be designed to operate mainly outside these regions of \( \delta \), since data are easier to analyze once \( \alpha_{a} \) is known.

In practice, a Tafel plot of experimental data will not extend as a straight line through the abscissa since, as \( \delta \rightarrow 0 \), the cathodic term of the Butler-Volmer equation becomes important. As is shown in figure 8, the common practice is to extend the straight part of the curve through \( \eta_{s,app} = 0 \), which gives \( i_{o,app} \). By determining the value of \( \delta \) at some point near which the slope of the curve
Figure 8. Simulated Butler-Volmer data, showing how experimental data may be expected to deviate from its Tafel slope.

- $i_o = 10^{-4} \text{A/cm}^2$
- $\kappa = 0.01 \text{(ohm-cm)}^{-1}$
- $\alpha_a = \alpha_c = 0.5$
- $T = 298.15 \text{ K}$
deviates from the Tafel slope, one can use figure 4 to calculate the true exchange current density. It is important to realize that, for a given average current density, the error becomes larger for low solution conductivities and large disk radii.

Whenever possible, exchange current densities should be determined from data taken in the linear kinetics region. Errors could then be determined from reference [3]. For high exchange current densities, sufficient data should be available in this linear region. For more practical reasons, it is also desirable to use linear data, since, in the Tafel region, ohmic potential drops may dominate the measurements.

Conclusions

This analysis again confirms suggestions that the reference electrode should be placed far from the disk when possible. In addition to the reduction in measurement errors, errors caused by the distortion of current lines near the working electrode can be avoided. Contamination of the working electrode due to the reference electrode can also be minimized.

In the literature, reported exchange current densities for a given system can vary by well over one hundred percent. Therefore, depending on the application, the magnitude of the errors shown in the analysis may be considered minor. For more complicated kinetics, though, the errors may become much more significant. For example, in a study of passivation phenomena, the use of a disk electrode could
easily lead to much larger errors than those calculated unless the nonuniform current distribution is explicitly taken into account [7].

In the study of such complex kinetics or when high precision is desired, a geometry with a uniform current distribution should be chosen. Better geometries include rotating cylinder and rotating hemisphere electrodes. The disk electrode, though, is easier to manufacture and polish. Therefore, for many applications, the disk will very likely remain a popular choice.

The rotating disk electrode can be a valuable tool when mass-transfer and concentration effects cannot be eliminated completely. Newman [1] outlined a method of studying electrode kinetics under such conditions. His analysis is valid for Butler-Volmer kinetics with a concentration dependent exchange current density. In the most general case, both $\delta$ and $J$ are important parameters. Additionally, a dimensionless mass-transfer rate, the order of the reaction, $\alpha_d/\alpha_c$, and the transference number of the reactant are important. Newman's approach involves determining the current density at the center of the disk for the appropriate set of parameters. Additionally, the potential at the center of the disk can be determined through knowledge of $i(r=0)/i_{avg}$, the disk radius, and the conductivity of the bulk electrolyte. True kinetic constants can then be determined. This approach may involve an iterative procedure.

The qualitative conclusions of this analysis are valid for any geometry with a nonuniform current distribution. In designing kinetic experiments, one should try to use a cell geometry that will
avoid these nonuniformities. Additionally, mass-transfer effects should be minimized by having uniformly accessible surfaces and operating under the proper hydrodynamic conditions.

Appendix

Axisymmetric boundary integral equations were used to calculate the current distribution (see chapter 2, equation (23)). For anodic currents, the Tafel relationship, in dimensionless form, can be written as

$$\frac{\partial \phi^*}{\partial z^*} = -A \exp\left(-\phi^*\right) \quad (A2)$$

where $z^* = z/r_o$.

$$\phi^* = \frac{a F \phi}{RT},$$

and $A$ is given by equation (8).

List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>dimensionless parameter, defined by equation (9)</td>
</tr>
<tr>
<td>$E$</td>
<td>dimensionless parameter, shown in figure 2</td>
</tr>
<tr>
<td>$g(\delta)$</td>
<td>function defined below equation (17)</td>
</tr>
<tr>
<td>$i$</td>
<td>current density, A/cm$^2$</td>
</tr>
<tr>
<td>$i_o$</td>
<td>exchange current density, A/cm$^2$</td>
</tr>
<tr>
<td>$J$</td>
<td>dimensionless exchange current density</td>
</tr>
<tr>
<td>$K(m)$</td>
<td>complete elliptic integral of the first kind</td>
</tr>
<tr>
<td>$r$</td>
<td>radial position coordinate, cm</td>
</tr>
</tbody>
</table>
\( r_o \)  
radius of the disk, cm

\( r_q \)  
radial position at which the potential is being solved, cm

\( R \)  
universal gas constant, 8.3143 J/mol-K

\( T \)  
absolute temperature, K

\( V \)  
electrode potential, V

\( z \)  
distance from electrode surface, cm

\( \alpha_a, \alpha_c \)  
transfer coefficients

\( \delta \)  
dimensionless average current

\( \eta_s \)  
surface overpotential, defined by equation (3), V

\( \kappa \)  
solution conductivity, mho/cm

\( \pi \)  
3.141592654

\( \Phi \)  
potential of the solution, V

\( \chi \)  
dimensionless parameter defined in equation (20)

\( \psi \)  
potential defined in figure 1, V

Subscripts

\( a \)  
anodic

\( app \)  
apparent

\( avg \)  
average

\( c \)  
cathodic

References


CHAPTER 6
Interpretation of Kinetic Data Taken in a Channel Flow Cell

It has long been recognized that a nonuniform reaction distribution on an electrode can lead to difficulties in the interpretation of current-overpotential data [1]. Tiedemann et al. quantified this observation for linear kinetic measurements on a disk electrode [2]. Chapter 5 gives results for the more complicated case of Tafel kinetics on a disk electrode.

Measurements are sometimes taken in the channel geometry. This geometry is useful because it has well-characterized (but nonuniform) mass-transfer rates and can be useful because of ease of construction. It also approximates popular cell configurations used to study solid electrolytes. This analysis would be particularly applicable to these systems since, if the electrolyte contains only one charge carrier, concentration variations do not exist. It will also become evident that this analysis is especially relevant to solid electrolytes since their conductivities are often low (compared to aqueous solutions).

The channel geometry has already been studied extensively; see especially, papers by Wagner [3] and by Parrish and Newman [4]. The key assumption of the analysis in this paper is that concentration variations can be neglected, which implies that $\frac{i}{i_{\text{avg}}} \ll i_{\text{lim}}$, where $i_{\text{lim}}$ is the average limiting current density. The validity of this assumption can be tested easily by calculating $i_{\text{lim}}$ through knowledge of the transport properties and the flow conditions.
The channel geometry is characterized by the two lengths shown in figure 1. The ratios $h/L$ of 1.0, 0.5, and 0.0 are investigated. Small ratios are chosen because they tend to make current distributions more uniform and tend to reduce the ohmic drop of the cell. The ratio $h/L = 0$ corresponds to a thin-gap cell, which is studied by Edwards and Newman [5], and physically means that $L \gg h$.

The average surface overpotential is assumed to be determined by the interruption of current. Additionally, the working electrode is taken to be an anode, although the results can be applied to the investigation of cathodic reactions. The counterelectrode is assumed to have the same kinetics as the working electrode, and the restrictiveness of this assumption is shown.

The emphasis of the results is on the placement of the reference electrode adjacent to the edge of the working electrode or very far from the electrode. To determine what can be considered very far from the working electrode the primary potential distribution along the insulator is shown in figure 2. At a distance $h$ from the edge of the working electrode the potential has fallen by roughly 95% of the total potential drop to infinity. Within the resolution of the graph, the distribution for all three ratios of $h/L$ is identical.

Analysis

In the absence of concentration variations, the distribution of current density is governed by Laplace’s equation. The working and counter electrodes are assumed to operate in the same reaction regime
Figure 1. Cell geometry, showing the two characteristic lengths, the coordinate system, and possible reference electrode placements.
Figure 2. Primary potential distribution along the insulator, measured from the edge of the electrode, for $h/L = 0$, $h/L = 0.5$, and $h/L = 1.0$. 
and to have identical exchange current densities and transfer coefficients. The appendix gives details of the solution procedure.

In addition to $h/L$, it is necessary to know the ratio of the ohmic to kinetic resistances to characterize how the data should be interpreted. Following Newman [6], the additional parameter for linear kinetics is

$$J = \frac{(\alpha_a + \alpha_c)F\eta_1}{RT\kappa}, \quad (1)$$

and for Tafel kinetics,

$$\delta = \frac{\alpha_a F\eta_{\text{avg}}}{RT\kappa}. \quad (2)$$

The characteristic length used in these definitions is chosen because it is the important length as $h/L \rightarrow 0$.

A nonuniform potential distribution on the electrode complicates the interpretation of data taken with the aid of current interruption. The apparent surface overpotential determined by this method is [7]

$$\eta_{s,\text{app}} = \nu - \Phi(x,y) - \Phi(0,h/2) + \Phi(x,y), \quad (3)$$

where $\Phi(x,y)$ is the potential of the reference electrode, and $\Phi(0,h/2) - \Phi(x,y)$ is the change in potential after the interruption of current and corresponds to the potential drop for a primary distribution with the same average current density.

---

$^\dagger$ The reference electrode is assumed to be the same kind as the working electrode, but passes no current, and is in equilibrium with the solution.
Results for Linear Kinetics

For linear kinetics, the current density is described by

\[ i = \frac{i_o (\alpha + \alpha_c) F \eta_s}{RT} \]  

(4)

where \( \eta_s = V - \Phi(x,h/2) \). Assuming that \( \alpha + \alpha_c \) is known, an apparent exchange current density can be defined by

\[ i_{avg} = \frac{i_{o,app} (\alpha + \alpha_c) F \eta_{s,app}}{RT} \]  

(5)

Combining equations (4) and (5) gives

\[ \frac{i}{i_{o,app}} = \frac{(\alpha + \alpha_c) F i_o}{RT} \frac{\eta_{s,app}}{i_{avg}} \]  

(6)

For a reference electrode adjacent to the edge of the electrode, equation (6) reduces to

\[ \frac{i}{i_{o,app}} = \frac{i_{edge}}{i_{avg}} \]  

(7)

Results obtained from equation (6) and the numerical procedure described in the appendix are shown in figures 3 and 4 for various reference electrode placements. \( J_{app} \) is introduced to facilitate the use of these figures and is defined by

\[ J_{app} = \frac{(\alpha + \alpha_c) F h i_{o,app}}{RT \kappa} \]  

(8)

Results for Tafel Kinetics

The important parameter for the characterization of Tafel kinetics is a dimensionless average current density. Since the proper interpretation of the data changes with the polarization parameter, a
Figure 3. Correction factor for the exchange current density for linear kinetics for a reference electrode placed adjacent to the working electrode and for one placed very far from the working electrode.
Figure 4. Correction factor for the exchange current density for linear kinetics, $L \gg h$, and four reference electrode placements.
Tafel plot of data is not expected to fall on a straight line, even if the Tafel equation exactly describes the kinetics of the reaction. This complicates the analysis for Tafel kinetics.

Reaction rates described by Tafel kinetics are given by

\[ i = i_o \exp \left( \frac{\alpha_a F \eta_s}{RT} \right) \]  \hfill (9)

Since local current densities and local surface overpotentials are not measurable, apparent kinetic parameters must be defined and should be related to measured quantities:

\[ i_{avg} = i_{o,app} \exp \left( \frac{\alpha_{a,app} F \eta_{s,app}}{RT} \right) \]  \hfill (10)

As chapter 5 discusses, a desired procedure for analyzing data is to define more precisely \( i_{o,app} \) as the apparent exchange current density obtained when a line of slope \( RT/\alpha_a F \) is fitted through the experimental data. It is, therefore, most interesting to report values of \( i/o_{o,app} \) for the case of \( \alpha_a = \alpha_{a,app} \). With this assumption, equations (9) and (10) give

\[ \frac{i_o}{i_{o,app}} = \frac{i_o}{i_{avg}} \exp \left( \frac{\alpha_a F \eta_{s,app}}{RT} \right) \]  \hfill (11)

For a reference electrode placed adjacent to the edge of the working electrode, equation (11) reduces to equation (7). Results for various reference electrode placements are shown in figures 5 and 6.

Before \( i_o \) can be obtained from \( i_{o,app} \), it is necessary to know \( \alpha_a \), which can be determined from \( \alpha_{a,app} \)
Figure 5. Correction factor for the exchange current density for Tafel kinetics, two reference electrode placements, and two ratios of h/L.
Figure 6: Correction factor for the exchange current density for Tafel kinetics, $L \gg h$, and four reference electrode placements.
Combining equations (11) and (12) gives

$$\alpha_{a,app} = \frac{RT}{F} \frac{d\ln \eta_{s,app}}{d\eta_{s,app}}.$$  \hspace{1cm} (12)

where the right side of equation (13) is evaluated assuming that 

$$\alpha_a = \alpha_{a,app}.$$  Equation (13) is shown in figures 7 and 8, where

$$\delta_{app} = \frac{\alpha_{a,app} F \frac{\eta_{avg}}{RT \kappa}}{F \frac{d\eta}{d\eta}}.$$  \hspace{1cm} (14)

Precisely obtaining \( i_o \) and \( \alpha_a \) from Tafel data can be difficult. The procedure that one might take is outlined as follows:

1. Determine \( \alpha_{a,app} \) from the slope of the data (\( \ln \eta_{avg} vs. \eta_{s,app} \)).
2. Calculate \( \delta_{app} \) from the value of \( i_{avg} \) at which the "apparent" Tafel slope was determined.
3. Obtain \( \alpha_a \) from figure 7 or 8.
4. Determine \( i_{o,app} \) from a line with the correct Tafel slope drawn through the value of \( i_{avg} \) used to calculate \( \delta_{app} \).
5. Use figure 5 or 6 to calculate \( i_o \).
Figure 7. Correction factor for the transfer coefficient as a function of the apparent dimensionless average current density for two reference electrode placements and two ratios of h/L.
Figure 8. Correction factor for the transfer coefficient as a function of the apparent dimensionless average current density for $L \gg h$ and for various positions of the reference electrode.
Discussion

Figure 3 shows $i_o/i_{o,app}$ for linear kinetics. As might be expected [2], the correction to $i_{o,app}$ can be much lower for a reference electrode placed at infinity. Unfortunately, it is not always possible to place the reference electrode far from the working electrode because the ohmic potential may dominate the measurements.

For a reference electrode placed adjacent to the working electrode, the errors are the greater (for a given $J$) the smaller the ratio, $h/L$. This result is surprising because a smaller ratio should decrease the necessary correction. This apparent inconsistency is explained by realizing that the choice of $h$ in the definition of $J$ is arbitrary, and perhaps $L$ would be a more physically significant length in describing the ratio of the ohmic to kinetic resistances. This is indeed true as $h/L \rightarrow \infty$.

Figure 4 shows $i_o/i_{o,app}$ for linear kinetics and $L \gg h$. For this ratio, errors are always zero for a reference electrode placed at infinity. Three intermediate reference electrode placements are also given. These positions correspond to positions along the insulator where the primary potential difference, $\Phi(0,h/2) - \Phi(x,h/2)$, is twenty, forty, and eighty percent of $\Phi(0,h/2) - \Phi(\infty,h/2)$.

Figures 5 and 6 show $i_o/i_{o,app}$ for Tafel kinetics. As chapter 5 discusses, a Tafel plot of data cannot be extended through $\delta = 0$ because the cathodic term of the Butler-Volmer equation becomes important. $i_{o,app}$, then, is determined by extrapolating a line of slope $RT/\alpha_d F$ through the Tafel portion of the data. A point near
which the data deviate from this Tafel slope determines the value of 
\( \delta \) that gives the correction factor to \( i_{o,app} \).

Figures 7 and 8 show \( \alpha_a/\alpha_{a,app} \). As \( \delta \to 0 \), \( \alpha_a = \alpha_{a,app} \) for any reference electrode placement. For a reference electrode placed adjacent to the edge of the working electrode, \( \alpha_a = 2\alpha_{a,app} \) as \( \delta \to \infty \). This is the same result obtained for the rotating disk electrode. Smyrl and Newman [8] show that this result holds for any reference electrode placed at the edge of a coplanar electrode and insulator. For any other reference electrode placement, \( \alpha_a = \alpha_{a,app} \) as \( \delta \to \infty \).

For a reference electrode placed next to an electrode edge, results from chapter 3 can show that, \( \alpha_a/\alpha_{a,app} = 2\beta/\pi \) as \( \delta \to \infty \), where \( \beta \) is the interior angle between the electrode and insulator. The results also show that, for linear kinetics, \( i_o \propto \frac{i_{o,app}^{2\beta/\pi}}{\beta} \) as \( J \to \infty \), for a reference electrode placed adjacent to the edge. For Tafel kinetics, \( i_o \propto i_{o,app}^{2\beta/\pi-1} \) as \( \delta \to \infty \).

The counter and working electrodes have been assumed to be in the same reaction regime and to have identical kinetic parameters. Figure 9 indicates how restrictive this assumption is. It shows \( i_o/i_{o,app} \) for a reference electrode placed adjacent to the working electrode for Tafel kinetics and for a counterelectrode with very fast kinetics, very slow kinetics, and with identical kinetics to the working electrode. To simulate slow kinetics, a constant current density is used as the counterelectrode boundary condition. Fast kinetics is simulated by prescribing a current distribution on the
Figure 9. Correction factor to the exchange current density for a reference electrode placed adjacent to the working electrode for $h/L = 0.5$ and slow kinetics, identical kinetics, and fast kinetics on the counterelectrode.
counterelectrode identical to that obtained when the overpotential is zero on both electrodes (what might be called the primary current distribution for this two-electrode system). For other reference electrode placements, the differences are smaller.

Conclusions

Results are given for the interpretation of current-overpotential measurements taken in the linear and Tafel kinetics regimes. They show that a reference electrode should be placed far from the working electrode, and it is shown what can be considered very far. We also show the effect that the current distribution on the counterelectrode has on the current distribution on the working electrode. To avoid large ohmic potential drops, it may be necessary to place the reference electrode close to the working electrode. If this procedure is necessary, the apparent kinetic parameters can be corrected.

It is worth noting that uncertainty in the placement of the reference electrode causes greater uncertainties in the interpretation of data for a reference electrode placed closer to the working electrode. This is explained completely by figure 2, which shows that the potential changes most rapidly near the working electrode.

Appendix

We used boundary integral methods, discussed in chapter 2. To facilitate the use of the numerical procedure, the channel geometry was mapped conformally into the geometries shown in figure 10.
Newman [9], [10] followed a similar procedure, except that he mapped the two electrodes so that they are coplanar (which is an intermediate Schwarz-Christoffel transformation used in the conformal mapping given here).

To solve for the current and potential distributions in the transformed geometry, the boundary conditions along the electrodes are (for non-zero \( h/L \))

\[
\frac{d\Phi}{dv_r} = f(\Phi_o) g_v(v_1),
\]

where \( f(\Phi_o) \) is given by the right side of equation (4) or (9), and

\[
g_v(v_1) = -\frac{h}{\pi} \left( \cosh^2 \epsilon - w^2 \right)^{\frac{1}{2}},
\]

where

\[
w = -j \sinh \left( \frac{\pi z}{h} \right)
\]

and

\[
\epsilon = \frac{\pi L}{2h}.
\]

\( v \) is related to \( w \) through

\[
v = -\int_0^w \frac{dw}{(w^2 - 1)^{\frac{1}{2}} (w^2 - \cosh^2 \epsilon)^{\frac{1}{2}}}.
\]

For \( h/L = 0 \), the boundary condition along the electrode is given by

\[
\frac{d\Phi}{dt_i} = f(\Phi_o) g_t(t_r),
\]

and \( g_t(t_r) \) is given by
Figure 10. Original and transformed geometries, showing the working and counter-electrodes.
\[ g_t(t_x) = -\frac{h}{\pi} \left( 1 - e^{-2\pi x'/h} \right)^{1/2}. \]  

(21)

t is related to \( z' \) through

\[ t = \sin^{-1}\exp\left( \frac{\pi z'}{h} \right). \]  

(22)

\( z' \) is related to the original coordinate system by a shift in the origin.

The advantage of using conformal mapping prior to the boundary integral technique is that the mapping tends to provide automatically a mesh spacing appropriate for a given geometry. It can also reduce the time necessary for programming a new problem because many geometries can be mapped into one.

