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# CURRENT DISTRIBUTION AND MASS TRANSFER IN ELECTROCHEMICAL SYSTEMS

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# Current Distribution and Mass Transfer in Electrochemical Systems

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## Abstract

Principles of current distribution are related to fundamental transport equations. Application of these principles in the past has followed mainly two courses - treatment of systems analogous to those of heat and nonelectrolytic mass transfer and applications of potential theory, where the potential distribution satisfies Laplace's equation. These results are illustrated for two plane electrodes forming part of the walls of a flow channel. Problems of an intermediate nature include the effect of ionic migration on limiting currents and current distribution below the limiting current.

# Introduction

Fundamental equations describing transport in dilute electrolytic solutions have been known since the turn of the century. In an electrochemical system, many processes occur simultaneously, and the treatment of such problems involves consideration of the ohmic potential drop, concentration changes near electrodes, and the kinetics of the heterogeneous electrode reaction.

Application of these principles has followed two main courses. There are systems where the ohmic potential drop can be neglected. The current distribution is then determined by the same principles which apply to heat transfer and non-electrolytic mass transfer. This usually involves systems operated at the limiting current with an excess of supporting electrolyte, because below the limiting current it is usually not justified to neglect the ohmic potential drop and because the presence of the supporting electrolyte allows the effect of ionic migration in the diffusion layer to be ignored. Furthermore, the concentration of the reactant is zero at the electrode surface, and the treatment becomes simplified. Let us call these "convective-transport problems."

At currents much below the limiting current, it is possible to neglect concentration variations near the electrodes. The current distribution is then determined by the ohmic potential drop in the solution and by electrode overpotentials. Mathematically, this means that the potential satisfies Laplace's equation, and many results of potential theory, developed in electrostatics, the flow of inviscid fluids, and steady heat conduction in solids, are directly applicable. Let us call these "potential-theory problems." The electrode kinetics provide boundary conditions which are usually different from those encountered in other applications of potential theory.

Problems have been treated which do not fall within either of these two classes. Some problems can be regarded as an extension of the convective-transport problems. At the limiting current the ohmic potential drop in the bulk of the solution may still be negligible, but the electric field in the diffusion layer near electrodes may lead to an enhancement of the limiting current. The current density is then distributed along the electrode in the same manner as when migration is neglected, but the magnitude of the current density at all points is increased or diminished by a constant factor which depends upon the bulk composition of the solution.

At currents below, but at an appreciable fraction of, the limiting current, diffusion and convective transport are essential, but neither concentration variations near the electrode nor the ohmic potential drop in the bulk solution can generally be neglected. These problems are complex because all the factors are involved at once.

In porous electrodes convection may not be present, but it is usually necessary to consider the ohmic potential drop, concentration variations, and electrode kinetics. Most treatments adopt a macroscopic model which does not take account of the detailed, random geometry of the porous structure. Results of potential theory are then not applicable since Laplace's equation does not hold. Because porous electrodes do not fit in well with the other electrolytic cells considered, their treatment is omitted from this paper.

## Fundamental Equations

### Transport in electrolytic solutions

The laws of transport in dilute electrolytic solutions have been known for many years and have been discussed in detail elsewhere[1,2]. The flux of a species is due to migration in an electric field, diffusion due to a concentration gradient, and convection with the fluid velocity.

$$\underline{N}_i = -z_i u_i F c_i \nabla\Phi - D_i \nabla c_i + \underline{v} c_i \ . \qquad (1)$$

A material balance for a small volume element leads to the differential conservation law:

$$\frac{\partial c_i}{\partial t} = -\nabla\cdot\underline{N}_i + R_i \ . \qquad (2)$$

Since reactions are frequently restricted to the surfaces of electrodes, the bulk reaction term $R_i$ is often zero in electrochemical systems. To a very good approximation the solution is electrically neutral,

$$\sum_i z_i c_i = 0, \qquad (3)$$

except in the diffuse part of the double layer very close to an interface. The current density in an electrolytic solution is due to the motion of charged species:

$$\underline{i} = F \sum_i z_i \underline{N}_i \ . \qquad (4)$$

These laws provide the basis for the analysis of electrochemical systems. The flux relation (1) defines transport coefficients--the mobility $u_i$ and the diffusion coefficient $D_i$ of an ion in a dilute solution. Many electrochemical systems involve flow of the electrolytic solution. The fluid velocity is to be determined from the Navier-Stokes equation