List of Symbols

- **F**: Faraday's constant, 96487 C/equiv
- **\( g_t, g_v \)**: functions relating derivatives in the transformed and original coordinate systems
- **h**: interelectrode distance, cm
- **i**: current density, A/cm\(^2\)
- **\( i_o \)**: exchange current density, A/cm\(^2\)
- **\( \overline{I}_{\text{lim}} \)**: average limiting current density, A/cm\(^2\)
- **j**: \( \sqrt{-1} \)
- **J**: dimensionless exchange current density
- **L**: electrode length, cm
- **R**: universal gas constant, 8.3143 J/mol-K
- **T**: absolute temperature, K
\( t, v, w, z, z' \) complex coordinates

\( V \) electrode potential, V

\( x, y \) cartesian coordinates, cm

\( x', y' \) modified coordinate system for \( h/L = 0 \), cm

\( \alpha_a, \alpha_c \) transfer coefficients

\( \beta \) interior angle between insulator and electrode, radians

\( \delta \) dimensionless average current density

\( \epsilon \) ratio defined by equation (18)

\( \eta_s \) surface overpotential, V

\( \kappa \) specific conductivity, \( \Omega^{-1}\text{cm}^{-1} \)

\( \pi \) 3.141592654

\( \phi \) solution potential, V

\( \bar{\phi} \) primary solution potential, V

**Subscripts**

app apparent

avg average

edge electrode/insulator interface

**References**


CHAPTER 7
The Ohmic Resistance of a Recessed Disk Electrode

The primary current distribution and ohmic resistance are evaluated for a disk electrode recessed in an insulating plane (see figure 1). The analysis can also be used to determine the ohmic resistance to flow of current through a pore of a separator. Additionally, the errors that might occur by approximating an axisymmetric geometry by its two-dimensional analog are elucidated.

For steady-state diffusion relevant in biological systems, Kelman [1,2] investigated the mathematically identical problem. He used a separation of variables technique that utilizes Bessel functions in the "pore" and Legendre polynomials in the region outside the pore. The coefficients of the two series are determined by matching everywhere along the pore mouth the potential and the z derivative of the potential. He gave a formal solution that is complicated and difficult to use. Furthermore, he does not present his solution in a graphical manner, so it is difficult to evaluate the validity of his solution. We compare his solution for the ohmic resistance of this cell with our calculations, obtained from axisymmetric boundary integral equations.

Analysis

The primary current distribution is valid when concentration variations are negligible and when the resistance of the interfacial reaction is zero. For these conditions, the distribution of current
Figure 1. Schematic diagram of a recessed disk electrode.
density and potential is given by Laplace's equation. The boundary conditions are

$$\Phi = 0 \text{ as } z^2 + r^2 \to \infty,$$  \hspace{1cm} (1)

$$\Phi = V \text{ at } z = 0 \text{ and } r < r_0,$$ \hspace{1cm} (2)

$$\frac{\partial \Phi}{\partial z} = 0 \text{ at } z = L \text{ and } r > r_0,$$ \hspace{1cm} (3)

and

$$\frac{\partial \Phi}{\partial r} = 0 \text{ at } r = r_o \text{ and } 0 < z < L.$$ \hspace{1cm} (4)

The outer radius of the insulating plane (at $z = L$) is assumed to be much larger than $r_o$.

Axisymmetric boundary integral equations were used to solve this problem for various values of the aspect ratio, $L/r_o$. A summary of the solution procedure is given in Appendix A. The solution for $L/r_o = 0$ is given by Newman [3]. As $L/r_o \to \infty$, the current distribution on the electrode is uniform, and the ohmic resistance becomes infinite.

The resistance of this geometry can be approximated by the resistance of a disk electrode (when $L/r_o = 0$) plus the resistance to flow of current along the axis of a tube with insulating walls. The order of magnitude of the correction to this approximation is expected to be the same order of magnitude as the resistance of a disk electrode.
Results and Discussion

The distribution of current density on the electrode is shown in figure 2 for various aspect ratios. Except for the undulations, the current distribution for \( L/r_0 = 0.01 \) might appear to be approximately correct, but an asymptotic analysis, given in Appendix C, indicates that the calculated current density near the edge is likely to be in error by nearly 100 percent. The difficulties in calculating the distribution for small aspect ratios are discussed in Appendix A.

The ohmic resistance \( R \) for current flow from the recessed disk to a counterelectrode at infinity can be given by

\[
R \kappa r_o = \frac{1}{4} + \frac{L}{\pi r_o} + h(L/r_0).
\]  

(5)

\( h(L/r_0) \) is the explicit correction to the estimate of the resistance given by the other two terms. Maxwell [4] estimated an upper bound for \( h(L/r_0) \) to be 0.02019, and Rayleigh [5] gave a refined maximum estimate of 0.01235.

Kelman [1,2] gave three asymptotic formulae, valid for different ranges of \( L/r_0 \), that can be used to estimate the resistance of the cell. These formulae, when expanded, predict that \( h(L/r_0) \to 0.011 \) as \( L/r_0 \to \infty \), and \( h(L/r_0) \to 0.067 L/r_0 \ln(L/r_0) \) as \( L/r_0 \to 0 \). A preliminary analysis, discussed briefly in Appendix C, also suggests the same relation for small aspect ratios, but the coefficient has yet to be determined. The formulae are shown by the solid line of figure 3.
Figure 2. The primary current distribution on a recessed disk electrode for various values of the aspect ratio.
Figure 3. A correction to an estimation of the ohmic resistance of a recessed disk electrode as calculated by Kelman's formulae [1,2] and by the numerical procedure described in Appendix A.
Kelman estimated that these formulae for the resistance give a maximum relative error of 0.0341 in the total current for a set potential difference between the counter and working electrodes. Kelman's estimated error translates into an absolute error for $h(L/r_o)$ of at least 0.0085, larger than or nearly as large as $h(L/r_o)$ itself. The points shown in figure 3 are our numerical results. We calculate that, for $L/r_o = 10$, $h(L/r_o) = 0.011$. Because this problem is relatively expensive to solve, we have not tested thoroughly the validity of our results. For the reasons outlined in Appendix B, one might also be suspicious of Kelman's results. Further work is necessary if more definite conclusions are required. We estimate that the maximum relative error in the resistance, when predicted by the first two terms of equation (5), is 0.03 and occurs near $L/r_o = 0.1$.

Since two-dimensional geometries are often easier to solve (for example, because conformal mapping procedures might be possible), it may be tempting to approximate an axisymmetric geometry with its two-dimensional analog. Such approximations are often rationalized by noting that the current density has the same asymptotic behavior near the edge of an electrode because, in this region, curvature effects can justifiably be neglected. Quantitative agreement is unlikely since the average current density will usually be influenced by curvature.

To elaborate further, the results are compared with results for this geometry's two-dimensional analog, given by Diem et al. [6]. The geometry is shown in figure 4, where the geometric ratios held
Figure 4. Two-dimensional analog to figure 1. Adapted from reference [6].

\[
\frac{h}{L-m} = 1.622 \\
\frac{h}{n} = 5.0 \\
m/n \text{ varies}
\]
constant in their analysis are also given. The ratio \( m/n \) is analogous to \( L/r_o \).

Since, in two dimensions, currents cannot flow to infinity without an infinite potential drop, the counterelectrode is placed at a finite distance from the working electrode. Placing the counterelectrode too close to the working electrode distorts the current distribution on the supposedly "isolated working electrode." Here, the distortions are minimal, as is seen by comparing \( \frac{i_{\text{center}}}{i_{\text{avg}}} = 0.66 \) for \( m/n = 0 \) with \( \frac{i_{\text{center}}}{i_{\text{avg}}} = 2/\pi \) for an isolated electrode. Comparisons between the two-dimensional and axisymmetric geometries are summarized in table 1. The reported values of \( h(L/r_o) \) are based on our analysis. The correction to the ohmic resistance of the two-dimensional cell is given by Diem's \( \Delta_1 \) and is similar to \( h(L/r_o) \). The current distribution for \( L/r_o = 0.04 \) displayed similar undulations to the distribution shown for \( L/r_o \); therefore, as Appendix C also indicates, the values given for \( L/r_o = 0.04 \) are suspicious.

A conclusion drawn from table 1 is that an axisymmetric geometry should generally not be approximated by a two-dimensional analog, if quantitative results are desired. If only qualitative results are required, numerical calculations may be unnecessary.

Conclusions

The primary current distribution and ohmic resistance for various aspect ratios are given. The results can be used to design a
Table 1. A comparison between results for two-dimensional and axisymmetric geometries.

<table>
<thead>
<tr>
<th>$L/r_o$</th>
<th>$i_{center}/i_{avg}$</th>
<th>$i_{edge}/i_{avg}$</th>
<th>$h(L/r_o)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2-D</td>
<td>axi</td>
<td>2-D</td>
</tr>
<tr>
<td>0.0</td>
<td>0.66</td>
<td>0.5</td>
<td>$\infty$</td>
</tr>
<tr>
<td>0.04</td>
<td>0.70</td>
<td>0.56</td>
<td>2.87</td>
</tr>
<tr>
<td>0.2</td>
<td>0.79</td>
<td>0.71</td>
<td>1.47</td>
</tr>
<tr>
<td>0.4</td>
<td>0.87</td>
<td>0.84</td>
<td>1.18</td>
</tr>
<tr>
<td>2.5</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$\infty$</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

cell that would have an approximately uniform current distribution in the absence of concentration variations. With convection, the mass-transfer limited current distribution can be nonuniform.

Appendix A. The Solution Procedure

Equations (14) through (19) of chapter 2 give an expression for the potential on the boundary. Finite-difference approximations of these equations were solved with an iterative procedure. The problem was solved as one with a prescribed current distribution on the electrode. Corresponding distributions of potential on the working electrode were superimposed until the constant boundary condition was satisfied.
The current distributions that were superimposed are

$$\frac{\partial \Phi}{\partial z} = P_{2n} \left[ \sin \left( \frac{\pi r}{2r_o} \right) \right],$$

(A.1)

where $P_{2n}$ are the even Legendre polynomials. It was found that the polynomials from $2n - 0$ to $2n - 24$ were sufficient. Additional polynomials did not change appreciably the distribution. The argument for the polynomials is chosen so that the radial derivative of the current density is zero at the center and edge of the electrode. The recurrence formula used to evaluate the polynomials is given in Hildebrand [7] and Abramowitz and Stegun [8].

The undulations in the current distribution for $L/r_o = 0.01$ are caused by inaccuracies in the numerical procedure. A more natural set of functions to describe the current density is suggested by Kelman [1,2]:

$$\frac{\partial \Phi}{\partial z} = A_o + \sum_{n=1}^{N} A_n J_0(\alpha_n r/r_o),$$

(A.2)

where $J_0(x)$ is the Bessel function of the first kind of order zero, and $\alpha_n$ is the $n^{th}$ root of $J_1(x)$. By letting $N = 12$, we determined the current distribution for $L/r_o = 0.01$. Abramowitz and Stegun [9] gave approximations for $J_0(x)$. The resulting current distribution is nearly identical (including the undulations) to the distribution shown in figure 2. This indicates that the inaccuracy is not caused by the choice of current functions. The reason that such inaccuracies exist is suggested by chapters 2 and 3. For such small aspect ratios, the edge regions are not completely isolated, and it is not
obvious where the asymptotic behavior dictated by one angle of intersection ends and the other begins. We did not pursue this problem in greater detail because it is relatively expensive to solve. Appendix C provides a starting point for a more involved investigation of the behavior of the current distribution for small aspect ratios.

For this cell geometry, other techniques [10] for determining the current density on an electrode with a constant potential boundary condition might give accurate solutions. For cells with obtuse angles of intersection between the electrode and insulator, the infinite current densities that arise can not be calculated accurately unless the correct form of the singularity is imbedded into the problem. Miksis and Newman [11] and Pierini and Newman [12] followed this procedure.

One alternative to the solution procedure outlined above is to solve directly for the gradient of the potential. The gradient of equation (5) of chapter 2 is

$$-\alpha_3 \nabla q \Phi = \int \left( -\frac{\partial \Phi}{\partial n} \frac{1}{\xi_3} \nabla q \xi_3 + \Phi \left( \frac{1}{\xi_3^2} \nabla q \left( \frac{\partial \xi_3}{\partial n} \right) - \frac{2}{\xi_3^3} \frac{\partial \xi_3}{\partial n} \nabla q \xi_3 \right) \right) dA, \quad (A.3)$$

where $\nabla q$ emphasizes that we are taking the gradient with respect to $x_q, y_q, z_q$.

A specific form of equation (A.3) was used to determine the current distribution on the counterelectrode in the slotted-electrode cell of chapter 4. The solution procedure worked, but the calculated current density near the edge was very sensitive to the placement of
the nodes.

For the recessed disk, after the \( \theta \) dependence of equation (A.3) is eliminated, the \( z \) derivative of the potential along the disk can be described by

\[
\frac{\partial \Phi}{\partial z} = \frac{2}{\pi} \int_0^\infty \frac{(\Phi-V)E(m)rdr}{((r-r_q)^2+L^2)((r+r_q)^2+L^2)^{1/2}}
\]

\[
-\frac{2}{\pi} \int_0^\infty \frac{(\Phi-V)rL^2}{((r+r_q)^2+L^2)^{3/2}} \left[ \frac{4E(m)(r^2+r_q^2+L^2)}{(r-r_q)^2+L^2} - K(m) \right] dr
\]

\[
+ \frac{3L}{\pi} \int_0^L \frac{(\Phi-V)E(m)zdz}{((r-r_q)^2+z^2)((r+r_q)^2+z^2)^{1/2}}
\]

\[
+ \frac{2L}{\pi} \int_0^L \frac{(\Phi-V)z(r_o^2-r_q^2-z^2)}{((r_o-r_q)^2+z^2)((r_o+r_q)^2+z^2)^{3/2}} \left[ \frac{2(r_o^2+r_q^2+z^2)E(m)}{(r_o-r_q)^2+z^2} - \frac{K(m)}{2} \right] dz
\]

We did not have great success with equation (A.4). Away from \( r = r_o \), the current distribution gave what appeared to be the correct behavior, but, near the edge, the current distribution was very sensitive to the node placement. Because this equation is relatively expensive to solve and other solution procedures were available, we did not investigate thoroughly why equation (A.4) caused difficulties. For the case of \( L/r_o = 0 \), equation (A.4) reduces to equation (23) of chapter 2, which, when integrated numerically, showed good agreement with the known, analytic solution.

A situation may arise where the procedure described here is the best method. We have, therefore, documented our efforts in the hope
that they may be useful.

Appendix B. A Discussion of Kelman's Analysis

Near \( z = L, \ r = r_0 \) (see figure 1), Laplace's equation can be solved to show that

\[
\Phi(\rho, \theta) \propto \rho^{2/3} \cos(2\theta/3),
\]

(B.1)

where \( \rho \) is the radial distance from the singular point and \( \theta \) is the angular coordinate with \( \theta = 0 \) corresponding to \( z = L, \ r > r_0 \) and \( \theta = \frac{3\pi}{2} \) corresponding to \( r = r_0, \ z < L \). This implies that along the mouth of the pore,

\[
\lim_{r \to r_0} \frac{\partial \Phi}{\partial z} \propto \rho^{-1/3},
\]

which is singular at \( r = r_0 \). A corresponding behavior for the radial derivative of potential prevails on the insulating plane near the opening.

We can ask whether Kelman's two series can give this behavior. Inside the pore, his expression for the current density at \( z = L \) can be written as

\[
\frac{\partial \Phi}{\partial z} = A_0 + \sum_{n=1}^{\infty} A_n J_n(\alpha_n r/r_0).
\]

(B.3)

Since the Bessel functions \( J_n(x) \) are well-behaved, it is difficult for this series to converge for all \( r > r_0 \) and still to give the correct asymptotic behavior near \( r = r_0 \).

In the outer region, his expression for the current density can be written as
\[
\frac{d\Phi}{dz} = \frac{1}{\eta} \sum_{n=0}^{\infty} B P_{2n}(\eta),
\]  
(B.4)

where \( \eta = (1 - r^2/r_o^2)^{1/2} \). Since the \( P_{2n}(\eta) \) are well-behaved, equation (B.4) is also unlikely to converge for all \( r = r_o \) and to give the correct asymptotic behavior near \( r = r_o \). Note that, when \( L/r_o = 0 \), the nature of the singularity changes, and the solution is valid because the term multiplying the summation goes to infinity in the correct manner as \( r \to r_o \).

In summary, we indicate that the "solution" given by Kelman is not reasonable because the series represented by equations (B.3) and (B.4) do not have the correct asymptotic behavior. This does not imply that Kelman's results should be completely disregarded because numerical solutions that are clearly in error near a singular point have been observed to be approximately correct over the remainder of the domain.

Appendix C. Small Aspect Ratios

Away from the electrode edge, for very small aspect ratios, the current distribution is indistinguishable from the current distribution for \( L/r_o = 0 \). Near the edge, the deviation from a zero aspect ratio has a major influence on the distribution. In this region, the curvature of the axisymmetric geometry can be neglected, and the problem can be considered two dimensional. Hence, the treatment given here is applicable for both the recessed disk and the two-dimensional analog, shown in figure 4.
To investigate the region near the edge, we used conformal mapping to obtain a solution to Laplace's equation. The current distribution on the electrode is described by

\[-\kappa \frac{\partial \Phi}{\partial y} = \frac{\sqrt{\pi L/2}}{\sqrt{1 - u}} P_o,\]  

(C.1)

where the coordinates are shown in figure 5, and \( w \) and \( z \) are related through

\[-z = \frac{z}{L} - \frac{2}{\pi} \frac{w\sqrt{w-1}}{\sqrt{w}} + \frac{1}{\pi} \ln \left( \frac{\sqrt{1 + \sqrt{w}}}{\sqrt{1 - \sqrt{w}}} \right),\]  

(C.2)

\( P_o \) is the parameter introduced by Smyrl and Newman [13] and generalized in chapter 3. To apply equations (C.1) and (C.2) to the two-dimensional analog, \( L \) should be replaced with \( m \). For the recessed disk,

\[ P_o = \sqrt{r_o} \frac{8}{\pi} i_{avg} \]  

(C.3)

and, for the two-dimensional analog in the case where \( L - m \gg n \),

\[ P_o = \sqrt{2n} \frac{8}{\pi} i_{avg} \]  

(C.4)

Equations (C.1), (C.3), and (C.4) show that the current distribution near the edge is inversely proportional to the square root of the aspect ratio. When evaluated at \( u = 0 \), equation (C.1), with \( P_o \) given by equation (C.4), is in good agreement with the result for \( m/n = 0.04 \). Equations (C.1) and (C.3) cast serious doubt on the current distribution calculated for \( L/r_o = 0.01 \). Current distributions, as given by equations (C.1) through (C.3), are shown in figure 6 for various, small aspect ratios.
Figure 5. The original and transformed coordinate systems used to elucidate the current distribution near the edge of a recessed disk for small aspect ratios. The mapping is achieved by requiring that

\[ \frac{dz}{dw} = \frac{2 \sqrt{w-1}}{\pi \sqrt{w}} \]
Figure 6. The distribution of current density, valid for small aspect ratios, near the edge of a recessed disk. The dashed lines were obtained from equations (C.1) (C.2), and (C.3), and the solid line is the primary current distribution for a disk electrode, as given by Newman [3].
To design an accurate, boundary-integral procedure for a complete study of the current distribution on a recessed disk, it is important to have an *a priori* estimate of the potential distribution along the insulating wall and plane near the pore mouth. This analysis gives

$$\frac{\kappa(V - \Phi)}{r_0 i \text{avg}} = \sqrt{u/\pi},$$

where, on the insulating wall, $u$ and $\bar{y}$ are related through

$$\bar{y} = \frac{2}{\pi} \left( u - u^2 \right)^{\frac{1}{4}} + \frac{1}{\pi} \tan^{-1} \left( \frac{2(u - u^2)^{\frac{1}{4}}}{1 - 2u} \right).$$

Along the insulating plane, $\bar{x}$ and $u$ are related through

$$\bar{x} = \frac{2}{\pi} \left( u^2 - u \right)^{\frac{1}{4}} + \frac{1}{\pi} \ln \left( \frac{\sqrt{u} - \sqrt{u-1}}{\sqrt{u} + \sqrt{u-1}} \right).$$

These equations can be expanded to show that the tangential gradients of potential satisfy the proportionality (B.2) near the singular point.

We should also be able to determine, in general, the order of magnitude of the correction to the resistance, but, to date, we have been unsuccessful. The evidence, though, strongly suggests

$$\lim_{L/r_0 \to 0} h(L/r_0) \propto L/r_0 \ln(L/r_0).$$

This result agrees with Kelman's analysis and is partly arrived at by determining the ohmic resistance of a recessed, planar electrode, similar to the cell in figure 4, with the counterelectrode replaced with a hemicylinder at a distance very far from the counterelectrode.
To determine the correction to the ohmic resistance for this cell, the mappings shown in figure 7 are useful. When the constants \(a\) and \(C\) are related to \(m\) and \(n\), the ohmic resistance of the cell can be determined. For small \(m/n\), these constants are given by

\[
m = \frac{\pi}{2} aC
\]

and

\[
n = C \left(1 - \frac{a}{2} \ln a\right).
\]

With these relations it can be shown that

\[
\lim_{m/n \to 0} h(m/n) = -\frac{1}{\pi^2} \frac{m}{n} \ln(m/n),
\]

which is in good agreement with the results given by Diem et al. [6].

List of Symbols

- \(A_n\), \(B_n\) coefficients in a series
- \(h(L/r_o)\) correction to estimate of cell resistance
- \(i\) current density, \(A/cm^2\)
- \(J_0\) Bessel function of the first kind of order zero
- \(L\) wall length, cm
- \(m/n\) ratio of lengths, given by figure 4
- \(P_{2n}\) even Legendre polynomials
- \(r, z\) cylindrical coordinates
- \(r_o\) radius of the disk electrode, cm
- \(R\) cell resistance, ohm
- \(V\) electrode potential, V
Figure 7. A schematic of the mappings used to determine the ohmic resistance of a recessed, planar electrode, with a counterelectrode placed at a distance very far from the working electrode. Also shown are the coordinate transformations that provide the mappings.
η rotational elliptic coordinate used in equation (B.4)
κ specific conductivity, \( \Omega^{-1}\text{cm}^{-1} \)
π \( 3.141592654 \)
ρ, θ cylindrical coordinates used near \( r = r_0, z = L \)
∅ solution potential, \( V \)

Subscripts

avg average
center center
dge edge
q denotes a point at which the potential is solved

References


CHAPTER 8
The Dissolution Kinetics of FeSO₄ Films

Introduction

The dissolution of iron in sulfuric acid has been extensively investigated. Russell [1], [2] and Haii [3] recently reviewed these studies. The most significant development that has arisen since their reviews is the recognition of the importance of certain, universal phenomena observed in nonlinear systems. These lines of inquiry may provide the means to analyze data and to compare quantitatively experiments with numerical simulations. Papers that are relevant to iron dissolution include [4], [5], and [6].

Sustained periodic and aperiodic dynamic behavior, which occurs in a potential range within the limiting current plateau which is presumably caused by a ferrous-sulfate film, is one of the more interesting phenomena observed in this system. Russell and Newman [1], [2] attempted to explain this behavior. Their work is probably the most complete theoretical investigation of such problems. Coupled transport equations within the ferrous-sulfate film and in the bulk electrolyte were used. One assumption in their model is that the concentration of ferrous ions at the solution/salt-film interface is equal to the saturation value. The goal of the experiments discussed here is to test the validity of this assumption. If it is not valid, a kinetic rate constant that could be used to describe the rate of dissolution might be determined. If the results indicate that it is necessary, a rather minor modification of Russell and
Newman's model could be made, and better agreement between experiments and theory might be possible. Otherwise, more extensive modifications to the model are necessary.

We use a ring-disk electrode system, where ferrous ions produced by the dissolution of the iron disk electrode or by the dissolution of the FeSO₄ film are oxidized on a platinum ring. After the interruption of current on the disk, the ferrous-sulfate film dissolves and is the only source of Fe²⁺. Through the collection efficiency, the rate of dissolution of the salt film might be estimated. Previously, Okinaka [7] used a similar procedure to estimate the dissolution kinetics of a cadmium-hydroxide film in concentrated, alkaline solution. For the conditions that he investigated, the films dissolved over a time of the magnitude of hundreds of seconds. Prater and Bard [8] modeled the transient response of the ring current after a step change in the disk current. They showed that, after the interruption of disk current, the ring current, if the only available reactant is produced at the disk, will decay to zero in a time of roughly

\[ t \approx 5.0 \, S_c^{1/3} \, \omega^{-1} \]  

where Sc is the Schmidt number and \( \omega \) is the rotation speed of the disk. Hence, if the rate of dissolution of the FeSO₄ film is to be determined with this experiment, its time constant for dissolution should be greater than a second.

When these experiments were carried out at room temperature, the current on the ring decayed to zero within a time consistent with the
model of Prater and Bard. It is, therefore, not possible to deduce from these experiments any quantitative information about the dissolution kinetics of the ferrous-sulfate film. Since the rate of a reaction is expected to decrease significantly with temperature, we repeated the experiments at 0°C, and we, again, obtained no quantitative information about the dissolution kinetics. In the remainder of the chapter, we describe the experimental procedure and briefly discuss the implications that these results have on further modeling efforts.

**Experimental Procedure**

The rotating ring-disk electrode consisted of an iron disk with a 0.4 cm diameter and a platinum ring with an inner diameter of 0.75 cm and an outer diameter of 0.85 cm. All experiments used 1 M sulfuric acid solutions. The glass cell that was used was shown and described by Russell and Newman [9]. The temperature was controlled with a constant-temperature bath at 25.0±0.1°C or 0.0±0.3°C. Before each experiment, N₂ was bubbled through the electrolyte for 1 to 2 hours, and the ring-disk electrode system was polished with 9, 3, and 1 micron diamond paste.

All experiments used a Hg/Hg₂SO₄ reference electrode and a platinum counterelectrode, both placed at distances very far from the working electrode. The ring-disk rotation speed was set at either 83.8 or 41.9 sec⁻¹. The potential of the disk was slowly swept until current oscillations were observed. The potential was then slowly decreased until the oscillations stopped. The ring electrode was set
at a potential so that the oxidation of the ferrous ions was clearly
at a limiting current. Once the disk and ring currents were steady,
the potential of the disk was stepped to a potential near -1.0 V.
The ring and disk currents were recorded with a Nicolet digital
oscilloscope.

Results and Discussion

The theoretical collection efficiency, when it is taken into
consideration that the disk electrode reaction involves two electrons
and the ring electrode reaction involves one, is 0.108 [10]. As was
briefly discussed in the Introduction, the time constant for dissolu-
tion of the film was found to be at least as small as the time con-
stant described by Prater and Bard [8]. The experiments were there-
fore repeated at 0°C. Polarization curves obtained at two different
sweep rates with the ring at open circuit are shown in figure 1. The
behavior was qualitatively the same as that observed at room tempe-
tature. Complicated dynamic behavior appeared at the slower sweep
rate, and, if the potential was held constant in this range, sus-
tained unsteady behavior was observed.

Figure 2 shows a typical ring-disk experiment. The time lag
observed on the ring electrode is consistent with the predictions of
Prater and Bard [8]. Prater and Bard showed the effects of varying
the ratios of the three characteristic radii of a ring-disk system.
It can be seen that, even with a very small gap between the disk and
ring, the time constant is probably too large to obtain information
about the dissolution kinetics of FeSO₄.
Figure 1. Polarization curves for iron dissolution at a rotation speed of 41.9 sec⁻¹.
Figure 2. A typical ring-disk experiment at a rotation speed of 41.9 sec$^{-1}$. 
Any attempt to estimate a rate constant from these experiments would be meaningless. The rate of dissolution of a salt film can often be described by [11]

\[ N_{Fe^{2+}} = k_d(c_{sat} - c_o), \]  

where \( c_o \) is the concentration of ferrous ions at the film/solution interface and \( c_{sat} \) is the equilibrium concentration of \( Fe^{2+} \). If \( k_d \) is very large, this reaction can be considered mass-transfer limited. More specifically, for the rotating-disk electrode, if \( \frac{D}{\delta k_d} \) is very small, the kinetics of dissolution can be neglected. \( D \) is the diffusion coefficient of \( Fe^{2+} \), and \( \delta \) provides an estimate of the size of the mass-transfer boundary layer and is given by [12]

\[ \delta = 1.61 Sc^{-1/3} \sqrt{\nu/\omega}. \]  

Since even at 0°C the rate of dissolution of the FeSO₄ is fast enough that it could not be measured, it is unlikely that the simplified boundary condition used by Russell and Newman is a major source of discrepancy between theory and experiment. More complicated changes, therefore, are necessary to obtain agreement. For example, radial variations in the potential and surface concentration might need to be accounted for more accurately, or perhaps it may be necessary to account more explicitly for changing film porosity.

As a further check on the rate of dissolution of the salt film, the concentration of the \( Fe^{2+} \) at the film/solution interface could be estimated from the ring current and the theoretical collection efficiency. The surface concentration \( c_o \), using the theoretical
collection efficiency, would be estimated by

\[ c_o = \frac{\delta I_{ring}}{2FDA 0.108}, \]  \hspace{1cm} (4)

where \( A \) is the surface area of the disk and \( F \) is Faraday's constant.

Using Russell and Newman's [13] estimates of \( D \) and \( \nu \), we estimate for the experiments at 25°C that \( c_o = 3.3 \pm 0.1 \text{ M} \) for \( \omega = 83.8 \text{ sec}^{-1} \) and that \( c_o = 3.4 \pm 0.1 \text{ M} \) for \( \omega = 41.9 \text{ sec}^{-1} \). These concentrations are greater than 1.88 M, the estimated saturation value.

This discrepancy is explained by figure 5 of Russell and Newman. It shows that the pH increases significantly in the mass-transfer boundary layer and that the concentration of \( \text{Fe}^{2+} \) is around an order of magnitude greater than the concentration of \( \text{H}^+ \). Hence, a term accounting for migration must be included in equation (4). Using the physical property data given by Russell and Newman [13], the surface concentration of the ferrous species was determined with a modified version of program MIGR [14]. In the first case, it was assumed that the \( \text{H}_2\text{SO}_4 \) dissociated into \( \text{H}^+ \) and \( \text{SO}_4^{2-} \), and in the second case, the supporting ionic species were assumed to be \( \text{H}^+ \) and \( \text{HSO}_4^- \). For the first case, the surface concentration was found to be 2.3 M, and, for the second case, the surface concentration was found to be 1.6 M. The actual concentration at the surface should be intermediate between these two values.

Because of the complexity of the solution chemistry and limited physical property data, it is not possible to determine precisely the surface concentration of \( \text{Fe}^{2+} \). Consequently, the most important con-
clusion from these results is that the concentrations obtained from the two different rotation speeds are the same to within the experimental uncertainty. This confirms that the rate of dissolution of FeSO$_4$ can be considered mass-transfer limited.

Conclusions

The kinetics of dissolution of ferrous-sulfate films in a sulfuric acid medium is sufficiently fast that it can be considered mass-transfer limited. It is valid in most models to assume that the concentration of ferrous ions adjacent to the salt film is given by its saturation value. Thus, for Russell and Newman’s model to show better agreement with experiments, it is most likely necessary to switch to a two-dimensional model. Simulations of dynamic behavior may, therefore, be quite expensive.

List of Symbols

\begin{align*}
A & \quad \text{surface area of the disk electrode, cm}^2 \\
c_0 & \quad \text{concentration of Fe}^{2+} \text{ at the film/solution interface, mol/cm}^3 \\
c_{sat} & \quad \text{saturation concentration of Fe}^{2+}, \text{ mol/cm}^3 \\
D & \quad \text{diffusion coefficient, cm}^2/\text{sec} \\
F & \quad \text{Faraday’s constant, } 96487 \text{ C/equiv} \\
I & \quad \text{current, A} \\
k_d & \quad \text{dissolution rate constant, cm/sec} \\
N_{Fe^{2+}} & \quad \text{flux of ferrous ions, mol sec}^{-1} \text{ cm}^{-2}
\end{align*}
\[ Sc \] Schmidt number
\[ \tau \] time, sec
\[ \delta \] mass-transfer boundary layer thickness, cm
\[ \nu \] kinematic viscosity, cm\(^2\)/sec
\[ \omega \] disk rotation speed, sec\(^{-1}\)

References


Corrosion, Orlando, FL (June 1, 1987).


[12] Veniamin G. Levich, ibid., p. 64.


APPENDIX
Computer Programs

The following are program listings used for work presented in this thesis. The code which generates information used as input for john.for is given by Orazem.†

1. wedge.for (chapter 3)
2. john.for‡ (chapter 4)
3. alan.for (chapter 4)
4. scchan.for (chapter 6)
5. scinf.for (chapter 6)
6. luggin.for (chapter 7)

‡written by Johannes H. Sukamto
program wedge
implicit double precision(a-h,o-z)
dimension x(201),s(201),phi(2,201),rl(2,2,201,201),phio(201),
lr(2,2,201,201),cdl(201),as(2,201)
common x,phi,rl,r2,my,mx,cdl,xmax,as,pp,pi

read*,angle
print*,'beta-pi*',angle
pi=3.14159265358979d0
beta=angle*pi
damp=0.1d0
read*,ikinet
call tread
call fillmat(beta)
call asymp(beta)

iter=1
if (ikinet.eq.1)then
  print*,'linear kinetics'
else
  print*,'Tafel kinetics'
end if

initial guess
do 3 i=1,mx
  phi(1,i)=-1.0d0
100 call current(1,ikinet,beta)

solve for phi1
do 15 i=1,mx
  phio(i)=as(1,i)
10 do 16 j=1,mx-1
  al=fa(cdl(j),cdl(j+1),x(j),x(j+1))
  bl=fb(cdl(j),cdl(j+1),x(j),x(j+1))
16 phio(i)=phio(i)+al*rl(1,1,i,j)+bl*rl(1,2,i,j)
15 phio(i)=phio(i)/pi/2.0d0
if (ikinet.eq.1)then
  const=xmax**(0.5d0-beta/pi)-phio(mx)
else
  const=dlog(xmax**(0.5d0-beta/pi))-phio(mx)
end if
555 phio(i)=phio(i)+const

check for errors
error=0.0d0
30 error=dmax1(error,dabs(phi(1,i)-phio(i)))
if (error.gt.1.d-5) then
  do 35 i=1,mx
35 phi(1,i)=phi(1,i)+damp*(phio(i)-phi(1,i))
iter = iter + 1
if (iter .ge. 800) then
  print*, 'greater than 300 iterations', 'error=', error
  goto 999
end if
  goto 100
end if
999  call tprint(iter, ikinet, beta)
end

subroutine fillmat(beta)
implicit double precision(a-h,o-z)
dimension x(201), s(201), phi(2,201), r1(2,2,201,201), phio(201),
    r2(2,2,201,201), cd1(201), as(2,201)
common x, phi, r1, r2, my, mx, cd1, xmax, as, pp, pi
en = beta / pi - 1.0d0
enl = en + 1.0d0
mm = 100
do 1 i = 1, mx
  do 1 j = 1, mx - 1
    call integrate(x(j+1), x(j), x(i), en, mm)
    r1(1,1,i,j) = beta / pi * pp
    call integrate(x(j+1), x(j), x(i), enl, mm)
    r1(1,2,i,j) = beta / pi * pp
  end do 1
continue
return
end

subroutine current(ielec, ikinet, beta)
implicit double precision(a-h,o-z)
dimension x(201), s(201), phi(2,201), r1(2,2,201,201), phio(201),
    r2(2,2,201,201), cd1(201), as(2,201)
common x, phi, r1, r2, my, mx, cd1, xmax, as, pp, pi
if (ikinet .eq. 1) then
  do 1 i = 1, mx
    cd1(i) = phi(1,i)
  end do 1
else
  do 3 i = 1, mx
    cd1(i) = -dexp(-phi(1,i))
  end do 3
end if
return
end

function fa(pl, p2, z1, z2)
implicit double precision(a-h,o-z)
fa = pl - (p2 - pl) * z1 / (z2 - z1)
return
end

function fb(pl, p2, z1, z2)
implicit double precision(a-h,o-z)
FB = (P2-P1)/(Z2-Z1)
return
end

subroutine tread
implicit double precision(a-h,o-z)
dimension x(201), s(201), phi(2,201), rl(2,2,201,201), phio(201),
lr2(2,2,201,201), cd1(201), as(2,201)
common x, phi, rl, r2, my, mx, cd1, xmax, as, pp, pi
read*, mx
read*, xmax
do 1 i=1,mx
1 x(i) = xmax*(dfloat(i-1)/dfloat(mx-1))**2
return
end

subroutine tprint(iter, ikinet, beta)
implicit double precision(a-h,o-z)
dimension x(201), s(201), phi(2,201), rl(2,2,201,201), phio(201),
lr2(2,2,201,201), cd1(201), as(2,201)
common x, phi, rl, r2, my, mx, cd1, xmax, as, pp, pi
print*, 'Along electrode:'
do 21 i=1,mx
21 print*, x(i)**(0.5d0), char(9), dabs(cd1(i))
if (iter.ge.800) then
   print*, 'The last run did not converge'
   stop
end if
return
end

subroutine asymp(beta)
implicit double precision(a-h,o-z)
dimension x(201), s(201), phi(2,201), rl(2,2,201,201), phio(201),
lr2(2,2,201,201), cd1(201), as(2,201)
common x, phi, rl, r2, my, mx, cd1, xmax, as, pp, pi
en = -0.5d0
mm = 1000
call integrate(xmax, 0.0d0, 0.0d0, en, mm)
as(1,1) = beta/pi*pp
do 3 i=2,mx-1
3 call integrate(x(i), 0.0d0, x(i), en, mm)
   temp = pp
   call integrate(xmax, x(i), x(i), en, mm)
   as(1,i) = (pp+temp)*beta/pi
continue
call integrate(xmax, 0.0d0, xmax, en, mm)
as(1,mx) = pp*beta/pi
return
end
subroutine integrate(b,a,xq,en,mm)
implicit double precision(a-h,o-z)
dimension x(201),s(201),phi(2,201),rl(2,2,201,201),phio(201),
1 r2(2,2,201,201),cdl(201),as(2,201)
common x,phi,rl,r2,my,mx,cdl,xmax,as,pp,pi
if (dabs(xq).le.1.e.-5)then
  if (a.ne.0.0d0)then
    pp-b**(en+1.0d0)/(en+1.0d0)*dlog(b**2)-2.0d0*b**(en+1.0d0)/
1 (en+1.0d0)**2-
1 (a**(en+1.0d0)/(en+1.0d0)*dlog(a**2)-2.0d0*a**(en+1.0d0)/
1 (en+1.0d0)**2)
  else
    pp-b**(en+1.0d0)/(en+1.0d0)*dlog(b**2)-2.0d0*b**(en+1.0d0)/
1 (en+1.0d0)**2
  end if
else
  if (dabs(en).le.1.e.-3)then
    pp=2.0d0*fln(b,a,xq)
  else if (en.gt.0.0d0)then
    eps=(b-a)/dfloat(mm-1)
    pp=xq**en*2.0d0*fln(b,a,xq)
x1=a
z1=f1(x1,xq,en)
do 1 i=1,mm-1
  x2=x1+eps
  z2=f1(x2,xq,en)
  pp=pp+(z2+z1)*eps/2.0d0
  z1=z2
  x1=x2
1 continue
else if (en.lt.0.0d0)then
  pp=xq**en*2.0d0*fln(b,a,xq)
  bns=b**(en+1.0d0)
  ans=a**(en+1.0d0)
  eps=(bns-ans)/dfloat(mm-1)
x1=ans
z1=f2(x1,xq,en)
do 2 i=1,mm-1
  x2=x1+eps
  z2=f2(x2,xq,en)
  pp=pp+(z2+z1)*eps/2.0d0
  z1=z2
  x1=x2
2 continue
end if
end if
return
end

function fln(b,a,xq)
implicit double precision(a-h,o-z)
if (a.eq.xq) then
    fa=0.0d0
else
    fa=(a-xq)*(dlog(dabs(a-xq))-1.0d0)
end if
if (b.eq.xq) then
    fb=0.0d0
else
    fb=(b-xq)*(dlog(dabs(b-xq))-1.0d0)
end if
fln=fb-fa
return
end

function f1(z,xq,en)
    implicit double precision(a-h,o-z)
    if (z.eq.xq) then
        f1=0.0d0
    else
        f1=(z**en-xq**en)*dlog((z-xq)**2)
    end if
    return
end

function f2(z,xq,en)
    implicit double precision(a-h,o-z)
    x=z**(1.0d0/(en+1.0d0))
    if (x.eq.xq) then
        f2=0.0d0
    else
        f2=((1.0d0-xq**en*x**(en-1)*dlog((x-xq)**2))/(en+1.0d0)
    end if
    return
end
program john

Written by Johannes H. Sukamto

The program calculates the relationships between the different coordinates for the slotted-electrode cell.