$$\rho \left( \frac{\partial \underline{v}}{\partial t} + \underline{v}\cdot\nabla\underline{v} \right) = -\nabla p - \mu\nabla^2\underline{v} + \rho\underline{g} \qquad (5)$$

and the continuity equation

$$\nabla\cdot\underline{v} = 0 \ . \qquad (6)$$

## Electrode kinetics

The differential equations describing the electrolytic solution require boundary conditions in order for the behavior of an electrochemical system to be predicted. The most complex of these concerns the kinetics of electrode reactions. A single electrode reaction can be written in symbolic form as

$$\sum_i s_i M_i^{z_i} \rightarrow ne^- \; . \tag{7}$$

Then the normal component of the flux of a species is related to the normal component of the current density, that which contributes to the external current to the electrode.

$$N_{in} = - \frac{s_i}{nF} i_n \; . \tag{8}$$

This equation is restricted not only to a single electrode reaction but also to the absence of an appreciable charging of the double layer, a process which does not follow Faraday's law.

Next one needs an equation describing the kinetics of the electrode reaction, that is, an equation which relates the normal component of the current density to the surface overpotential at that point and the composition of the solution just outside the diffuse part of the double layer. The motivation of the electrochemical engineer in this regard is basically different from that of an electrochemist. The object is to predict the behavior of a complex electrochemical system rather than to elucidate the mechanism of an electrode reaction. For this purpose one needs an equation which describes accurately how the interface behaves during the passage of current, and for this purpose the interface includes the diffuse part of the double layer.

The surface overpotential $\eta_s$ can be defined as the potential of the working electrode relative to a reference electrode of the same kind located just outside the double layer. Then one seeks a kinetic expression of the form

$$i_n = f(\eta_s, c_i) , \tag{9}$$

where charging of the double layer is again ignored. The concentrations $c_i$ here refer to the point just outside the double layer. Such an expression thus describes the interface since $i_n$, $\eta_s$, and $c_i$ are all local quantities. In particular, the concentration variation between the interface and the bulk solution and the ohmic potential drop in the solution have only an incidental bearing on events at the interface. At the same time no attempt is made to give a separate account of the diffuse part of the double layer.

The function f in equation (9) is in general complicated. However, there is ample evidence that there is a large class of electrode reactions for which the current density depends exponentially on the surface overpotential in the following form:

$$i_n = i_o \left[ \exp \left\{ \frac{\alpha n F}{RT} \eta_s \right\} - \exp \left\{ - \frac{(1-\alpha) n F}{RT} \eta_s \right\} \right] , \tag{10}$$

where $i_o$ is the exchange current density and depends on the concentrations $c_i$. This latter dependence can frequently be expressed as a product of powers of the concentrations. In this equation, $i_n$ and $\eta_s$ are positive for anodic processes, negative for cathodic processes. Both $\alpha$ and n are kinetic parameters and must be determined to agree with experimental data.

Information on electrode kinetics can be found in the literature[3,4,5]. This is often interpreted from the point of view of reaction mechanisms and not with the object of predicting the behavior of electrochemical systems.

## Convective-Transport Problems

For the reaction of minor ionic species in a solution containing excess supporting electrolyte, it should be permissible to neglect the contribution of ionic migration to the flux of the reacting ions, so that equation (1) becomes

$$\underline{N}_i = -D_i \nabla c_i + \underline{v} c_i \, , \tag{11}$$

and substitution into equation (2) yields

$$\frac{\partial c_i}{\partial t} + \underline{v} \cdot \nabla c_i = D_i \nabla^2 c_i \, . \tag{12}$$

This may be called the equation of convective diffusion. A similar equation applies to convective heat transfer and convective mass transfer in non-electrolytic solutions. Since these fields have been studied in detail, it is possible to apply many results to electrochemical systems which obey equation (12). At the same time electrochemical systems sometimes provide the most convenient experimental means of testing these results or arriving at new results for systems too complex to analyze.

Essential to the understanding of convective-transport problems is the concept of the diffusion layer. Frequently, due to the small value of the diffusion coefficient, the concentrations differ significantly from their bulk values only in a thin region near the surface of an electrode. In this region the velocity is small, and diffusion is important to the transport process. The thinness of this region permits a simplification in the analysis, but it is erroneous to treat the diffusion layer as a stagnant region. Figure 1 shows the concentration profile in the diffusion layer, with the electrode surface at the left. Far from the surface, convective transport dominates, while at the surface itself there is only diffusion.

The systems typically studied in heat and mass transfer involve laminar and turbulent flow with various geometric arrangements. The flow may be due to some more or less well characterized stirring (forced convection)

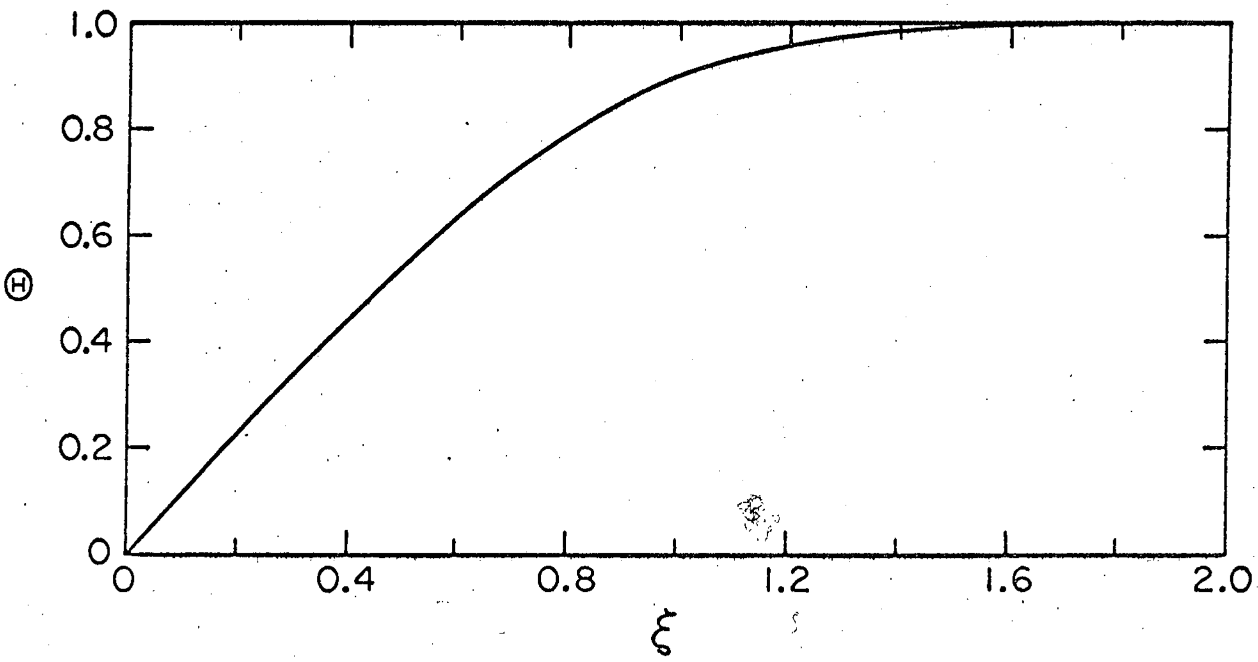

Figure 1. Concentration profile in the diffusion layer.

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or may be the result of density differences created in the solution as part of the transfer process (free convection). We shall discuss here a few examples, although there is no need to be exhaustive since convective heat and mass transfer is thoroughly treated in many texts and monographs[6,7,8,9]. There are also several reviews of mass transfer in electrochemical systems [10,11,12]. The examples selected are primarily those which have been studied with electrochemical systems. In addition certain theoretical results of general validity are included because they are particularly applicable to electrolytic solutions, where the Schmidt numbers are invariably large.

## The annulus

Axial flow in the annular space between two concentric cylinders provides a convenient situation for experimental studies of mass transfer. In the work of Lin, Denton, Gaskill, and Putnam[13] the electrode of interest formed part of the inner cylinder while the outer cylinder formed the counter electrode. However, their experimental results and theoretical treatment have been severely criticized by Friend and Metzner[14]. Ross and Wragg[15] reviewed the problem and performed additional experiments with a similar arrangement. A circular tube with no inner cylinder is a limiting case of the annular geometry and has been studied by Van Shaw, Reiss, and Hanratty[16]. Another limiting case investigated by Tobias and Hickman[17] is the flow between two plane electrodes.

Let the radius of the outer cylinder be R, and the radius of the inner cylinder be $\kappa R$. The electrode of interest is of length L and is located far enough downstream in the annulus that the velocity distribution is fully developed before this electrode is reached. A limiting current is reached at this electrode when the concentration of the reactant drops to zero at the surface.