Its input is obtained from a slightly modified version of PROGRAM RCALC of Orazem.

dimension fintga(100000), fintgc(100000), tta(100000), ttc(100000),
  +  xa(500), xc(500), ga(500), za(500), zc(500), gc(500)
common/int/numint1, numint2, numint3, numint4, numint5,
  +  numint6, numint7, numx, dl, tg
common/const/a, b, c, d, xmax, wimax, rescd
common/limit/limit1, limit2
common/points/fintga, fintgc, tta, ttc, xa, xc
common/calc/ga, za, zc, gc
complex za, zc
call input
call cxmax
call cxcz
call output
stop
end

subroutine input
common/int/numint1, numint2, numint3, numint4, numint5,
  +  numint6, numint7, numx, dl, tg
common/const/a, b, c, d, xmax, wimax, rescd
c a, b, c, d = A, B, C, D in original geometry
wimax = y-max
dl = length of electrode
rescd = ohmic resistance

c numint's = Number of intervals for integration; they do not require any changes unless 'max' and 'min' (look at output) differ significantly. Have the same number for the first 4, and the same number for the last 2.
numx = number of evenly spaced nodes, rectangular geometry
read*, a, b, c, d
read*, wimax
read*, dl
read*, rescd
read*, numint1, numint2, numint3, numint4, numint5, numint6, numint7
read*, numx
return
end

subroutine cxmax
c: calculate xmax
dimension fintga(100000),fintgc(100000),tta(100000),ttc(100000),
    xa(500),xc(500),ga(500),za(500),zc(500),gc(500)
common/int/numint1,numint2,numint3,numint4,numint5,
    numint6,numint7,numx,dl,tg
common/const/a,b,c,d,xmax,wimax,rescd
common/limit/limit1,limit2
common/points/fintga,fintgc,tta,ttc,xa,xc

c a to I
   tta(1)=a
   width=sqrt((b-a)/2.)/float(numint1)
   beta=0.
   xmax=0.
   first=fax(tta(1))
   fintga(1)=0.
   do 10 i=2,numint1
      beta=beta+width
      tta(i)=a+beta**2
      second=fax(tta(i))
      fintga(i)=fintga(i-1)+.5*(first+second)*width
      first=second
   10 continue
   tta(numint1+1)=(a+b)/2.
   second=fax(tta(numint1+1))
   fintga(numint1+1)=fintga(numint1)+.5*(first+second)*width

c I to b
   limit=numint1+numint2
   beta=sqrt((b-a)/2.)
   width=(0.-sqrt((b-a)/2.))/float(numint2)
   first=fbx(tta(numint1+1))
   do 20 i=numint1+2,limit
      beta=beta+width
      tta(i)=b-beta**2
      second=fbx(tta(i))
      fintga(i)=fintga(i-1)+.5*(first+second)*width
      first=second
   20 continue
   tta(limit+1)=b
   second=fbx(tta(limit+1))
   fintga(limit+1)=fintga(limit)+.5*(first+second)*width
   limit1=limit+1

c -c to -I
   ttc(1)=-c
   width=sqrt((d-c)/2.)/float(numint3)
   beta=0.
   first=fcx(ttc(1))
   fintgc(1)=0.
   do 30 i=2,numint3
      beta=beta+width
      ttc(i)=-c-beta**2
      second=fcx(ttc(i))
      fintgc(i)=fintgc(i-1)+.5*(first+second)*width
   30 continue
first=second
30 continue
ttc(numint3+1)=-(c+d)/2.
second=fcx(ttc(numint3+1))
fintgc(numint3+1)=fintgc(numint3)+.5*(first+second)*width
c -I to -d
limit=numint3+numint4
beta=sqrt((d-c)/2.)
width=sqrt((d-c)/2.)/float(numint4)
first=fdx(ttc(numint3+1))
do 40 i=numint3+2,limit
   beta=beta+width
   ttc(i)=beta**2-d
   second=fdx(ttc(i))
   fintgc(i)=fintgc(i-1)+.5*(first+second)*width
   first=second
40 continue
ttc(limit+1)=d
second=fdx(ttc(limit+1))
fintgc(limit+1)=fintgc(limit)+.5*(first+second)*width
limit2=limit+1
xmax=(fintga(limit1)+fintgc(limit2))/2.
return
end

subroutine cxcz
  c calculate relations between derivatives of original and
  c rectangular geometries
    dimension fintga(100000),fintgc(100000),tta(100000),ttc(100000),
    + xa(500),xc(500),ga(500),za(500),zc(500),gc(500)
    common/int/numint1,numint2,numint3,numint4,numint5,
    + numint6,numint7,numx,dl,tg
    common/const/a,b,c,d,xmax,wimax,rescd
    common/limit/limit1,limit2
    common/points/fintga,fintgc,tta,ttc,xa,xc
    common/calc/ga,za,zc,gc
    complex za,zc
    logical flag1,flag2
  c integrate up to a
    temp=0.
5. sumrl=0.
    sumil=0.
    widthz=a/float(numint5)
t=0.
    first=fazrl(t)
do 10 i=2,numint5
       t=t+widthz
       second=fazrl(t)
       sumrl=sumrl+.5*(first+second)*widthz
       first=second
10. continue.
second=0.
sumrl=sumrl+.5*(first+second)*widthz
del=abs(1.-temp/sumrl)
if (del.gt.1.e-4) then
  if (numint5.gt.1000) then
    print*, 'PROBLEM WITH CONVERGENCE z-t, 0 to a'
    stop
  endif
  numint5=2*numint5
temp=sumrl
goto 5
endif
first=0.
sumr2=sumrl
za(1)=complx(sumrl,sumil)

C integrate from a to b
numint=2*(numint1+numint2)/numx
width=xmax/float(numx-1)
xa(1)=0.
x=0.
j=2
temp=sqrt(b-a)
first=0.
ga(1)=gxa(tta(1))
do 20 i=2,numx-1
  x=x+width
  30 if ((x.ge.fintga(j)).and.(j.lt.limitl)) then
    j=j+1
    goto 30
  endif
  if (j.eq.limitl) goto 300
  xa(i)=fintga(j)
ga(i)=gxa(tta(j))
  widthz=(sqrt(b-tta(j))-temp)/float(numint)
  beta=temp
  temp=sqrt(b-tta(j))
do 40 k=2,numint+1
    beta=beta+widthz
    t=b-beta**2
    second=fbzil(t)
    sumil=sumil+.5*(first+second)*widthz
    first=second
  40 continue
  za(i)=complx(sumrl,sumil)
  continue
  300 xa(numx)=xmax
  ga(numx)=gxa(tta(limitl))
  widthz=-temp/float(numint)
  beta=temp
  do 50 k=2,numint+1
    beta=beta+widthz
  50 continue
\begin{verbatim}
t=b-beta**2
second=fbzil(t)
sumil=sumil+.5*(first+second)*widthz
first=second
50 continue
za(numx)=cmplx(sumril,sumil)
sumi2=sumil
c integrate from -b to -c
c integrate from -b to -I
templ=0.
55 temp2=0.
beta=0.
widthz=sqrt((c-b)/2.)/float(numint6)
t=-b
first=fbzr2(t)
do 60 i=2,numint6+1
beta=beta+widthz
t=-b-beta**2
second=fbzr2(t)
temp2=temp2+.5*(first+second)*widthz
first=second
60 continue
c integrate from -I to -c
beta=sqrt((c-b)/2.)
widthz=-beta/float(numint7)
t=-(c+b)/2.
first=fczr2(t)
do 70 i=2,numint7
beta=beta+widthz
t=beta**2-c
second=fczr2(t)
temp2=temp2+.5*(first+second)*widthz
first=second
70 continue
t=-c
second=fczr2(t)
temp2=temp2+.5*(first+second)*widthz
del=abs(1.-temp1/temp2)
if (del.gt.1.e-4) then
  if (numint6.gt.1.e-000) then
    print*, 'PROBLEM WITH CONVERGENCE, z-t, b to c'
    stop
  endif
  numint6=2*numint6
  numint7=2*numint7
  templ=temp2
  goto 55
endif
sumr2=sumr2+temp2
zc(1)=cmplx(sumr2,sumi2)
c integrate from -c to -d
\end{verbatim}
numint=2*(numint3+numint4)/numx
xc(1)=0.
gc(1)=gxc(ttc(1))
x=0.
j=2
temp=0.
beta=temp
flag1=.true.
flag2=.true.
do 80 i=2,numx-1
   x=x+width
      if ((x.ge.fintgc(j)).and.(j.le.limit2)) then
         j=j+1
         go to 90
      endif
      if (j.gt.limit2) then
         print*, 'OUTSIDE OF REGION 2, c TO d'
         stop
      endif
      xc(i)=fintgc(j)
gc(i)=gxc(ttc(j))
      if (abs(ttc(j)).lt.((c+d)/2.)) then
         widthz=(sqrt(-ttc(j)-c)-temp)/float(numint)
         beta=temp
         temp=sqrt(-ttc(j)-c)
         if (flag1) then
            t=c
            first=fcz12(t)
            flag1=.false.
         endif
         do 100 k=2,numint+1
            beta=beta+widthz
            t=c-beta**2
            second=fcz12(t)
            sumi2=sumi2+.5*(first+second)*widthz
            first=second
            continue
         zc(i)=cmplx(sumr2,sumi2)
      else
         if (flag2) then
            t=c-temp**2
            first=fdzi2(t)
            temp=sqrt(d+t)
            flag2=.false.
         endif
         widthz=(sqrt(d+ttc(j))-temp)/float(numint)
         beta=temp
         temp=sqrt(d+ttc(j))
         do 110 k=2,numint+1
            beta=beta+widthz
            t=beta**2-d
second=fdzi2(t)
sumi2=sumi2+.5*(first+second)*widthz
first=second
continue
zc(i)=cmplx(sumr2,sumi2)
endif
continue
zc(numx)=cmplx(sumr2,sumi2)
return
end

subroutine output
dimension fintga(100000),fintgc(100000),tta(100000),ttc(100000),
+ xa(500),xc(500),ga(500),za(500),zc(500),gc(500)
common/int/numint1,numint2,numint3,numint4,numint5,
+ numint6,numint7,numx,d1,tg
common/const/a,b,c,d,xmax,wimax,rescd
common/points/fintga,fintgc,tta,ttc,xa,xc
common/calc/ga,za,zc,gc
complex za,zc
print100,xmax,wimax
100 format (2e17.8)
print150,b,c,d
150 format (3e17.8)
print160,d1
160 format (el17.8)
print*,numx
print160,rescd
do 10 i=1,numx
    print200,xa(i),ga(i),xc(i),gc(i)
10 continue
200 format (4e17.8)
do 20 i=1,numx
    print300,za(i),zc(i)
20 continue
300 format (4e17.8)
error1=0.
error2=1000.
do 30 i=2,numx
    error1=amax1(error1,abs(xa(i)-xa(i-1)),abs(xc(i)-xc(i-1)))
    error2=amin1(error2,abs(xa(i)-xa(i-1)),abs(xc(i)-xc(i-1)))
30 continue
continue
print*, 'max. = ', error1
print*, 'min. = ', error2
return
end

function fax(t)
common/const/a,b,c,d,xmax,wimax,rescd
fax=2./sqrt(b-t)/sqrt(c+t)/sqrt(d+t)
return
end

function fbx(t)
common/const/a,b,c,d,xmax,wimax,rescd
fbx=2./sqrt(t-a)/sqrt(c+t)/sqrt(d+t)
return
end

function fcx(t)
common/const/a,b,c,d,xmax,wimax,rescd
fcx=2./sqrt(a-t)/sqrt(b-t)/sqrt(d+t)
return
end

function fdx(t)
common/const/a,b,c,d,xmax,wimax,rescd
fdx=2./sqrt(a-t)/sqrt(b-t)/sqrt(-c-t)
return
end

function fazrl(t)
common/const/a,b,c,d,xmax,wimax,rescd
if (t.eq.a) goto 10
fazrl=2.*sqrt(a**2-t**2)/sqrt(b+t)/sqrt(c**2-t**2)/sqrt(d**2-t**2)
return
10 fazrl=0.
return
end

function fbzil(t)
common/const/a,b,c,d,xmax,wimax,rescd
if (t.eq.a) goto 10
fbzil=2.*sqrt(t**2-a**2)/sqrt(b+t)/sqrt(c**2-t**2)/sqrt(d**2-t**2)
return
10 fbzil=0.
return
end

function fbzi2(t)
common/const/a,b,c,d,xmax,wimax,rescd
if (t.eq.a) goto 10
fbzi2=-2.*sqrt(a-t)*sqrt(-a-t)/sqrt(b-t)/sqrt(c**2-t**2)/
   + sqrt(d**2-t**2)
return
10
fbzi2=0.
return
end

function fbzr2(t)
common/const/a,b,c,d,xmax,wimax,rescd
fbzr2=-2.*sqrt(a-t)*sqrt(-a-t)/sqrt(b-t)/sqrt(c**2-t**2)/
   + sqrt(d**2-t**2)
return
end

function fczr2(t)
common/const/a,b,c,d,xmax,wimax,rescd
fczr2=-2.*sqrt(a-t)*sqrt(-a-t)/sqrt(b-t)/sqrt(-b-t)/
   + sqrt(c-t)/sqrt(d**2-t**2)
return
end

function fczi2(t)
common/const/a,b,c,d,xmax,wimax,rescd
fczi2=fczr2(t)
return
end

function fdzi2(t)
common/const/a,b,c,d,xmax,wimax,rescd
fdzi2=-2.*sqrt(a-t)*sqrt(-a-t)/sqrt(b-t)/sqrt(-b-t)/
   + sqrt(c-t)/sqrt(-c-t)/sqrt(d-t)
return
end

function gxa(t)
common/const/a,b,c,d,xmax,wimax,rescd
gxa=(t-a)*sqrt(t+a)/sqrt(b+t)/sqrt(c-t)/sqrt(d-t)
return
end

function gxc(t)
common/const/a,b,c,d,xmax,wimax,rescd
gxc=(a-t)*sqrt(-t-a)/sqrt(-t-b)/sqrt(c-t)/sqrt(d-t)
return
end
program alan
implicit double precision(a-h,o-z)
character*72 11
dimension x(51),y(51),phi(4,51),rl(4,2,51,51),phio(51),
1 r2(4,2,51,51),r3(4,2,51,51),r4(4,2,51,51),cd(51),g(100),phio3(51)
1 ,za(51),zc(51),x3(51),g3(100)
common x,y,phi,rl,r2,r3,r4,my,mx,cd,xmax,ymax,g,xmaxi,za,zc,bj,
1 dj

x,y are the coordinates of the rectangle.
phi stores the values of the unknowns on the four sides.
phi(3,i) is the current density on side 3. phi(1,i), phi(2,i) and
phi(3,i) are the values of the potentials on the four sides.
rl, r2, r3, and r4 store the values of the integrand for each side.
cd(i) is used to store the current density on side 1.

pi=3.14159265358979d0
read*,iflag
read*,imax,damp,dj,djinc,djmax
tdamp=damp
read*,mx,my
read*,xmaxi,y maxi
read*,bt,ct,dt
read*,dl,tg,dum
read*,numpts
read*,resis
write(1,*),resis
write(2,*),resis
bj=dj*resis/dl
ymax=y maxi/x maxi
xmax=1.0d0
read*,x(1),g(1),x3(1),g3(1)
limit=(numpts-1)/(mx-1)-1
do 78 i=2,mx
  do 77 j=1,limit
    read*,dum,dum,dum,dum
  77 read*,x(i),g(i),x3(i),g3(i)
read*,dum,za(1),dum,zc(1)
do 80 i=2,mx
do 79 j=1,limit
  79 read*,dum,dum,dum,dum
read*,dum,za(i),dum,zc(i)
do 1 i=1,mx
  1 x(i)=x(i)/xmaxi
do 2 i=1,my
  2 y(i)=ymax*d float(i-1)/d float(my-1)
call fillmat

initial guess
if (iflag.eq.1) then
call read guess
else
    do 3 i=1,mx
        phi(1,i)=ymax*xmaxi*g(i)
    3
    do 4 i=1,my
        phi(2,i)=phi(1,1)*(ymax-y(i))/ymax
    4
end if

100 call current

c solve for phi2
    do 6 i=2,my-1
        phi(2,i)=0.0d0
    do 7 j=1,mx-1
        a2=fa(phi(1,j),phi(1,j+1),x(j),x(j+1))
        b2=fb(phi(1,j),phi(1,j+1),x(j),x(j+1))
        a1=fa(cd(j),cd(j+1),x(j),x(j+1))
        b1=fb(cd(j),cd(j+1),x(j),x(j+1))
        a3=fa(phi(3,j),phi(3,j+1),x(j),x(j+1))
        b3=fb(phi(3,j),phi(3,j+1),x(j),x(j+1))
    7
    phi(2,i)=phi(2,i)+a2*r2(2,1,i,j)+b2*r2(2,2,i,j)+a3*r2(3,1,i,j)+b3*r2(3,2,i,j)
    do 8 j=1,my-1
        a=fa(phi(4,j),phi(4,j+1),y(j),y(j+1))
        b=fb(phi(4,j),phi(4,j+1),y(j),y(j+1))
    8
    phi(2,i)=phi(2,i)+a*r2(4,1,i,j)+b*r2(4,2,i,j)

6 phi(2,i)=phi(2,i)/pi
phi(2,1)=phi(1,1)
phi(2,my)=0.0d0

c solve for phi4
    do 9 i=2,my-1
        phi(4,i)=0.0d0
    do 10 j=1,mx-1
        a2=fa(phi(1,j),phi(1,j+1),x(j),x(j+1))
        b2=fb(phi(1,j),phi(1,j+1),x(j),x(j+1))
        a1=fa(cd(j),cd(j+1),x(j),x(j+1))
        b1=fb(cd(j),cd(j+1),x(j),x(j+1))
        a3=fa(phi(3,j),phi(3,j+1),x(j),x(j+1))
        b3=fb(phi(3,j),phi(3,j+1),x(j),x(j+1))
    10
    phi(4,i)=phi(4,i)+a1*r4(1,1,i,j)+b1*r4(1,2,i,j)+
        a2*r4(2,1,i,j)+b2*r4(2,2,i,j)+a3*r4(3,1,i,j)+b3*r4(3,2,i,j)
    do 11 j=1,my-1
        a=fa(phi(2,j),phi(2,j+1),y(j),y(j+1))
        b=fb(phi(2,j),phi(2,j+1),y(j),y(j+1))
    11
    phi(4,i)=phi(4,i)+a*r4(4,1,i,j)+b*r4(4,2,i,j)

9 phi(4,i)=phi(4,i)/pi
phi(4,1)=phi(1,mx)
phi(4,my)=0.0d0
c solve for 13
   do 12 i-l,mx
      phi03(i)=phi(3,i)
      phi(3,i)=0.0d0
   do 13 j-l,mx-1
      a1=fa(phi(1,j),phi(1,j+1),x(j),x(j+1))
      b1(fb(phi(1,j),phi(1,j+1),x(j),x(j+1))
      a2=fa(cd(j),cd(j+1),x(j),x(j+1))
      b2=fb(cd(j),cd(j+1),x(j),x(j+1))
   13 phi(3,i)=phi(3,i)+a1*r3(1,1,i,j)+b1*r3(1,2,i,j)+
      1 a2*r3(2,1,i,j)+b2*r3(2,2,i,j)
   do 14 j-l,my-l
      a1=fa(phi(2,j),phi(2,j+1),y(j),y(j+1))
      b1=fb(phi(2,j),phi(2,j+1),y(j),y(j+1))
      a2=fa(phi(4,j),phi(4,j+1),y(j),y(j+1))
      b2=fb(phi(4,j),phi(4,j+1),y(j),y(j+1))
   14 phi(3,i)=phi(3,i)+a1*r3(3,1,i,j)+b1*r3(3,2,i,j)+
      1 a2*r3(4,1,i,j)+b2*r3(4,2,i,j)
   ph1(3,1)=phi(3,1)/pi
12 phi(3,1)=phi03(i)-damp*(phi03(i)-phi(3,i))
   c solve for phi
   do 15 i-l,mx
      phi0(i)=0.0d0
   do 16 j-l,mx-1
      a2=fa(phi(3,j),phi(3,j+1),x(j),x(j+1))
      b2=fb(phi(3,j),phi(3,j+1),x(j),x(j+1))
      a1=fa(cd(j),cd(j+1),x(j),x(j+1))
      b1=fb(cd(j),cd(j+1),x(j),x(j+1))
   16 phi0(i)=phi0(i)+a1*r1(1,1,i,j)+b1*r1(1,2,i,j)+
      1 a2*r1(3,1,i,j)+b2*r1(3,2,i,j)
   do 17 j-l,my-l
      a1=fa(phi(2,j),phi(2,j+1),y(j),y(j+1))
      b1=fb(phi(2,j),phi(2,j+1),y(j),y(j+1))
      a2=fa(phi(4,j),phi(4,j+1),y(j),y(j+1))
      b2=fb(phi(4,j),phi(4,j+1),y(j),y(j+1))
   17 phi0(i)=phi0(i)+a1*r1(2,1,i,j)+b1*r1(2,2,i,j)+
      1 a2*r1(4,1,i,j)+b2*r1(4,2,i,j)
15 phi0(i)=phi0(i)/pi
   c check for errors
   error=0.0d0
   do 30 i-2,mx
30   error=dmaxl(error,dabs(1.0d0-phi0(i)/phi(1,i)))
   if (error.gt.1.d-4) then
      do 35 i-1,mx
35   phi(1,i)=phi(1,i)+damp*(phi0(i)-phi(1,i))
      iter=iter+1
      if (iter.ge.imax) then
         print*, 'the number of iterations exceeds ', imax
         print*, 'error. = ', error
goto 999
end if

goto 100
end if

c  Print results
print*, "'
print*, "'
print*, 'J = ',dj
print*, 'resis. = ',resis