For laminar flow in the annulus, the local, limiting current density should follow the theoretical expression

$$i_n = 0.8546 \frac{nF D_i c_\infty}{s_i} \left( \frac{\langle v \rangle \phi}{(1-\kappa) R D_i x} \right)^{1/3} , \tag{13}$$

where $\langle v \rangle$ is the average velocity in the annulus, x is the distance from the upstream edge of the electrode, and $\phi^{1/3}$ is a function of the geometric parameter $\kappa$ and is shown in figure 2 for both the inner and the outer electrode.

Mass transfer in laminar flow is very similar to the classical Graetz-Nusselt-Lévêque problem (see Jakob[18]). Equation (13) is valid only when the concentration variation is confined to a thin diffusion layer near the electrode surface, as it is for small values of x. However, for electrochemical systems the diffusion coefficient is small, and consequently the diffusion layer grows in thickness slowly with increasing x. It might be estimated[15] that equation (13) is valid for

$$x < 0.01 \text{ Re Sc } d_e , \tag{14}$$

where $d_e = 2(1-\kappa)R$ is the equivalent diameter of the annulus, $Re = d_e \langle v \rangle / \nu$ is the Reynolds number, and $Sc = \nu/D_i$ is the Schmidt number. For Sc = 2,000 and Re = 500, this condition yields

$$x < 10^4 d_e , \tag{15}$$

and is usually satisfied in the experiments.

In order to facilitate comparison of results for different systems and with the standard correlations of heat and mass transfer, equation (13) is frequently written in dimensionless form.

$$Nu(x) = 1.0767 (\phi \text{ Re Sc } d_e/x)^{1/3} , \tag{16}$$

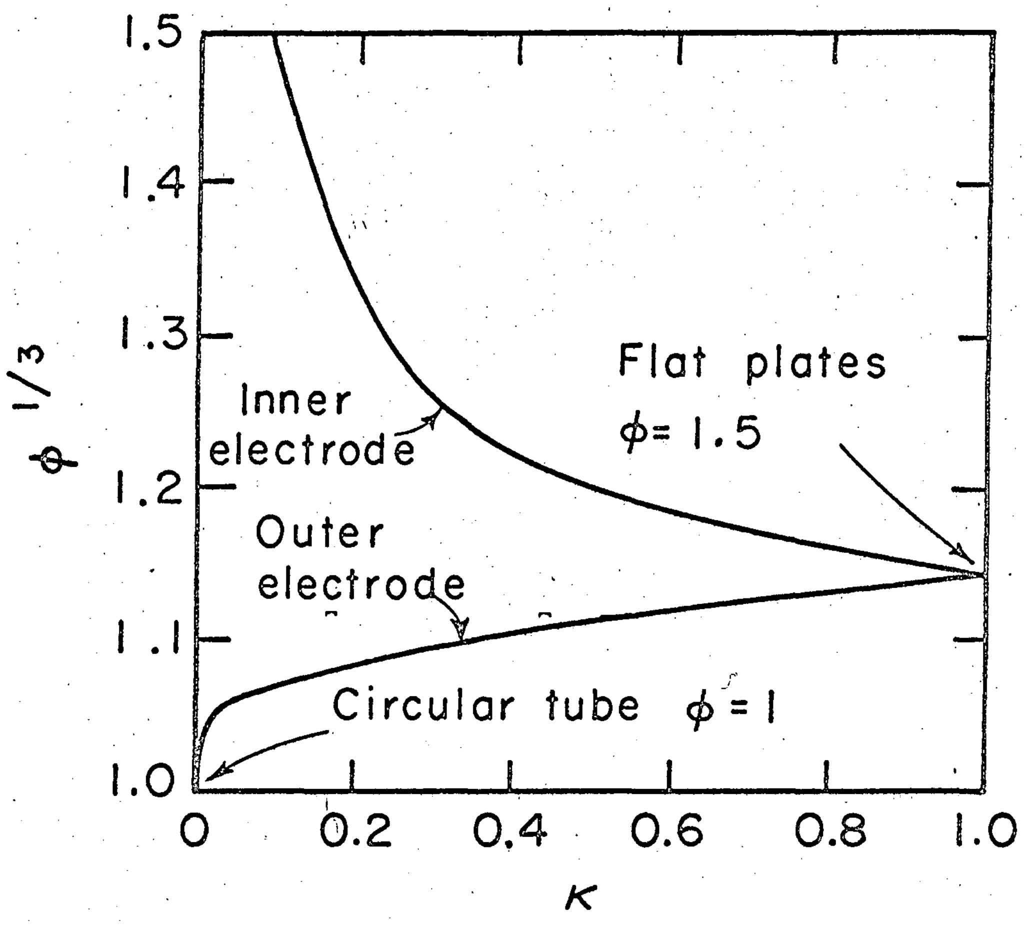

Figure 2. Coefficient for mass transfer in annuli.

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where the Nusselt number is a dimensionless mass-transfer rate:

$$Nu(x) = -N_i d_e / c_\infty D_i \ . \tag{17}$$

The average value of the Nusselt number, corresponding to the average mass-transfer rate over the length L, is

$$Nu_{avg} = 1.6151 \ (\phi \ Re \ Sc \ d_e/L)^{1/3} \ . \tag{18}$$

As $\kappa \rightarrow 1$, these results apply to the flow between two flat plates, parts of which form plane electrodes. Then $\phi = 1.5$, and equations (13), (16), and (18) become

$$i_n = 0.9783 \ \frac{nF \ D_i \ c_\infty}{s_i} \left( \frac{\langle v \rangle}{h \ D_i \ x} \right)^{1/3} , \tag{19}$$

where $h = (1-\kappa)R$ is the distance between the planes,

$$Nu(x) = 1.2325 \ (Re \ Sc \ d_e/x)^{1/3} , \tag{20}$$

$$Nu_{avg} = 1.8488 \ (Re \ Sc \ d_e/L)^{1/3} . \tag{21}$$

In figure 3 the curve denoted "limited by convection and diffusion" depicts the local current density as a function of position along the electrode. The mass-transfer rate is infinite at the upstream edge of the electrode where fresh solution is brought in contact with the electrode. The current decreases with increasing x since the solution in the diffusion layer has already been depleted by the electrode reaction further upstream. Later it will be instructive to compare this current distribution with that which would be obtained when the ohmic potential drop in the solution is controlling.

The results of Lin, Denton, Gaskill, and Putnam[13] for laminar flow fall roughly 17 percent below the values predicted by equation (18). Part of this discrepancy can be attributed to the fact that some of the diffusion coefficients were determined by fitting these experimental results to an