999 print*,'Number of iterations:',iter

c average current

cd(1)=bj*(1.0d0-phi(1,1))
sum=0.0d0
do 250 i=2,mx
  cd(i)=bj*(1.0d0-phi(1,i))
  sum=sum+.5d0*(cd(i)+cd(i-1))*(za(i)-za(i-1))
do 300 i=1,mx
  za(i)=(za(i)-za(1))/(za(mx)-za(1))
300 cd(i)=cd(i)/sum

eta=sum/bj
phimax=dabs(phi(1,1)-phi(1,mx))
write(1,*) dj,eta,phimax
if ( (dj.eq.5.) .or. (dj.eq.10.) .or. (dj.eq.20.) .or. (dj.eq.50.)
  + .or. (dj.eq.100.) ) then
  write(2,*),dj
  do 500 i=1,mx
    write(2,*),za(i),char(9),cd(i)
  endif
  write(3,*),'J = ',dj
  do 8000 nni=1,mx
 8000 write(3,*),phi(1,nni),phi(2,nni),phi(3,nni),phi(4,nni)
c increment dj
if (dj.lt.djmax) then
  dj=dj+djinc
  bj=dj*resis/dl
  iter=0
  damp=tdamp
  goto 100
endif
eende

c subroutine fillmat
implicit double precision(a-h,o-z)
dimension x(51),y(51),phi(4,51),rl(4,2,51,51),phio(51),
r2(4,2,51,51),r3(4,2,51,51),r4(4,2,51,51),cd(51),g(100),
za(51),zc(51),x3(51),g3(100)
common x,y,phi,rl,r2,r3,r4,my,mx,cd,xmax,ymax,g,xmaxi,za,zc,bj,
dj
do 1 i=1,mx
  do 1 j=1,mx
    rl(1,1,i,j)=f1(x(j+1),x(i))-f1(x(j),x(i))
    rl(1,2,i,j)=f2(x(j+1),x(i))-f2(x(j),x(i))
    rl(3,1,i,j)=0.5d0*(f3(x(j+1),ymax)-f3(x(j),ymin))
    rl(3,2,i,j)=x(i)*rl(3,1,i,j)-
      (f4(x(j+1)-x(i),ymin)-f4(x(j)-x(i),ymin))*0.5d0
    r3(1,1,i,j)=(f5(x(j+1)-x(i),ymin)-f5(x(j)-x(i),ymin)+2.0d0*
      ymax)**2*(f7(x(j+1)-x(i),ymin)-f7(x(j)-x(i),ymin))
    r3(1,2,i,j)=x(i)*r3(1,1,i,j)+
      2.0d0*ymax**2*(f8(x(j+1)-x(i),ymin)-
      f8(x(j)-ymin,x(i),ymin))
  end if
  if (i.eq.1) then
    rl(2,1,i,j)=0.0d0
    rl(2,2,i,j)=0.0d0
    r3(3,1,i,j)=0.0d0
    r3(3,2,i,j)=0.0d0
  else
    rl(2,1,i,j)=x(i)*(f5(y(j+1),x(i))-f5(y(j),x(i)))-
      f5(y(j),ymin,x(i))
    rl(2,2,i,j)=(f6(x(j+1),x(i))-f6(x(j),x(i)))*
      r3(3,1,i,j)+2.0d0*x(i)*(f9(y(j+1)-ymin,x(i))-f9(y(j)-ymin,x(i)))-
      f8(y(j)-ymin,x(i))
    r3(3,2,i,j)=ymax*r3(3,1,i,j)+2.0d0*x(i)*
      (f9(y(j+1)-ymin,x(i))-f9(y(j)-ymin,x(i)))-
      f8(y(j),ymin,x(i))
  end if
  if (i.eq.mx) then
    rl(4,1,i,j)=0.0d0
    rl(4,2,i,j)=0.0d0
    r3(4,1,i,j)=0.0d0
    r3(4,2,i,j)=0.0d0
  else
    rl(4,1,i,j)=(xmax-x(i))*f5(y(j+1),x(i))-f5(y(j),x(i))-
      f5(y(j),xmax-x(i))
    rl(4,2,i,j)=(xmax-x(i))*f6(y(j+1),x(i))-f6(y(j),xmax-x(i))-
      f6(y(j),xmax-x(i))
    r3(4,1,i,j)=2.0d0*(xmax-x(i))*f8(y(j+1)-ymin,x(i))-
      (xmax-x(i))*f8(y(j)-ymin,x(i))
    r3(4,2,i,j)=ymax*r3(4,1,i,j)+2.0d0*(xmax-x(i))*
      (f9(y(j+1)-ymin,x(i))-f9(y(j)-ymin,x(i)))-
      f8(y(j),ymin,x(i))
  end if
  continue
  do 2 i=1,mx
    do 2 j=1,mx
      if (i.eq.1) then
        rl(2,1,i,j)=0.0d0
        rl(2,2,i,j)=0.0d0
        r3(3,1,i,j)=0.0d0
        r3(3,2,i,j)=0.0d0
      else
        rl(2,1,i,j)=x(i)*(f5(y(j+1),x(i))-f5(y(j),x(i)))-
          f5(y(j),ymin,x(i))
        rl(2,2,i,j)=(f6(x(j+1),x(i))-f6(x(j),x(i)))*
          r3(3,1,i,j)+2.0d0*x(i)*(f9(y(j+1)-ymin,x(i))-f9(y(j)-ymin,x(i)))-
          f8(y(j),ymin,x(i))
        r3(3,2,i,j)=ymax*r3(3,1,i,j)+2.0d0*x(i)*
          (f9(y(j+1)-ymin,x(i))-f9(y(j)-ymin,x(i)))-
          f8(y(j),ymin,x(i))
      end if
      if (i.eq.mx) then
        rl(4,1,i,j)=0.0d0
        rl(4,2,i,j)=0.0d0
        r3(4,1,i,j)=0.0d0
        r3(4,2,i,j)=0.0d0
      else
        rl(4,1,i,j)=(xmax-x(i))*f5(y(j+1),x(i))-f5(y(j),x(i))-
          f5(y(j),xmax-x(i))
        rl(4,2,i,j)=(xmax-x(i))*f6(y(j+1),x(i))-f6(y(j),xmax-x(i))-
          f6(y(j),xmax-x(i))
        r3(4,1,i,j)=2.0d0*(xmax-x(i))*f8(y(j+1)-ymin,x(i))-
          (xmax-x(i))*f8(y(j)-ymin,x(i))
        r3(4,2,i,j)=ymax*r3(4,1,i,j)+2.0d0*(xmax-x(i))*
          (f9(y(j+1)-ymin,x(i))-f9(y(j)-ymin,x(i)))-
          f8(y(j),ymin,x(i))
      end if
      continue
      do 3 i=1,mx
        do 3 j=1,mx
          r2(1,1,i,j)=0.5d0*(f3(x(j+1),y(i))-f3(x(j),y(i)))-
            f3(x(j),ymin)-f3(x(j),xmax-x(i))
          r2(1,2,i,j)=0.5d0*(f4(x(j+1),y(i))-f4(x(j),y(i)))-
            f4(x(j),ymin)-f4(x(j),xmax-x(i))
        end do 3 j
      end do 3 i
    continue
  end do 2 i
end do 1 j
\[
\begin{align*}
r_2(2,1,1,j) &= y(i)*(f_5(x(j+1),y(i)) - f_5(x(j),y(i))) \\
r_2(2,1,2,j) &= y(i)*(f_6(x(j+1),y(i)) - f_6(x(j),y(i))) \\
r_2(3,1,1,j) &= -0.5d_0*(f_3(x(j+1),ymax-y(i))) \\
r_2(3,2,1,j) &= -0.5d_0*(f_4(x(j+1),y(i)) - y(i)*(f_5(x(j+1),y(i)) - f_5(x(j),y(i)))) \\
r_2(3,2,2,j) &= -0.5d_0*(f_6(x(j+1),y(i)) - f_6(x(j),y(i))) \\
r_2(4,1,1,j) &= -0.5d_0*(f_3(x(j+1) - xmax, y(i)) - f_3(x(j) - xmax, y(i))) \\
r_2(4,1,2,j) &= -0.5d_0*(f_4(x(j+1) - xmax, y(i)) - f_4(x(j) - xmax, y(i))) \\
r_2(4,2,1,j) &= -0.5d_0*(f_5(y(j+1) - y(i)) - f_5(y(j) - y(i))) \\
r_2(4,2,2,j) &= -0.5d_0*(f_6(y(j+1) - y(i)) - f_6(y(j) - y(i))) \\
r_4(1,1,1,j) &= r_2(1,1,1,j) \\
r_4(1,1,2,j) &= r_2(1,1,2,j) \\
r_4(2,1,1,j) &= r_2(2,1,1,j) \\
r_4(2,1,2,j) &= r_2(2,1,2,j) \\
r_4(3,1,1,j) &= r_2(3,1,1,j) \\
r_4(3,1,2,j) &= r_2(3,1,2,j) \\
r_4(3,2,1,j) &= r_2(3,2,1,j) \\
r_4(3,2,2,j) &= r_2(3,2,2,j) \\
r_4(4,1,1,j) &= r_2(4,1,1,j) \\
r_4(4,1,2,j) &= r_2(4,1,2,j) \\
r_4(4,2,1,j) &= r_2(4,2,1,j) \\
r_4(4,2,2,j) &= r_2(4,2,2,j)
\end{align*}
\]

c The two following do loops account for the fact the interior angles at the corners are twice as small.

do 5 j=1, mx-1
\[
\begin{align*}
r_3(1,1,1,j) &= 2.0d_0*r_3(1,1,1,j) \\
r_3(1,2,1,j) &= 2.0d_0*r_3(1,2,1,j) \\
r_3(2,1,1,j) &= 2.0d_0*r_3(2,1,1,j) \\
r_3(2,2,1,j) &= 2.0d_0*r_3(2,2,1,j) \\
r_3(1,1,mx,j) &= 2.0d_0*r_3(1,1,mx,j) \\
r_3(1,2,mx,j) &= 2.0d_0*r_3(1,2,mx,j) \\
r_3(2,1,mx,j) &= 2.0d_0*r_3(2,1,mx,j) \\
r_3(2,2,mx,j) &= 2.0d_0*r_3(2,2,mx,j) \\
r_1(1,1,1,j) &= 2.0d_0*r_1(1,1,1,j) \\
r_1(1,2,1,j) &= 2.0d_0*r_1(1,2,1,j) \\
r_1(2,1,1,j) &= 2.0d_0*r_1(2,1,1,j) \\
r_1(3,1,1,j) &= 2.0d_0*r_1(3,1,1,j) \\
r_1(3,2,1,j) &= 2.0d_0*r_1(3,2,1,j) \\
r_1(1,1,mx,j) &= 2.0d_0*r_1(1,1,mx,j) \\
r_1(1,2,mx,j) &= 2.0d_0*r_1(1,2,mx,j) \\
r_1(3,1,mx,j) &= 2.0d_0*r_1(3,1,mx,j) \\
r_1(3,2,mx,j) &= 2.0d_0*r_1(3,2,mx,j)
\end{align*}
\]

do 6 j=1, my-1
\[
\begin{align*}
r_3(3,1,mx,j) &= 2.0d_0*r_3(3,1,mx,j) \\
r_3(3,2,mx,j) &= 2.0d_0*r_3(3,2,mx,j) \\
r_3(4,1,1,j) &= 2.0d_0*r_3(4,1,1,j)
\end{align*}
\]
SUBROUTINE CURRENT IS WHERE THE KINETICS AND THE INFORMATION FROM THE SCHWARZ-CHRISTOFFEL TRANSFORMATION ARE INPUT

```fortran
subroutine current
  implicit double precision(a-h,o-z)
  dimension x(Sl),y(Sl),phi(4,Sl),r1(4,2,Sl,Sl),r2(4,2,Sl,Sl),r3(4,2,Sl,Sl),r4(4,2,Sl,Sl),cd(Sl),g(lOO),
1za(Sl),zc(Sl),x3(Sl),g3(100)
  common x,y,phi,r1,r2,r3,r4,my,mx,cd,xmax,ymax,g,xmaxi,za,zc,bj,
1 dj
  do 1 i=1,mx
1   cd(i)=bj*(l.OdO-phi(l,i))*g(i)*xmaxi
  return
end
```

THE FOLLOWING FUNCTIONS ARE INTEGRALS TO BE USED IN 2-D PROBLEMS. THEY ARE CALLED IN SUBROUTINE FILLMAT.

```fortran
function f1(b,a)
  implicit double precision(a-h,o-z)
  if (a.eq.b) then
    f1=0.0d0
  else
    f1=(b-a)*(dlog(dabs(b-a))-l.OdO)
  end if
  return
end
```

```fortran
function f2(b,a)
  implicit double precision(a-h,o-z)
  if (a.eq.b) then
    f2=0.0d0
  else
    te=(a-b)**2/2.0d0*(dlog(dabs(b-a)))-0.5d0
    f2=a*(b-a)*(dlog(dabs(b-a))-1.0d0)+te
  end if
  return
end
```

```fortran
function f3(b,a)
  implicit double precision(a-h,o-z)
  f3=b*dlog(b**2+a**2)-2.0d0*b+2.0d0*a*datan(b/a)
```

```
6
  r3(4,2,1,j)=2.0d0*r3(4,2,1,j)
  r1(2,1,mx,j)=2.0d0*r1(2,1,mx,j)
  r1(2,2,mx,j)=2.0d0*r1(2,2,mx,j)
  r1(4,1,1,j)=2.0d0*r1(4,1,1,j)
  r1(4,2,1,j)=2.0d0*r1(4,2,1,j)
  return
end
```
function f4(b,a)
  implicit double precision(a-h.o-z)
  f4 = 0.5d0*(b**2+a**2)*dlog(b**2+a**2) - 0.5d0*b**2
  return
end

function f5(b,a)
  implicit double precision(a-h.o-z)
  f5 = datan(b/a)/a
  return
end

function f6(b,a)
  implicit double precision(a-h.o-z)
  f6 = 0.5d0*dlog(a**2+b**2)
  return
end

function f7(b,a)
  implicit double precision (a-h.o-z)
  f7 = (b/(a**2+b**2) - datan(b/a)/a)/2.0d0/a**2
  return
end

function f8(b,a)
  implicit double precision(a-h.o-z)
  f8 = -0.5d0/(b**2+a**2)
  return
end

function f9(b,a)
  implicit double precision(a-h.o-z)
  f9 = b/(b**2+a**2)/2.0d0+datan(b/a)/a/2.0d0
  return
end

function fa(pl,p2,zl,z2)
  implicit double precision(a-h.o-z)
  fa = pl-(p2-pl)*zl/(z2-zl)
  return
end

function fb(pl,p2,zl,z2)
  implicit double precision(a-h.o-z)
  fb = (p2-pl)/(z2-zl)
  return
end
subroutine readguess
implicit double precision(a-h,o-z)
dimension x(51),y(51),phi(4,51),r1(4,2,51,51),phio(51),
1 r2(4,2,51,51),r3(4,2,51,51),r4(4,2,51,51),cd(51),g(100),
1 za(51),zc(51),x3(51),g3(100)
common x,y,phi,r1,r2,r3,r4,my,mx,cd,xmax,ymax,g,xmaxi,za,zc,bj,
1 dj
    do 1 i=1,mx
    read*,phi(1,i),phi(2,i),phi(3,i)
1  read*,phi(4,i)
    return
end
program scchan
implicit double precision(a-h,o-z)
character*72 ll

dimension x(51),y(51),phi(4,51),r1(5,2,51,51),phio(51),
lr2(5,2,51,51),r3(5,2,51,51),r4(5,2,51,51),cdl(51),g(100),phio3(51)
l,vj(200),vr(200),wins(200),wele(200),xins(200),xele(200),cd3(51)
common x,y,phi,r1,r2,r3,r4,my,mx,cdl,xmax,ymax,g,xmaxi
1,vj,vr,wins,wele,xins,xele,cd3,hl

read*,djint
dj=djint
pi=3.14159265358979d0
damp=0.5d0
read*,ikinet
if (ikinet.eq.1) then
print*, 'linear kinetics'
l1='J' i(L)/iavg Bl'
print*,ll
else if (ikinet.eq.2) then
print*, 'Tafel kinetics'
l1='delta' i(L)/iavg ln(Ec) ln(g)'
print*,ll
else
print*, 'constant current'
l1='delta' i(L)/iavg ln(Ec) ln(g)'
print*,ll
l1='J'
print*,ll
end if

call tread
call fillmat
iter=1

C initial guess
iflag=0
if (iflag.eq.1) then
  call readguess
else
  do 3 i=1,mx
    phi(1,i)=ymax*gi)
  3 phi(3,i)=0.1d0
end if
call current(3,ikinet,dj)
do 4 i=1,my
  phi(2,i)=(phi(1,1)-phi(3,1))*(ymax-y(i))/ymax+phi(3,1)
  phi(4,1)=(phi(1,mx)-phi(3,mx))*(ymax-y(i))/ymax+phi(3,mx)
4

C solve for phi2
do 6 i=2,my-1
\phi(2, i) = 0.0d0

do 7 j = 1, mx - 1
    a2 = f_a(\phi(1, j), \phi(1, j+1), x(j), x(j+1))
    b2 = f_b(\phi(1, j), \phi(1, j+1), x(j), x(j+1))
    a1 = f_a(cdl(j), cdl(j+1), x(j), x(j+1))
    b1 = f_b(cdl(j), cdl(j+1), x(j), x(j+1))
    a3 = f_a(cd3(j), cd3(j+1), x(j), x(j+1))
    b3 = f_b(cd3(j), cd3(j+1), x(j), x(j+1))
    a4 = f_a(\phi(3, j), \phi(3, j+1), x(j), x(j+1))
    b4 = f_b(\phi(3, j), \phi(3, j+1), x(j), x(j+1))

7 \phi(2, i) = \phi(2, i) + a1 * r2(1, 1, i, j) + a2 * r2(1, 2, i, j) +
a2 * r2(2, 1, i, j) + b2 * r2(2, 2, i, j) + a3 * r2(3, 1, i, j) + b3 * r2(3, 2, i, j) +
a4 * r2(5, 1, i, j) + b4 * r2(5, 2, i, j)

do 8 j = 1, my - 1
    a = f_a(\phi(4, j), \phi(4, j+1), y(j), y(j+1))
    b = f_b(\phi(4, j), \phi(4, j+1), y(j), y(j+1))

8 \phi(2, i) = \phi(2, i) + a * r2(4, 1, i, j) + b * r2(4, 2, i, j)

6 \phi(2, i) = \phi(2, i) / pi
\phi(2, 1) = \phi(1, 1)
\phi(2, my) = \phi(3, 1)

---

\textbf{solve for } \phi_4

do 9 i = 2, my - 1
\phi(4, i) = 0.0d0

do 10 j = 1, mx - 1
    a2 = f_a(\phi(1, j), \phi(1, j+1), x(j), x(j+1))
    b2 = f_b(\phi(1, j), \phi(1, j+1), x(j), x(j+1))
    a1 = f_a(cdl(j), cdl(j+1), x(j), x(j+1))
    b1 = f_b(cdl(j), cdl(j+1), x(j), x(j+1))
    a3 = f_a(cd3(j), cd3(j+1), x(j), x(j+1))
    b3 = f_b(cd3(j), cd3(j+1), x(j), x(j+1))
    a4 = f_a(\phi(3, j), \phi(3, j+1), x(j), x(j+1))
    b4 = f_b(\phi(3, j), \phi(3, j+1), x(j), x(j+1))

10 \phi(4, i) = \phi(4, i) + a1 * r4(1, 1, i, j) + a2 * r4(1, 2, i, j) +
a2 * r4(2, 1, i, j) + b2 * r4(2, 2, i, j) + a3 * r4(3, 1, i, j) + b3 * r4(3, 2, i, j) +
a4 * r4(5, 1, i, j) + b4 * r4(5, 2, i, j)

do 11 j = 1, my - 1
    a = f_a(\phi(2, j), \phi(2, j+1), y(j), y(j+1))
    b = f_b(\phi(2, j), \phi(2, j+1), y(j), y(j+1))

11 \phi(4, i) = \phi(4, i) + a * r4(4, 1, i, j) + b * r4(4, 2, i, j)

9 \phi(4, i) = \phi(4, i) / pi
\phi(4, 1) = \phi(1, mx)
\phi(4, my) = \phi(3, mx)

---

\textbf{solve for } \phi_3

do 12 i = 1, mx
\phi(3, i) = \phi(3, i)
\phi(3, i) = 0.0d0

do 13 j = 1, mx - 1
    a1 = f_a(\phi(1, j), \phi(1, j+1), x(j), x(j+1))
    b1 = f_b(\phi(1, j), \phi(1, j+1), x(j), x(j+1))
a2=fa(cdl(j), cd1(j+1), x(j), x(j+1))
b2=fb(cdl(j), cd1(j+1), x(j), x(j+1))
a3=fa(cd3(j), cd3(j+1), x(j), x(j+1))
b3=fb(cd3(j), cd3(j+1), x(j), x(j+1))

13 phi(3,i)=phi(3,i)+a3*r3(1,1,i,j)+b3*r3(1,2,1,i,j)+
a2*r3(3,1,i,j)+b2*r3(3,2,1,i,j)+a1*r3(5,1,i,j)+b1*r3(5,2,1,i,j)
do 14 j=1, my-1
   a1=fa(phi(2,j), phi(2,j+1), y(j), y(j+1))
b1=fb(phi(2,j), phi(2,j+1), y(j), y(j+1))
a2=fa(phi(4,j), phi(4,j+1), y(j), y(j+1))
b2=fb(phi(4,j), phi(4,j+1), y(j), y(j+1))
14 phi(3,i)=phi(3,i)+a1*r3(2,1,i,j)+b1*r3(2,2,1,i,j)+
a2*r3(4,1,i,j)+b2*r3(4,2,1,i,j)
phi(3,i)=phi(3,i)/pi
12 phi(3,i)=phio3(i)-damp*(phio3(i)-phi(3,i))
call current(3, ikinet, dj)
c
1 solve for phi1
   do 15 i=1, mx
      phio(i)=0.0d0
   do 16 j=1, mx-1
      a2=fa(cd3(j), cd3(j+1), x(j), x(j+1))
b2=fb(cd3(j), cd3(j+1), x(j), x(j+1))
a3=fa(phi(3,j), phi(3,j+1), x(j), x(j+1))
b3=fb(phi(3,j), phi(3,j+1), x(j), x(j+1))
al=fa(cdl(j), cdl(j+1), x(j), x(j+1))
b1=fb(cdl(j), cdl(j+1), x(j), x(j+1))
16 phio(i)=phio(i)+a1*rl(1,1,i,j)+b1*rl(1,2,1,i,j)+
a2*rl(3,1,i,j)+b2*rl(3,2,1,i,j)+a3*rl(5,1,i,j)+b3*rl(5,2,1,i,j)
do 17 j=1, my-1
   a1=fa(phi(2,j), phi(2,j+1), y(j), y(j+1))
b1=fb(phi(2,j), phi(2,j+1), y(j), y(j+1))
a2=fa(phi(4,j), phi(4,j+1), y(j), y(j+1))
b2=fb(phi(4,j), phi(4,j+1), y(j), y(j+1))
17 phio(i)=phio(i)+a1*rl(2,1,i,j)+b1*rl(2,2,1,i,j)+
a2*rl(4,1,i,j)+b2*rl(4,2,1,i,j)
phio(i)=phio(i)/pi
c
15 check for errors
   error=0.0d0
   do 30 i=2, mx
      error=dmax1(error, dabs(1.0d0-phio(i)/phi(1,i)))
      if (error.gt.1.d-4) then
         do 35 i=1, mx
            phi(1,i)=phi(1,i)+damp*(phio(i)-phi(1,i))
            iter=iter+1
            if (iter.ge.500) then
               print*, 'greater than 300 iterations', 'error=', error
go to 999
         end if
      end if
   end do
goto 100
end if

999 call tprint(iter,ikinet,dj)
dj=dj+djint
if (dj.lt.10.0d0*djint) then
  if (dj.ge.9.0d0)damp=0.1d0
  iter=1
  goto 100
end if
end

subroutine fillmat
implicit double precision(a-h,o-z)
dimension x(51),y(51),phi(4,51),rl(5,2,51,51),phi(51),
r2(5,2,51,51),r3(5,2,51,51),r4(5,2,51,51),cd1(51),g(100),cd3(51)
common x,y,phi,rl,r2,rs,my,mx,cd1,xmax,ymax,cd3,xmax
1,vj(200),vr(200),wens(200),wele(200),xens(200),xele(200),cd3,hl
x=1,i=1,mx-1
y=1,j=1,mx-1

  r1(1,1,i,j)=f1(x(j+1),x(i))-f1(x(j),x(i))
  r1(1,2,i,j)=f2(x(j+1),x(i))-f2(x(j),x(i))
  r1(3,1,i,j)=-0.5*d0*(f3(x(j+1)-x(i),ymax)-f3(x(j)-x(i),ymax))
  r1(3,2,i,j)=x(i)*r1(3,1,i,j)-
  (f4(x(j+1)-x(i),ymax)-f4(x(j)-x(i),ymax))*0.5d0
  r1(5,1,i,j)=ymax*(f5(x(j+1)-x(i),ymax)-f5(x(j)-x(i),ymax))
  r1(5,2,i,j)=x(i)*r1(5,1,i,j)+ymax*(f6(x(j+1)-x(i),ymax)-
  f6(x(j)-x(i),ymax))
  r3(1,1,i,j)=rl(1,1,i,j)
  r3(1,2,i,j)=rl(1,2,i,j)
  r3(3,1,i,j)=rl(3,1,i,j)
  r3(3,2,i,j)=rl(3,2,i,j)
  r3(3,2,1,i,j)=rl(3,2,1,i,j)
  r3(3,2,1,i,j)=rl(3,2,1,i,j)
  r3(3,2,1,i,j)=rl(3,2,1,i,j)
  continue
do 2 i=1,mx
  do 2 j=1,my-1
  if (i.eq.1) then
    r1(2,1,i,j)=0.0d0
    r1(2,2,i,j)=0.0d0
    r3(2,1,i,j)=0.0d0
    r3(2,2,i,j)=0.0d0
  else
    r1(2,1,i,j)=x(i)*(f5(y(j+1),x(i)))-f5(y(j),x(i))
    r1(2,2,i,j)=x(i)*(f6(y(j+1),x(i)))-f6(y(j),x(i))
    r3(2,1,i,j)=x(i)*(f5(ymax-y(j+1),x(i))-
    f5(ymax-y(j),x(i)))
    r3(2,2,i,j)=y(j)+r3(2,1,i,j)+
    x(i)*(f6(ymax-y(j+1),x(i))-f6(ymax-y(j),x(i)))
  end if
  if (i.eq.mx) then
    r1(4,1,i,j)=0.0d0
else
\textcolor{red}{rl(4,1,i,j)=\text{(xmax-x(i))*(f5(y(j+1),xmax-x(i))-f5(y(j),xmax-x(i)))}
\textcolor{red}{rl(4,2,i,j)=\text{(xmax-x(i))*(f6(y(j+1),xmax-x(i))-f6(y(j),xmax-x(i)))}
\textcolor{red}{r3(4,1,i,j)=\text{(xmax-x(i))*(f5(ymax-y(j+1),xmax-x(i))-f5(ymax-y(j),xmax-x(i)))}
\textcolor{red}{r3(4,2,i,j)=\text{ymax*r3(4,1,i,j)+
(xmax-x(i))*(f6(ymax-y(j+1),xmax-x(i))-f6(ymax-y(j),xmax-x(i)))}}
\textcolor{red}{\text{end if}}
\textcolor{red}{\text{end if}}
\textcolor{red}{2 continue}
do 3 i=2,my-1
\textcolor{red}{do 3 j=1,mx-1
\textcolor{red}{r2(1,1,i,j)=0.5d0*(f3(x(j+1),y(i))-f3(x(j),y(i)))
\textcolor{red}{r2(1,2,i,j)=0.5d0*(f4(x(j+1),y(i))-f4(x(j),y(i)))
\textcolor{red}{r2(2,1,i,j)=y(i)*(f5(x(j+1),y(i))-f5(x(j),y(i)))
\textcolor{red}{r2(2,2,i,j)=y(i)*(f6(x(j+1),y(i))-f6(x(j),y(i)))}}
o_{3,1,i,j}=0.5d0*(f3(x(j+1),ymax-y(i))-f3(x(j),ymax-y(i)))
o_{3,2,i,j}=0.5d0*(f4(x(j+1),ymax-y(i)))
The two following do loops account for the fact the interior angles at the corners are twice as small.

```
do 5  j-1, mx-1
   r3(1,1,1,j)=2.0d0*r3(1,1,1,j)
   r3(1,2,1,j)=2.0d0*r3(1,2,1,j)
   r3(3,1,1,j)=2.0d0*r3(3,1,1,j)
   r3(3,2,1,j)=2.0d0*r3(3,2,1,j)
   r3(5,1,1,j)=2.0d0*r3(5,1,1,j)
   r3(5,2,1,j)=2.0d0*r3(5,2,1,j)
   r3(1,1,mx,j)=2.0d0*r3(1,1,mx,j)
   r3(1,2,mx,j)=2.0d0*r3(1,2,mx,j)
   r3(3,1,mx,j)=2.0d0*r3(3,1,mx,j)
   r3(3,2,mx,j)=2.0d0*r3(3,2,mx,j)
   r3(5,1,mx,j)=2.0d0*r3(5,1,mx,j)
   r3(5,2,mx,j)=2.0d0*r3(5,2,mx,j)
   r1(l,1,1,j)=2.0d0*r1(l,1,1,j)
   r1(l,2,1,j)=2.0d0*r1(l,2,1,j)
   r1(3,1,1,j)=2.0d0*r1(3,1,1,j)
   r1(3,2,1,j)=2.0d0*r1(3,2,1,j)
   r1(5,1,1,j)=2.0d0*r1(5,1,1,j)
   r1(5,2,1,j)=2.0d0*r1(5,2,1,j)
   r1(1,1,mx,j)=2.0d0*r1(1,1,mx,j)
   r1(1,2,mx,j)=2.0d0*r1(1,2,mx,j)
   r1(3,1,mx,j)=2.0d0*r1(3,1,mx,j)
   r1(3,2,mx,j)=2.0d0*r1(3,2,mx,j)

5 do 6  j-1, my-1
   r3(2,1,mx,j)=2.0d0*r3(2,1,mx,j)
   r3(2,2,mx,j)=2.0d0*r3(2,2,mx,j)
   r3(4,1,1,j)=2.0d0*r3(4,1,1,j)
   r3(4,2,1,j)=2.0d0*r3(4,2,1,j)
   r1(2,1,mx,j)=2.0d0*r1(2,1,mx,j)
   r1(2,2,mx,j)=2.0d0*r1(2,2,mx,j)
   r1(4,1,1,j)=2.0d0*r1(4,1,1,j)
   r1(4,2,1,j)=2.0d0*r1(4,2,1,j)

6 return
end
```

SUBROUTINE CURRENT IS WHERE THE KINETICS AND THE INFORMATION FROM THE SCHWARZ-CHRISTOFFEL TRANSFORMATION ARE INPUT.
linear kinetics (ikinet=1)
Tafel kinetics (ikinet=2)
constant current (ikinet=3)

if (ikinet.eq.1) then
  if (ielec.eq.1) then
    do 1 i=1,mx
      cd1(i) = -d^2g(i)/(1.0d0-phi(1,i))
    else
      do 2 i=1,mx
      cd3(i) = -d^2g(i)*phi(3,i)
    end if
  else if (ikinet.eq.2) then
    if (ielec.eq.1) then
      do 3 i=1,mx
      cd1(i) = -g(i)*dexp(dj-phi(1,i))
    else
      do 4 i=1,mx
      cd3(i) = -g(i)*dexp(phi(3,i))
    end if
  else
    if (ielec.eq.1) then
      do 5 i=1,mx
      cd1(i) = g(i)
    else
      do 6 i=1,mx
      cd3(i) = g(i)
    end if
  end if
else
  if (ielec.eq.1) then
    do 5 i=1,mx
    cd1(i) = g(i)
  else
    do 6 i=1,mx
    cd3(i) = g(i)
  end if
end if
return
end

THE FOLLOWING FUNCTIONS ARE INTEGRALS TO BE USED IN 2-D PROBLEMS.
THEY ARE CALLED IN SUBROUTINE FILLMAT.

function fl(b,a)
  implicit double precision(a-h,o-z)
  if (a.eq.b) then
    fl=0.0d0
  else
    fl=(b-a)*(dlog(dabs(a-b))-1.0d0)
  end if
return
end

function f2(b,a)
  implicit double precision(a-h,o-z)
  if (a.eq.b) then
    f2=0.0d0
  else
    te=(a-b)**2/(2.0d0*(dlog(dabs(b-a))-0.5d0))


\[ f_2 = a \cdot (b - a) \cdot (d \log(d \text{abs}(b - a)) - 1.0 \cdot 0) + \text{te} \]

\end if

\end

\begin{verbatim}
function f3(b, a)
  implicit double precision(a-h, o-z)
  f3 = b \cdot d \log(b**2 + a**2) - 2.0 \cdot 0 \cdot b + 2.0 \cdot 0 \cdot a \cdot \text{datan}(b/a)
  return
end
\end{verbatim}

\begin{verbatim}
function f4(b, a)
  implicit double precision(a-h, o-z)
  f4 = 0.5 \cdot 0 \cdot (b**2 + a**2) \cdot d \log(b**2 + a**2) - 0.5 \cdot 0 \cdot b**2
  return
end
\end{verbatim}

\begin{verbatim}
function f5(b, a)
  implicit double precision(a-h, o-z)
  f5 = \text{datan}(b/a)/a
  return
end
\end{verbatim}

\begin{verbatim}
function f6(b, a)
  implicit double precision(a-h, o-z)
  f6 = 0.5 \cdot 0 \cdot d \log(a**2 + b**2)
  return
end
\end{verbatim}

\begin{verbatim}
function f7(b, a)
  implicit double precision (a-h, o-z)
  f7 = (b/(a**2 + b**2) - \text{datan}(b/a)/a)/2.0 \cdot 0 / a**2
  return
end
\end{verbatim}

\begin{verbatim}
function f8(b, a)
  implicit double precision(a-h, o-z)
  f8 = -0.5 / (b**2 + a**2)
  return
end
\end{verbatim}

\begin{verbatim}
function f9(b, a)
  implicit double precision(a-h, o-z)
  f9 = (b/(b**2 + a**2) + datan(b/a)/a)/2.0 \cdot 0 +datan(b/a)/a/2.0 \cdot 0
  return
end
\end{verbatim}

\begin{verbatim}
function fa(p1, p2, z1, z2)
  implicit double precision(a-h, o-z)
  fa = p1 - (p2 - p1) \cdot z1/(z2 - z1)
  return
\endfunction
\end{verbatim}
function fb(pl,p2,z1,z2)
imPLICIT double precision(a-h,o-z)
fb=(p2-p1)/(z2-z1)
return
end

subroutine readguess
implicit double precision(a-h,o-z)
dimension x(51),y(51),phi(4,51),rl(5,2,51,51),phio(51),
r2(5,2,51,51),r3(5,2,51,51),r4(5,2,51,51),cdl(51),g(100),cd3(51)
common x,y,phi,rl,r2,r3,r4,my,mx,cdl,xmax,ymax,g,cd3,hl
v(200),vr(200),wins(200),wle(200),xins(200),xele(200),cd3
do i=1,mx/2+1
read*,phi(1,2*i-1),phi(3,2*i-1)
do 2 i=2,mx-1,2
phi(1,i)=phi(1,i-1)+(-phi(1,i-1)+phi(1,i+1))/2.0d0
phi(3,i)=phi(3,i-1)+(-phi(3,i-1)+phi(3,i+1))/2.0d0
return
end

subroutine tread
implicit double precision(a-h,o-z)
dimension x(51),y(51),phi(4,51),rl(5,2,51,51),phio(51),
r2(5,2,51,51),r3(5,2,51,51),r4(5,2,51,51),cdl(51),g(100),cd3(51)
common x,y,phi,rl,r2,r3,r4,my,mx,cdl,xmax,ymax,g,cd3,hl
v(200),vr(200),wins(200),wle(200),xins(200),xele(200),cd3
read*,mx,my
print*, 'h/L-', h1
pi=3.14159265358979d0
do i=1,200
read*,vj(i),wle(i),xle(i)
do 2 i=1,200
read*,vr(i),wins(i),xins(i)
xmax=vj(200)
ymax=2.0d0*vr(200)
x(1)=0.0d0
ix=200/(mx-1)
iy=200/(my-1)*2
do 3 i=2,mx
x(i)=vj((i-1)*ix)
y(1)=0.0d0
y(my)=2.0d0*vr(200)
y(my/2+1)=vr(200)
do 4 i=2,my/2
y(my+i-1)=vr(200)+vr(200-(i-1)*iy)
y(i)=(vr(200)-vr(200-(i-1)*iy))
g(1)=dsqrt(wle(200)**2-wle(1)**2)/pi
do 5 i=2,mx-1
g(i)=dsqrt(wele(200)**2-wele((i-1)*ix)**2)/pi
5 continue
7 g(mx)=0.0d0
8 return
9 end

subroutine tprint(iter,ikinet,dj)
implicit double precision(a-h,o-z)
character*72 11

dimension x(51),y(51),phi(4,51),rl(5,2,51,51),phio(51),
1 r2(5,2,51,51),r3(5,2,51,51),r4(5,2,51,51),cdl(51),g(100),cd3(51)
common x,y,phi,rl,r2,r3,r4,my,mx,cdl,xmax,ymax,g, xmaxi
1,vj(200),vr(200),wins(200),wele(200),xins(200),xele(200),cd3,hl

del=average(ikinet)
delst=2.0d0*del*hl*x(mx)

if (ikinet.eq.1) then
bl=(1.0d0-phi(4,my/2+1))/del/y(my/2+1)
dil=dj*(1.0d0-phi(1,mx))
print101,dj,dil/delst,bl
else if (ikinet.eq.2) then
ec=dj-phi(4,my/2+1)-y(my/2+1)*del-dlog(delst)
gd=y(my/2+1)*del-phi(4,1)+phi(4,my/2+1)
dil=dexp(dj-phi(1,mx))
print102,delst,dil/delst,ec,gd
else
ec=dj-phi(4,my/2+1)-y(my/2+1)*del-dlog(delst)
gd=y(my/2+1)*del-phi(4,1)+phi(4,my/2+1)
bl=(1.0d0-phi(4,my/2+1))/del/y(my/2+1)
print103,1.0d0,1.0d0,gd
print104,1.0d0,bl
end if

if (iter.ge.500) then
print*, 'The last run did not converge'
stop
end if

101 format(3G13.6)
102 format(4G13.6)
103 format('infinity',4G13.6)
104 format('infinity',3G13.6)
return
end

CALCULATE THE AVERAGE CURRENT DENSITY

function average(ikinet)
implicit double precision(a-h,o-z)

dimension x(51),y(51),phi(4,51),rl(5,2,51,51),phio(51),
1 r2(5,2,51,51),r3(5,2,51,51),r4(5,2,51,51),cdl(51),g(100),cd3(51)
common x,y,phi,rl,r2,r3,r4,my,mx,cdl,xmax,ymax,g, xmaxi
1,vj(200),vr(200),wins(200),wele(200),xins(200),xele(200),cd3,hl
sum=0.0d0
do 1 i=2,mx
ex=(cdl(i)+cdl(i-1))*(x(i)-x(i-1))/2.0d0
sum=sum+ex
average=dabs(sum/x(mx))
return
end
program scinf
implicit double precision(a-h,o-z)
character*72 11
dimension x(51),y(51),phi(4,51),r1(5,2,51,51),phi0(51),
1r2(5,2,51,51),r3(5,2,51,51),r4(5,2,51,51),cdl(51),g(100),phi03(51)
1,l,vj(200),vr(200),wins(200),wele(200),xins(200),xele(200),cd3(51)
common x,y,phi,r1,r2,r3,r4,my,mx,cdl,xmax,ymax,g,xmaxi
1,l,vj,vr,wins,wele,xins,xele,cd3,hl

read*,djint
dj=djint
pi=3.14159265358979d0
damp=0.5d0
read*,ikinet
if (ikinet.eq.1)then
    print*,'linear kinetics'
    print*,i(L)/iavg
else if (ikinet.eq.2) then
    print*,'Tafel kinetics'
    print*,delta
else
    print*,'constant current'
end if

iter=1
c initial guess
do 3 i=1,mx
    philinf=(1.0d0+dj)/(2.0d0+dj)
    phi03inf=1.0d0/(dj+2.0d0)
    phi(1,i)=philinf-g(i)
    phi(3,i)=phi03inf-g(i)
c call current(3,ikinet,dj)
3 phi(2,i)=0.0d0
do 7 j=1,mx-1
    a2=fa(phi(1,j),phi(1,j+1),x(j),x(j+1))
    b2=fb(phi(1,j),phi(1,j+1),x(j),x(j+1))
    a1=fa(cdl(j),cdl(j+1),x(j),x(j+1))
    b1=fb(cdl(j),cdl(j+1),x(j),x(j+1))
    a3=fa(cd3(j),cd3(j+1),x(j),x(j+1))
    b3=fb(cd3(j),cd3(j+1),x(j),x(j+1))
    a4=fa(phi(3,j),phi(3,j+1),x(j),x(j+1))
    b4=fb(phi(3,j),phi(3,j+1),x(j),x(j+1))
100 call current(1,ikinet,dj)
c solve for phi2
    do 6 i=2,my-1
        phi(2,i)=0.0d0
    do 7 j=1,mx-1
        a2=fa(phi(1,j),phi(1,j+1),x(j),x(j+1))
        b2=fb(phi(1,j),phi(1,j+1),x(j),x(j+1))
        a1=fa(cdl(j),cdl(j+1),x(j),x(j+1))
        b1=fb(cdl(j),cdl(j+1),x(j),x(j+1))
        a3=fa(cd3(j),cd3(j+1),x(j),x(j+1))
        b3=fb(cd3(j),cd3(j+1),x(j),x(j+1))
        a4=fa(phi(3,j),phi(3,j+1),x(j),x(j+1))
        b4=fb(phi(3,j),phi(3,j+1),x(j),x(j+1))
\[
\phi(2,i) = \phi(2,i) + a1*r2(1,1,i,j) + b1*r2(1,2,i,j) + a2*r2(2,1,i,j) + b2*r2(2,2,i,j) + a3*r2(3,1,i,j) + b3*r2(3,2,i,j) + a4*r2(5,1,i,j) + b4*r2(5,2,i,j)
\]

\[
\phi(2,i) = \phi(2,i) / \pi
\]

\[
\phi(2,1) = \phi(1,1)
\]

\[
\phi(2,my) = \phi(3,1)
\]

\[
\text{solve for } \phi_3
\]

\[
\text{do 12 } i=1,mx
\]

\[
\phi_{io3}(i) = \phi(3,i)
\]

\[
\phi(3,i) = 0.0d0
\]

\[
\text{do 13 } j=1,mx-1
\]

\[
a1 = fa(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
b1 = fb(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
a2 = fa(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
b2 = fb(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
a3 = fa(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
b3 = fb(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
\]

\[
\phi(2,i) = \phi(2,i) + a1*r2(1,1,i,j) + b1*r2(1,2,i,j) + a2*r2(2,1,i,j) + b2*r2(2,2,i,j) + a3*r2(3,1,i,j) + b3*r2(3,2,i,j) + a4*r2(5,1,i,j) + b4*r2(5,2,i,j)
\]

\[
\phi(2,i) = \phi(2,i) / \pi
\]

\[
\text{do 12 } i=1,mx
\]

\[
\phi_{io4}(i) = \phi(3,i)
\]

\[
\phi(3,i) = 0.0d0
\]

\[
\text{do 16 } j=1,mx-1
\]

\[
a2 = fa(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
b2 = fb(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
a3 = fa(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
b3 = fb(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
a1 = fa(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
b1 = fb(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
\]

\[
\phi(2,i) = \phi(2,i) + a1*r2(1,1,i,j) + b1*r2(1,2,i,j) + a2*r2(2,1,i,j) + b2*r2(2,2,i,j) + a3*r2(3,1,i,j) + b3*r2(3,2,i,j) + a4*r2(5,1,i,j) + b4*r2(5,2,i,j)
\]

\[
\phi(2,i) = \phi(2,i) / \pi
\]

\[
\text{call current(3,ikinet,dj)}
\]

\[
\text{solve for } \phi_1
\]

\[
\text{do 15 } i=1,mx
\]

\[
\phi_{io}(i) = 0.0d0
\]

\[
\text{do 16 } j=1,mx-1
\]

\[
a2 = fa(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
b2 = fb(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
a3 = fa(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
b3 = fb(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
a1 = fa(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
b1 = fb(\phi(1,j), \phi(1,j+1), x(j), x(j+1))
\]

\[
\phi(2,i) = \phi(2,i) + a1*r1(1,1,i,j) + b1*r1(1,2,i,j) + a2*r1(2,1,i,j) + b2*r1(2,2,i,j) + a3*r1(3,1,i,j) + b3*r1(3,2,i,j) + a4*r1(5,1,i,j) + b4*r1(5,2,i,j)
\]

\[
\phi(2,i) = \phi(2,i) / \pi
\]

\[
\text{check for errors}
\]

\[
\text{error=0.0d0}
\]

\[
\text{do 30 } i=2,mx
\]

\[
\text{error=dmax1(error,dabs(\phi(1,i)-\phi_{io}(i)))}
\]
continue
if (error.gt.1.d-5) then
    do 35 i=1,mx
    phi(1,i)=phi(1,i)+damp*(phio(i)-phi(1,i))
    iter=iter+1
    if (iter.ge.500) then
        print*,'greater than 300 iterations','error=',error
        goto 999
    end if
    goto 100
end if
999 call tprint(iter,ikinet,dj)
dj=dj+djint
if (dj.lt.50.0d0*djint) then
    if (dj.ge.6.0d0)damp=0.1d0
    iter=1
    goto 100
end if
end
subroutine fillmat
implicit double precision(a-h,o-z)
dimension x(51),y(51),phi(4,51),r1(5,2,51,51),phio(51),
r2(5,2,51,51),r3(5,2,51,51),r4(5,2,51,51),cd1(51),g(100),cd3(51)
common x,y,phi,r1,r2,r3,r4,my,mx,cd1,xmax,ymax,g,xmaxi
1,vj(200),vr(200),wels(200),xins(200),xeli(200),cd3,hl
do 1 i=1,mx
    do 1 j=1,mx-1
        r1(1,1,i,j)=f1(x(j+1),x(i))-f1(x(j),x(i))
        r1(1,2,i,j)=f2(x(j+1),x(i))-f2(x(j),x(i))
        r1(3,1,i,j)=0.5d0*1(f3(x(j+1)-x(i),ymax)-f3(x(j)-x(i),ymax))
        r1(3,2,i,j)=x(i)*r1(3,1,i,j)-1(f4(x(j+1)-x(i),ymax)-f4(x(j)-x(i),ymax))*0.5d0
        r1(5,1,i,j)=ymax*(f5(x(j+1)-x(i),ymax)-f5(x(j)-x(i),ymax))
        r1(5,2,i,j)=x(i)*r1(5,1,i,j)+ymax*(f6(x(j+1)-x(i),ymax))-1
        r3(1,1,i,j)=-r1(1,1,i,j)
        r3(1,2,i,j)=-r1(1,2,i,j)
        r3(5,1,i,j)=r1(5,1,i,j)
        r3(5,2,i,j)=r1(5,2,i,j)
        r3(3,1,i,j)=-r1(3,1,i,j)
        r3(3,2,i,j)=-r1(3,2,i,j)
    continue
    do 2 i=1,mx
        do 2 j=1,my-1
            if (i.eq.1) then
                r1(2,1,i,j)=0.0d0
                r1(2,2,i,j)=0.0d0
                r3(2,1,i,j)=0.0d0
                r3(2,2,i,j)=0.0d0
            else
                print*,'greater than 300 iterations','error=',error
                goto 999
            end if
            r1(2,1,i,j)=0.0d0
            r1(2,2,i,j)=0.0d0
            r3(2,1,i,j)=0.0d0
            r3(2,2,i,j)=0.0d0
        end if
    end do
end subroutine fillmat
continue
\[ r_1(2,1,i,j) = x(i) \cdot (f_5(y(j+1),x(i)) - f_5(y(j),x(i))) \]
\[ r_1(2,2,i,j) = x(i) \cdot (f_6(y(j+1),x(i)) - f_6(y(j),x(i))) \]
\[ r_3(2,1,i,j) = -x(i) \cdot (f_5(y_{max}-y(j+1),x(i)) - f_5(y_{max}-y(j),x(i))) \]
\[ r_3(2,2,i,j) = ymax \cdot r_3(2,1,i,j) + x(i) \cdot (f_6(y_{max}-y(j+1),x(i)) - f_6(y_{max}-y(j),x(i))) \]
\[ end if \]
\[ continue \]
\[ do 3 \ i = 2, my - 1 \]
\[ do 3 \ j = 1, mx - 1 \]
\[ r_2(1,1,1,j) = 0.5d0 \cdot (f_3(x(j+1),y(i)) - f_3(x(j),y(i))) \]
\[ r_2(1,2,1,j) = 0.5d0 \cdot (f_4(x(j+1),y(i)) - f_4(x(j),y(i))) \]
\[ r_2(2,1,1,j) = (y(i) \cdot (f_5(x(j+1),y(i)) - f_5(x(j),y(i))) \]
\[ r_2(2,2,1,j) = (y(i) \cdot (f_6(x(j+1),y(i)) - f_6(x(j),y(i))) \]
\[ r_2(3,1,1,j) = -0.5d0 \cdot (f_3(x(j+1),y_{max}-y(i)) - f_3(x(j),y_{max}-y(i))) \]
\[ r_2(3,2,1,j) = -0.5d0 \cdot (f_4(x(j+1),y_{max}-y(i)) - f_4(x(j),y_{max}-y(i))) \]
\[ continue \]
\[ do 5 \ j = 1, mx - 1 \]
\[ r_3(1,1,1,j) = 2.0d0 \cdot r_3(1,1,1,j) \]
\[ r_3(1,2,1,j) = 2.0d0 \cdot r_3(1,2,1,j) \]
\[ r_3(3,1,1,j) = 2.0d0 \cdot r_3(3,1,1,j) \]
\[ r_3(3,2,1,j) = 2.0d0 \cdot r_3(3,2,1,j) \]
\[ r_3(5,1,1,j) = 2.0d0 \cdot r_3(5,1,1,j) \]
\[ r_3(5,2,1,j) = 2.0d0 \cdot r_3(5,2,1,j) \]
\[ r_3(1,1,\text{mx},j) = 2.0d0 \cdot r_3(1,1,\text{mx},j) \]
\[ r_3(1,2,\text{mx},j) = 2.0d0 \cdot r_3(1,2,\text{mx},j) \]
\[ r_3(3,1,\text{mx},j) = 2.0d0 \cdot r_3(3,1,\text{mx},j) \]
\[ r_3(3,2,\text{mx},j) = 2.0d0 \cdot r_3(3,2,\text{mx},j) \]
\[ r_3(5,1,\text{mx},j) = 2.0d0 \cdot r_3(5,1,\text{mx},j) \]
\[ r_3(5,2,\text{mx},j) = 2.0d0 \cdot r_3(5,2,\text{mx},j) \]
\[ r_1(1,1,1,j) = 2.0d0 \cdot r_1(1,1,1,j) \]
\[ r_1(1,2,1,j) = 2.0d0 \cdot r_1(1,2,1,j) \]
\[ r_1(3,1,1,j) = 2.0d0 \cdot r_1(3,1,1,j) \]
\[ r_1(3,2,1,j) = 2.0d0 \cdot r_1(3,2,1,j) \]
\[ r_1(5,1,1,j) = 2.0d0 \cdot r_1(5,1,1,j) \]
\[ r_1(5,2,1,j) = 2.0d0 \cdot r_1(5,2,1,j) \]
\[ r_1(1,1,\text{mx},j) = 2.0d0 \cdot r_1(1,1,\text{mx},j) \]
\[ r_1(1,2,\text{mx},j) = 2.0d0 \cdot r_1(1,2,\text{mx},j) \]
\[ r_1(5,1,\text{mx},j) = 2.0d0 \cdot r_1(5,1,\text{mx},j) \]
\[ r_1(5,2,\text{mx},j) = 2.0d0 \cdot r_1(5,2,\text{mx},j) \]
\[ r_1(3,1,\text{mx},j) = 2.0d0 \cdot r_1(3,1,\text{mx},j) \]
\[ r_1(3,2,\text{mx},j) = 2.0d0 \cdot r_1(3,2,\text{mx},j) \]
\[ do 6 \ j = 1, my - 1 \]
r3(2,1,mx,j)=2.0d0*r3(2,1,mx,j)
r3(2,2,mx,j)=2.0d0*r3(2,2,mx,j)
rl(2,1,mx,j)=2.0d0*rl(2,1,mx,j)
rl(2,2,mx,j)=2.0d0*rl(2,2,mx,j)
continue
return
end

c ____________________ ~

c SUBROUTINE CURRENT IS WHERE THE KINETICS AND THE INFORMATION FROM THE SCHWARZ-CHRISTOFFEL TRANSFORMATION ARE INPUT
c

c subroutine current(ielec,ikinet,dj)
implicit double precision(a-h,o-z)
dimension x(Sl),y(Sl),phi(4,Sl),rl(S,2,Sl,Sl),phio(Sl),
   r2(S,2,Sl,Sl),r3(S,2,Sl,Sl),r4(S,2,Sl,Sl),cdl(Sl),g(lOO),cd3(Sl)
common x,y,phi,rl,r2,r3,r4,my,mx,cdl,xmax,ymax,g,xmaxi
1,vj(200),vr(200),wins(200),wele(200),xins(200),xele(200),cd3,hl
c ________________
__
subroutine current(ielec,ikinet,dj)
implicit double precision(a-h,o-z)
dimension x(51),y(51),phi(4,51),rl(5,2,51,51),phio(51),
r2(5,2,51,51),r3(5,2,51,51),r4(5,2,51,51),cdl(51),g(100),cd3(51)
common x,y,phi,rl,r2,r3,r4,my,mx,cdl,xmax,ymax,g,xmaxi
1,vj(200),vr(200),wins(200),wele(200),xins(200),xele(200),cd3,hl

c linear kinetics (ikinet=1)
c Tafel kinetics (ikinet=2)
c constant current (ikinet=3)
c
if (ikinet.eq.1)then
   philinf=(1.0d0+dj)/(2.0d0+dj)
   phi3inf=1.0d0/(dj+2.0d0)
   if (ielec.eq.1)then
      do 1 i=1,mx
         cdl(i)=dj*g(i)*(1.0d0-phi(1,i)-philinf)-(phi3inf-philinf)
      else
         do 2 i=1,mx
         cd3(i)=g(i)*(phi(3,i)+phi3inf)-(phi3inf-philinf)
      end if
   else if (ikinet.eq.2) then
      if (ielec.eq.1)then
         do 3 i=1,mx
         cdl(i)=g(i)*dabs(dj)*dexp(-phi(1,i))+dabs(dj)
      else
         do 4 i=1,mx
         cd3(i)=g(i)*dabs(dj)*dexp(phi(3,i))+dabs(dj)
      end if
   else
      if (ielec.eq.1)then
         do 5 i=1,mx
         cdl(i)=-g(i)+1.0d0
      else
         do 6 i=1,mx
         cd3(i)=-g(i)+1.0d0
      end if
   end if
end if
return
end
THE FOLLOWING FUNCTIONS ARE INTEGRALS TO BE USED IN 2-D PROBLEMS.
They are called in subroutine FILLMAT.

```
c function f1(b,a)
   implicit double precision(a-h,o-z)
   if (a.eq.b) then
      f1=0.0d0
   else
      f1=(b-a)*(dlog(dabs(a-b))-1.0d0)
   end if
   return
end

c function f2(b,a)
   implicit double precision(a-h,o-z)
   if (a.eq.b) then
      f2=0.0d0
   else
      te=(a-b)**2/2.0d0*(dlog(dabs(b-a))-0.5d0)
      f2=a*(b-a)*(dlog(dabs(b-a))-1.0d0)+te
   end if
   return
end

c function f3(b,a)
   implicit double precision(a-h,o-z)
   f3=b*dlog(b**2+a**2)-2.0d0*b+2.0d0*a*datan(b/a)
   return
end

c function f4(b,a)
   implicit double precision(a-h,o-z)
   f4=0.5d0*(b**2+a**2)*dlog(b**2+a**2)-0.5d0*b**2
   return
end

c function f5(b,a)
   implicit double precision(a-h,o-z)
   f5=datan(b/a)/a
   return
end

c function f6(b,a)
   implicit double precision(a-h,o-z)
   f6=0.5d0*dlog(a**2+b**2)
   return
end

c function f7(b,a)
   implicit double precision (a-h,o-z)
```
f7=(b/(a**2+b**2)-datan(b/a)/a)/2.0d0/a**2
return
end

c________
function f8(b,a)
implicit double precision(a-h,o-z)
f8=-0.5d0/(b**2+a**2)
return
end

c________
function f9(b,a)
implicit double precision(a-h,o-z)
f9=-b/(b**2+a**2)/2.0d0+datan(b/a)/a/2.0d0
return
end

c________
function fa(p1,p2,z1,z2)
implicit double precision(a-h,o-z)
fa=p1-(p2-p1)*z1/(z2-z1)
return
end

c________
function fb(p1,p2,z1,z2)
implicit double precision(a-h,o-z)
fb=(p2-p1)/(z2-z1)
return
end

c________
subroutine tread
implicit double precision(a-h,o-z)
dimension x(51),y(51),phi(4,51),r1(5,2,51,51),phio(51),
r2(5,2,51,51),r3(5,2,51,51),r4(5,2,51,51),cdl(51),g(100),cd3(51)
common x,y,phi,r1,r2,r3,r4,my,mx,cd1,xmax,ymax,g,xmax
read*,mx,my
print*, 'h/L=',0'
p1=3.14159265358979d0
ymax=1.0d0
xmax=2.0d0
do 1 i=1,mx
x(i)=xmax*dfloat(i-1)/dfloat(mx-1)
pix=2.0d0*dlog(dcos(pi*x(i)))
g(i)=dsqrt(1.0d0-dexp(-pix))
1 continue
do 2 i=1,my
2 y(i)=ymax*dfloat(i-1)/dfloat(my-1)
return
end

c________
subroutine tprint(iter,ikinet,dj)
implicit double precision(a-h,o-z)
character*72

dimension x(51), y(51), phi(4,51), rl(5,2,51,51), phi0(51),
1 r2(5,2,51,51), r3(5,2,51,51), r4(5,2,51,51), cd1(51), g(100), cd3(51)
common x, y, phi, rl, r2, r3, r4, my, mx, cd1, xmax, ymax, g, xmai
1, vj(200), vr(200), wins(200), wele(200), xins(200), xele(200), cd3, hl
c
if (ikinet.eq.1) then
  philinf=(1.0d0+dj)/(2.0d0+dj)
  phi3inf=1.0d0/(dj+2.0d0)
  v=philinf-phi3inf
  b1=(1.0d0-phi(2,5)-philinf)*dj/v
  b2=(1.0d0-phi(2,9)-philinf)*dj/v
  b4=(1.0d0-phi(2,17)-philinf)*dj/v
  dil=dj*(1.0d0-phi(l,l)-philinf)/(phi3inf-philinf)
  print101,dj,dil,b1,b2,b4
else if (ikinet.eq.2) then
  g1=phi(2,5)
  g2=phi(2,9)
  g4=phi(2,17)
  g0=phi(2,1)
  print101,dj,g0,g1,g2,g4
else
  print*,'Along insulator:'
do 10 i=1,my
    print*,y(i),phi(2,i)+y(i)
  end do
  print*,'Along electrode:'
do 20 i=1,mx
    print*,x(i),phi(l,i)
end if
if (iter.ge.500) then
  print*,'The last run did not converge'
  stop
end if
101 format(5G13.6)
return
end
program luggin

implicit double precision(a-h,o-z)
dimension zw(0:5l),rd(0:5l),rp(101),y12(2,0:51,51),
y13(2,0:51,101),y21(2,51,51),y22(2,51,51),y31(2,101,51),
lphi3(101),lphi2n(0:5l),lphi3o(101),lphi2(0:5l),
y23a(51),y13a(0:51),cd(0:51),y23(2,51,101),y32(2,101,51)
1,phi1(0:51),y3lp(2,101,0:5l),y2lp(2,5l,5l),philcd(0:51)
common y21,y23,y31,y32,zw,rp,zstart,zstop,pl,ic,jc
l,rd,nd,np,nw,pp,damp,pi,y23a,y12,y13,y13a,philcd,y3lp,y2lp,cd
pi=3.14159265358979d0
c
pl= dimensionless length of capillary wall
nw= # of points on wall where potential is calculated
np= # of points on plane where potential is calculated
c
call pread
call fillmat
call current(O)
c
Initial guesses.
do 3 i=0,nw
3 phi2(i)=pl+1.0d0-(1.0d0-0.75d0/pl)*zw(i)
do 4 i=0,nd
phi1(i)=pl+1.0d0
4 continue
do 5 i=1,np
5 phi3o(i)=0.75d0*(1.0d0-2.0d0/pi*datan(rp(i)**2-l.0d0))
c
calculate the potential on the insulating plane
do 10 i=1,np
phi3(i)=0.0d0
do 11 j=1,nw
   a=fa(rd(j),rd(j-1),cd(j),cd(j-1))
   b=fb(rd(j),rd(j-1),cd(j),cd(j-1))
   c=fa(rd(j),rd(j-1),phi1(j),phi1(j-1))
   d=fb(rd(j),rd(j-1),phi1(j),phi1(j-1))
11 phi3(i)=phi3(i)+a*y3l(1,i,j)+b*y31(2,i,j)+
c*y3lp(1,1,j)+d*y3lp(2,1,j)
do 10 j=1,nw
phi3(i)=phi3(i)+a*y3l(1,i,j)+b*y31(2,i,j)+
c*y3lp(1,1,j)+d*y3lp(2,1,j)
c
calculate the potential on the disk electrode
do 70 i=0,nd
phi1(i)=philcd(i)+(0.6d0*phi3(i)+0.4d0*phi2(nw))*y13a(i)
do 71 j=1,np-1
   a=fa(rp(j+1)-1.d0,rp(j)-1.d0,phi3(j+1),phi3(j))
   b=fb(rp(j+1),rp(j),phi3(j+1),phi3(j))
71 phi1(i)=phi1(i)+a*y13(1,i,j)+b*y13(2,i,j)
do 72 j=1,nw
   a=fa(zw(j),zw(j-1),phi2(j),phi2(j-1))
   b=fb(zw(j),zw(j-1),phi2(j),phi2(j-1))
   ph1(i)=ph1(i)+a*y12(1,i,j)+b*y12(2,i,j)
70 continue
   ph1(nd)=2.0d0*ph1(nd)
   ph1(nd)=ph1(nd-1)
   ph12n(0)=ph1(nd)
   c calculate the potential on the wall
   do 20 i=1,nw
      ph12n(i)=(0.6d0*ph1(i)+0.4d0*ph12(nw))*y23a(i)
   do 21 j=1,np-1
      a=fa(rp(j+1)-1.d0,rp(j)-1.d0,phi3(j+1),phi3(j))
      b=fb(rp(j+1),rp(j),phi3(j+1),phi3(j))
   21 ph12n(i)=ph12n(i)+a*y23(1,i,j)+b*y23(2,i,j)
   do 22 j=1,nw
      a=fa(zw(j),zw(j-1),phi2(j),phi2(j-1))
      b=fb(zw(j),zw(j-1),phi2(j),phi2(j-1))
   22 ph12n(i)=ph12n(i)+a*y22(1,i,j)+b*y22(2,i,j)
   do 23 j=1,nd
      a=fa(rd(j),rd(j-1),cd(j),cd(j-1))
      b=fb(rd(j),rd(j-1),cd(j),cd(j-1))
      c=fa(rd(j),rd(j-1),phi1(j),phi1(j-1))
      d=fb(rd(j),rd(j-1),phi1(j),phi1(j-1))
   23 ph12n(i)=ph12n(i)+a*y21(1,i,j)+b*y21(2,i,j)+
      c*y21p(1,i,j)+d*y21p(2,i,j)
   20 continue
   ph12n(nw)=2.0d0/3.0d0*ph12n(nw)
   c Check for convergence
   error=0.0d0
   do 30 i=0,nw
   30 error=dmax1(dabs((phi2n(i)-phi2(i))/phi2(i)),error)
   if (error.le.1.d-5) goto 600
   if (error.le.1.d-3)damp=0.1d0
   do 35 i=0,nw
   35 phi2(i)=phi2(i)+damp*(phi2n(i)-phi2(i))
      iter=iter+1
   if(iter.le.500)goto 100
   600 continue
   if(iter.ge.500)print*, 'DID NOT CONVERGE, ERROR = ',error
   c PRINT RESULTS
   print *, 'wall'
   print*, zw(0),char(9),phi1(nd)
   do 500 i=1,nw
   500 print*, zw(i),char(9),phi2n(i)
   print*, 'insulating plane'
   do 501 i=1,np
   501 print.*, rp(i),char(9),phi3(i)
print*,'disk electrode'
do 502 i=0,nd
502 print*,rd(i),char(9),phil(i)
do 503 i=0,nd
503 write(7,*),rd(i),phil(i)
if (icurr.le.18) then
  icurr=icurr+2
  call current(icurr)
  iter=1
  goto 100
end if
end

C ________________
C Subroutine to fill the matrix
C subroutine fillmat
  implicit double precision (a-h,o-z)
dimension zw(0:51),rd(0:51),rp(101),y12(2,0:51,51),
   ly13(2,0:51,101),y21(2,51,51),y22(2,51,51),y31(2,101,51),
   phi3(101),phi2n(0:51),phi3o(101),phi2(0:51),
   ly23a(51),y13a(0:51),cd(0:51),y23(2,51,101),y32(2,101,51)
1,phi1(0:51),y31p(2,101,0:51),y2lp(2,51,51),phicl(0:51)
common y21,y22,y31,y32,zw,rp,zstart,zstop,pl,ic,jc
1,rd,nd,np,nw,pp,damp,pi,y23a,y12,y13,y13a,philcl,y31p,y21p,cd
mw=500
mp=500
md=500
do 1 ic=1,nw
do 2 jc=1,nw
if (ic.eq.jc).or.(ic.eq.(jc-1)) then
  call integ3(zw(jc),zw(jc-1),10*mw,8)
  y22(1,ic,jc)=pp
  call integ3(zw(jc),zw(jc-1),10*mw,9)
  y22(2,ic,jc)=pp
else
  call integ1(zw(jc),zw(jc-1),mw,1)
  y22(1,ic,jc)=pp
  call integ1(zw(jc),zw(jc-1),mw,2)
  y22(2,ic,jc)=pp
end if
continue
2 do 3 jc=1,nd
  call integ1(rd(jc),rd(jc-1),md,7)
  y21p(1,ic,jc)=pp
  call integ1(rd(jc),rd(jc-1),md,21)
  y21p(2,ic,jc)=pp
  call integ1(rd(jc),rd(jc-1),md,3)
  y21(1,ic,jc)=pp
  call integ1(rd(jc),rd(jc-1),md,4)
3 y21(2,ic,jc)=pp
do 1 jc=1,np-1
if (ic.eq.nw) then
y23(1,ic,jc)=0.0d0
y23(2,ic,jc)=0.0d0
else
    call integ2(rp(jc+1),rp(jc),mp,5)
y23(1,ic,jc)=pp
    call integ2(rp(jc+1),rp(jc),mp,6)
y23(2,ic,jc)=pp
end if
continue
do 10 ic=1,np
do 20 jc=1,nd
call integ1(rd(jc),rd(jc-1),mp,14)
y3lp(1,ic,jc)=pp
call integ1(rd(jc),rd(jc-1),mp,22)
y3lp(2,ic,jc)=pp
call integ1(rd(jc),rd(jc-1),mp,10)
y3l(1,ic,jc)=pp
call integ1(rd(jc),rd(jc-1),mp,11)
y3l(2,ic,jc)=pp
20
do 30 jc=1,nw
call integ1(zw(jc),zw(jc-1),mp,12)
y32(1,ic,jc)=pp
call integ1(zw(jc),zw(jc-1),mp,13)
y32(2,ic,jc)=pp
30
continue
do 100 ic=0,nd
do 200 jc=1,nw
if ((ic.eq.nd).and.(jc.eq.1)) then
call integ3(zw(jc),zw(jc-1),10*mw,26)
y12(1,ic,jc)=pp
call integ3(zw(jc),zw(jc-1),10*mw,25)
y12(2,ic,jc)=pp
else
call integ1(zw(jc),zw(jc-1),mw,15)
y12(1,ic,jc)=pp
call integ1(zw(jc),zw(jc-1),mw,16)
y12(2,ic,jc)=pp
end if
200
continue
do 300 jc=1,np-1
call integ2(rp(jc+1),rp(jc),mp,17)
y13(1,ic,jc)=pp
call integ2(rp(jc+1),rp(jc),mp,18)
y13(2,ic,jc)=pp
300
continue
return
end

* Basic Trapezoid integration
subroutine integ1(up,down,m,id)
imPLICIT DOUBLE PRECISION(a-h,o-z)
dimension zw(0:51), rd(0:51), rp(101), y12(2,0:51,51),
ly13(2,0:51,101), y21(2,51,51), y22(2,51,51), y31(2,101,51),
phi3(101), phi2n(0:51), phi3o(101), phi2(0:51),
ly23a(51), y13a(0:51), cd(0:51), y23(2,51,101), y32(2,101,51)
1, phi1(0:51), y31p(2,101,0:51), y21p(2,51,51), phi1cd(0:51)
common y21, y22, y23, y31, y32, zw, rp, zstart, zstop, pl, ic, jc
1, rd, nd, np, nw, pp, damp, pi, y23a, y12, y13, y13a, phi1cd, y31p, y21p, cd
pp=0.0d0
j=1
eps=(up-down)/dfloat(m-1)
do 1 j=2,m
  x=down+eps*dfloat(j-1)
  or2=ord(id,x)
  pp=pp+eps*(or2+or1)/2.0d0
1
or1=or2
return
end

c Integration "log style"
subroutine integ2(up,down,m,id)
  implicit double precision(a-h,o-z)
dimension zw(0:51), rd(0:51), rp(101), y12(2,0:51,51),
ly13(2,0:51,101), y21(2,51,51), y22(2,51,51), y31(2,101,51),
phi3(101), phi2n(0:51), phi3o(101), phi2(0:51),
ly23a(51), y13a(0:51), cd(0:51), y23(2,51,101), y32(2,101,51)
1, phi1(0:51), y31p(2,101,0:51), y21p(2,51,51), phi1cd(0:51)
common y21, y22, y23, y31, y32, zw, rp, zstart, zstop, pl, ic, jc
1, rd, nd, np, nw, pp, damp, pi, y23a, y12, y13, y13a, phi1cd, y31p, y21p, cd
upl=up-1.0d0
downl=down-1.0d0
xl=downl
h=dlog(upl/downl)/dfloat(m-1)
orl=ord(id,downl)
if (((id.eq.17).and.(jc.eq.1)) then
  y13a(ic)=orl*downl
else if (((jc.eq.1).and.(id.eq.5)) then
  y23a(ic)=orl*downl
end if
pp=0.0d0
do 1 j=2,m
  x2=downl*dexp(h*dfloat(j-1))
  or2=ord(id,x2)
b=dlog(or2/or1)/h
  pp=pp+(x2*or2-xl*or1)/(1.0d0+b)
  xl=x2
1
or1=or2
return
end

c This is for the addition and subtraction of singular values.
subroutine integ3(up,down,m,id)
implicit double precision(a-h,o-z)
dimension zw(0:51),rd(0:51),rp(101),y12(2,0:51,51),
lyl3(2,0:51,101),y21(2,51,51),y22(2,51,51),y31(2,101,51),
phi13(101),phi2n(0:51),phi3o(101),phi2(0:51),
ly23a(51),yl3a(0:51),cd(0:51),y23(2,51,101),y32(2,101,51)
1,phi1(0:51),y3lp(2,101,0:51),y2lp(2,51,51),phi1cd(0:51)
common y21,y22,y23,y31,y32,zw,rp,zstart,zstop,p1,ic,jc
1,rd,nd,np,nd,pp,damp,pi,y23a,y12,y13,y13a,phi1cd,y3lp,y2lp

call integ1(up,down,m,id)
dif=up-down
if (mod(id,2).ne.0) then
te=0.5d0*dif**2*(dlog(dif/4.0d0)-0.5d0)
if(id.eq.25) then
corr=te
goto 111
end if
if (dabs(zw(ic)-up).le.0.0001d0)te=te
corr=zw(ic)*dif*(dlog(dif/4.0d0)-1.0d0)+te
else
corr=dif*(dlog(dif/4.0d0)-1.0d0)
end if
111 pp=pp-corr/2.0d0/pi
return
end

subroutine integ4(up,down,m,id,icurr)
implicit double precision(a-h,o-z)
dimension zw(0:51),rd(0:51),rp(101),y12(2,0:51,51),
lyl3(2,0:51,101),y21(2,51,51),y22(2,51,51),y31(2,101,51),
phi13(101),phi2n(0:51),phi3o(101),phi2(0:51),
ly23a(51),yl3a(0:51),cd(0:51),y23(2,51,101),y32(2,101,51)
1,phi1(0:51),y3lp(2,101,0:51),y2lp(2,51,51),phi1cd(0:51)
common y21,y22,y23,y31,y32,zw,rp,zstart,zstop,p1,ic,jc
1,rd,nd,np,nd,pp,damp,pi,y23a,y12,y13,y13a,phi1cd,y3lp,y2lp,cd
jc=icurr
call integ1(up,down,m,id)
corr=0.0d0
if (id.eq.19) then
dif=up-down
corr=dif*(dlog(dif)-1.0d0)
y=dcos(pi/2.0d0*(1.0d0-rd(ic)))
pp=pp+corr/pi*P(icurr,y)
end if
return
end

function fa(x2,x1,p2,p1)
implicit double precision(a-h,o-z)
fa=p1-(p2-p1)*x1/(x2-x1)
return
end
function fb(x2,x1,p2,p1)
imPLICIT DOUBLE PRECISION(a-h,o-z)
fb=(p2-p1)/(x2-x1)
return
end

This simulates a Pascal case statement for use in integration.
function ord(id,x)
imPLICIT DOUBLE PRECISION(a-h,o-z)
dimension zw(0:51),rd(0:51),rp(101),y12(2,0:51,51),
y13(2,0:51,101),y21(2,51,51),y22(2,51,51),y31(2,101,51),
phi3(101),phi2n(0:51),phi3o(101),phi2(0:51),
y23a(51),y13a(0:51),cd(0:51),y23(2,51,101),y32(2,101,51)
1,phi1(0:51),y31p(2,101,0:51),y21p(2,51,51),philcd(0:51)
common y21,y22,y23,y31,y32,zw,rp,zstart,zstop,pl,ic,jc
1,rd,nd,mp,nw,pp,damp,pi,y23a,y12,y13,y13a,philcd,y31p,y21p,cd
if (id.eq.1) then
  ord--f2(x,zw(ic),1.0d0,1.0d0)
else if (id.eq.2) then
  ord--f2(x,zw(ic),1.0d0,1.0d0)*x
else if (id.eq.3) then
  ord--f1(0.0d0,zw(ic),x,1.0d0)*x
else if (id.eq.4) then
  ord--f3(pl,zw(ic),x+1.0d0,1.d0)*(x+1.0d0)
else if (id.eq.5) then
  ord--f3(pl,zw(ic),x+1.0d0,1.d0)*x**2
else if (id.eq.6) then
  ord--f3(pl,zw(ic),x+1.0d0,1.d0)*x*(x+1.0d0)
else if (id.eq.7) then
  ord--f3(0.0d0,zw(ic),x,1.0d0)*x
else if (id.eq.8) then
  if (dabs(x-zw(ic)).le.1d-8 then
    ord--0.5d0/pi*(1.0d0-dlog(2.0d0)
else
    ord--f2(x,zw(ic),1.0d0,1.0d0)+
1 dlog((x-zw(ic))**2/16.0d0)/4.0d0/pi
end if
else if (id.eq.9) then
  if (dabs(x-zw(ic)).le.1d-8 then
    ord--x/2.0d0/pi*(1.0d0-dlog(2.0d0))
else
    ord--(-f2(x,zw(ic),1.0d0,1.0d0)+dlog((x-zw(ic))**2/16.0d0)
1 /4.0d0/pi)*x
end if
else if (id.eq.10) then
  ord--f1(0.0d0,pl,x,rp(ic))*x
else if (id.eq.11) then
  ord--f1(0.0d0,pl,x,rp(ic))*x**2
else if (id.eq.12) then
  ord--f2(x,pl,1.0d0,rp(ic))
else if (id.eq.13) then
    ord=f2(x,pl,1.0d0,rp(ic))*x
else if (id.eq.14) then
    ord=f3(0.0d0,pl,x,rp(ic))*x
else if (id.eq.15) then
    ord=f2(x,0.0d0,1.0d0,rd(ic))
else if (id.eq.16) then
    ord=f2(x,0.0d0,1.0d0,rd(ic))*x
else if (id.eq.17) then
    ord=f3(pl,0.0d0,x+1.0d0,rd(ic))*(x+1.0d0)
else if (id.eq.18) then
    ord=f3(pl,0.0d0,x+1.0d0,rd(ic))*x*(x+1.0d0)
else if (id.eq.19) then
    yq=dcos(pi/2.0d0*(1.0d0-rd(ic))
    y=dcos(pi/2.0d0*(1.0d0-x))
    if (dabs(x-rd(ic)).le.1.0d-7) then
        ord=dlog(8.0d0*rd(ic))/pi*P(jc,yq)
    else
        ord=-f1(0.0d0,0.0d0,x+1.0d0,rd(ic))*x*P(jc,yq)
        P(jc,yq)*dlog((x-rd(ic))*2)/pi/2.0d0
    end if
else if (id.eq.20) then
    y=dcos(pi/2.0d0*(1.0d0-x))
    ord=-x/(rd(ic)+x)*P(jc,y)
else if (id.eq.21) then
    ord=f3(0.0d0,zw(ic),x,1.0d0)**2
else if (id.eq.22) then
    ord=f3(0.0d0,pl,x,rp(ic))*x**2
else if (id.eq.26) then
    if (x.1e.1d-8) then
        ord=-0.5d0/pi*(1.0d0-dlog(2.0d0))
    else
        ord=f2(x,0.0d0,1.0d0,1.0d0)+dlog(x**2/16.0d0)/4.0d0/pi
    end if
else if (id.eq.25) then
    if (x.1e.1d-8) then
        ord=x/2.0d0/pi*(1.0d0-dlog(2.0d0))
    else
        ord=((-f2(x,0.0d0,1.0d0,1.0d0)+dlog(x**2/16.0d0)/4.0d0/pi)*x
    end if
else
    print*, 'Invalid ID number'
    stop
end if
return
end if

This is the Green's function for axisymmetric problems.

function fl(z,zq,r,rq)
implicit double precision(a-h,o-z)
pi=3.14159265358979d0
$w = \frac{(r-rq)^2+(z-zq)^2}{((r+rq)^2+(z-zq)^2)}$

$f1 = 2.0d0/pi*e1(w)/dsqrt((z-zq)^2+(r+rq)^2)$

return
end

---

This is the $r$-component of the gradient of the Green's function

function f2(z,zq,r,rq)
  implicit double precision(a-h,o-z)
  pi=3.14159265358979d0
  $w = \frac{(r-rq)^2+(z-zq)^2}{((r+rq)^2+(z-zq)^2)}$
  $zd = z-zq$
  f2 = -(e2(w)*((r**2-rq**2-zd**2)/((r-rq)^2+zd^2)) + e1(w))/2.0d0/r/
  1 dsqrt((r+rq)**2+zd**2)*2.0d0/pi
  return
end

---

This is the $z$-component of the gradient of the Green's function.

function f3(z,zq,r,rq)
  implicit double precision(a-h,o-z)
  pi=3.14159265358979d0
  $w = \frac{(r-rq)^2+(z-zq)^2}{((r+rq)^2+(z-zq)^2)}$
  $zd = z-zq$
  f3 = -2.0d0/pi*zd*e2(w)/(r+rq)**2+zd**2)/dsqrt(zd**2+(r+rq)**2)
  return
end

---

Complete Elliptic Integral of the First Kind

function e1(w)
  implicit double precision (a-h,o-z)
  dimension a(5),b(5)
  data a / 1.38629436112d0, .09666344259d0, 0.03590092383d0
  1, .0374263713d0, .01451196212d0/
  data b / .5d0, .12498593597d0, .06880248576d0,
  1 .03328355346d0, .00441787012d0/
  a = a(1) + a(2)*w + a(3)*w**2 + a(4)*w**3 + a(5)*w**4
  e1 = d + (b(1) + b(2)*w + b(3)*w**2 + b(4)*w**3 + b(5)*w**4)*dlog(1.0d0/w)
  return
end

---

Complete Elliptic Integral of the Second Kind

function e2(w)
  implicit double precision (a-h,o-z)
  dimension c(4),d(4)
  data c / .44325141463d0, .0626061220d0, 0.04757383546d0,
  1 .01736506451d0/
  data d / .2498386831d0, .09200180037d0, .04069697526d0,
  1 .0052644639d0/
  a = a(1) + a(2)*w + a(3)*w**2 + a(4)*w**3 + a(5)*w**4
  e2 = a + (d(1)*w + d(2)*w**2 + d(3)*w**3 + d(4)*w**4)*dlog(1.0d0/w)
  end
subroutine pread
implicit double precision(a-h,o-z)
dimension zw(0:51),rd(0:51),rp(101),y12(2,0:51,51),
ly13(2,0:51,101),y21(2,51,51),y22(2,51,51),y31(2,101,51),
phi3(101),phi2n(0:51),phi30(101),phi2(0:51),
ly23a(51),y13a(0:51),cd(0:51),y23(2,51,101),y32(2,101,51)
1,phi1(0:51),y3lp(2,101,0:51),y2lp(2,51,51),philcd(0:51)
common y21,y22,y23,y31,y32,zw,rp,zstart,zstop,pl,ic,jc
1,rd,nd,np,nw,pp,damp,pi,y23a,y12,y13,y13a,philcd,y3lp,y2lp,cd
read*,np,nw,nd
read*,pl
zstop=100.00d0
zstart=0.01d0
damp=0.5d0
hp=dlog(zstop/zstart)/(dfloat(np-1))
do 1 i=0,nw-5
1 zw(i)=(pl-0.1d0)*dfloat(i)/dfloat(nw-5)
do 100 i=1,5
100 zw(nw-5+i)=pl-0.1d0+0.1d0*dfloat(i)/dfloat(5)
do 2 i=1,np
2 rp(i)=1.0d0-zstart*exp(hp*dfloat(i-1))
do 3 i=0,nd
3 rd(i)=dfloat(i)/dfloat(nd)
returnend

subroutine current(icurr)
implicit double precision(a-h,o-z)
dimension zw(0:51),rd(0:51),rp(101),y12(2,0:51,51),
ly13(2,0:51,101),y21(2,51,51),y22(2,51,51),y31(2,101,51),
phi3(101),phi2n(0:51),phi30(101),phi2(0:51),
ly23a(51),y13a(0:51),cd(0:51),y23(2,51,101),y32(2,101,51)
1,phi1(0:51),y3lp(2,101,0:51),y2lp(2,51,51),philcd(0:51)
common y21,y22,y23,y31,y32,zw,rp,zstart,zstop,pl,ic,jc
1,rd,nd,np,nw,pp,damp,pi,y23a,y12,y13,y13a,philcd,y3lp,y2lp,cd
do 1 i=0,nd
x=dcos(pi/2.0d0*(1.0d0-rd(i)))
1 cd(i)=-P(icurr,x)
md=1000
do 2 ic=1,nd-1
  call integ4(rd(ic),0.0d0,md,19,icurr)
  philcd(ic)=-pp
  call integ4(1.0d0,rd(ic),md,19,icurr)
  philcd(ic)=philcd(ic)-pp
2 continue
ic=nd
do 1000
continue
ic=0
call integ4(1.0d0,0.0d0,md,20,icurr)
philcd(0)=-pp
Calculation of Legendre Polynomials

function P(n,x)
implicit double precision(a-h,o-z)
p1=1.d0
p2=x
if(n-1)1,2,3
1 P=p1
return
2 P=p2
return
3 nml=n-1
do 4 nu=1,nml
P=(x*dfloat(2*nu+1)*p2-dfloat(nu)*p1)/dfloat(nu+1)
p1=p2
4 p2=P
return
end