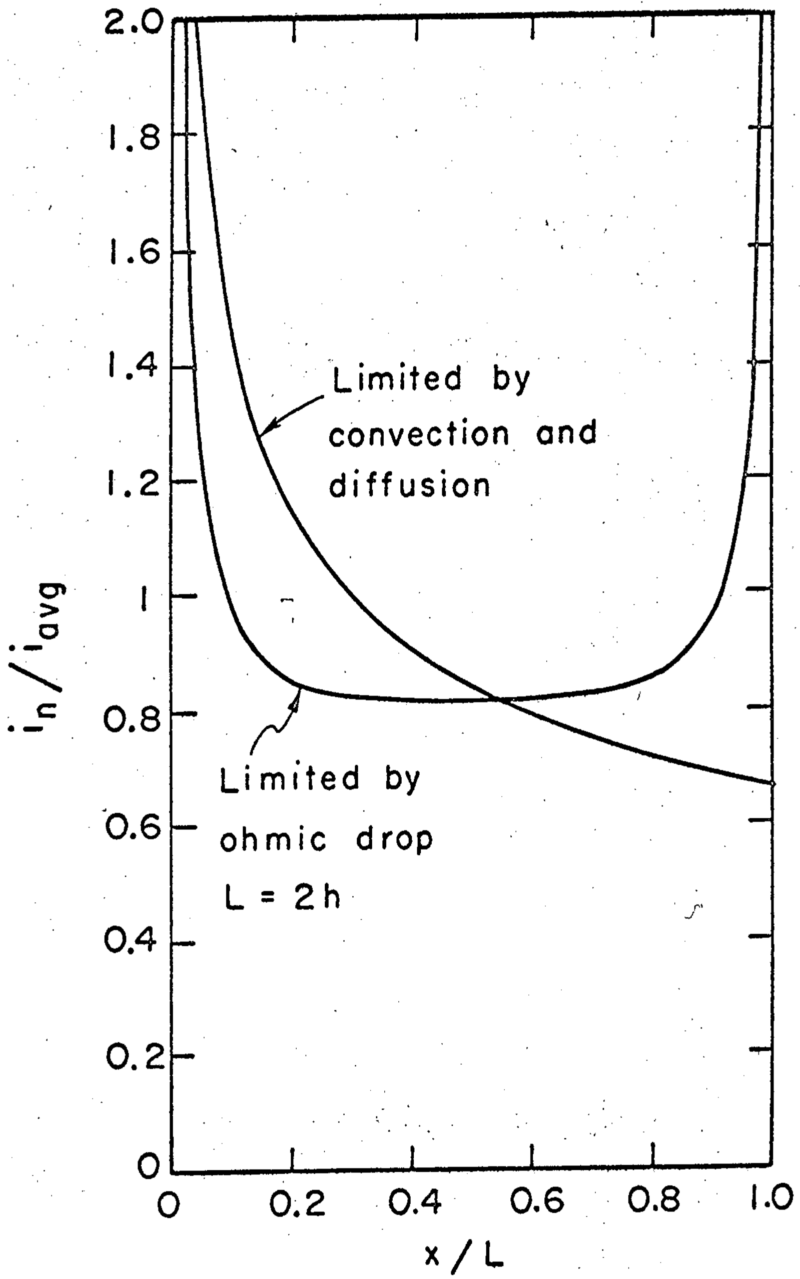

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Figure 3. Current distribution on planar electrodes.

erroneous equation. Ross and Wragg's[15] laminar results are 9 to 13 percent below those predicted, while those of Tobias and Hickman[17] scatter within 7 percent of the values predicted by equation (21).

Turbulent flow is characterized by rapid and random fluctuations of the velocity and pressure about their average values. The turbulence is greater at a distance from solid walls, and the fluctuations gradually go to zero as the wall is approached. The fluctuations in velocity result in fluctuations in concentration and also in enhanced rates of mass transfer. Near the wall the fluctuations go to zero, and mass transfer at the wall is by diffusion. The details of the nature of the fluctuations are important in the region near the wall where diffusion and turbulent transport contribute roughly equally to the mass transfer rate.

In the mass-transfer entry region in turbulent flow, Van Shaw, Reiss, and Hanratty[16] expect the average Nusselt number in circular tubes to be given by

$$Nu_{avg} = 0.276\ Re^{0.58} Sc^{1/3} (d_e/L)^{1/3} \ . \tag{22}$$

The experimental results fall 7 percent below these values but exhibit the same dependence upon the Reynolds number and the electrode length. The data of Ross and Wragg[15] for the inner cylinder of an annulus with $\kappa = 0.5$ are correlated by equation (22). However, in this geometry, those authors expect the coefficient to be 9 percent higher.

The mass-transfer entry region where equation (22) applies is much shorter in turbulent flow than in laminar flow. The results of Van Shaw, Reiss, and Hanratty[16] indicate that this length ranges from 2 diameters to 0.5 diameter as the Reynolds number ranges from 5,000 to 75,000.

Beyond this short entry region, the Nusselt number rapidly approaches a constant value, corresponding to fully-developed mass transfer. It is surprising that fully-developed mass transfer has not been studied more extensively with electrochemical systems. The results of Lin, Denton, Gaskill, and Putnam[13] agree well with the equation of Chilton and Colburn[19] for heat transfer:

$$Nu_{avg} = 0.023\ Re^{0.8} Sc^{1/3} . \tag{23}$$

Friend and Metzner[14] discuss critically the applicability of such an equation for Schmidt numbers as large as those encountered in electrochemical systems. However, Hubbard[20] also obtained agreement with this equation.

<u>Two-dimensional diffusion layers in laminar forced convection</u>

In 1942 Levich[21], in treating electrolytic mass transfer to a rotating disk, remarked that in the case of diffusion, particularly the diffusion of ions, the Schmidt number reaches the value of several thousands. "Thus, in this case we deal with a peculiar limiting case of hydrodynamics, which may be called the hydrodynamics of Prandtl's [or Schmidt's] large numbers." Lighthill[22] developed a solution for the heat-transfer rate applicable when the region of temperature variation is thin compared to the region of velocity variation. Acrivos[23] realized that this method is applicable to a wide range of problems when the Schmidt number is large. Thus, for electrochemical systems where the Schmidt number is generally large, it is frequently possible to obtain the concentration distribution and the rate of mass transfer for steady problems when the velocity distribution near the electrode is known in advance. Many results for electrolytic mass transfer can be regarded as special cases of the application of this method.

The concentration distribution in a thin diffusion layer near an electrode is governed by the equation

$$v_x \frac{\partial c_i}{\partial x} + v_y \frac{\partial c_i}{\partial y} = D_i \frac{\partial^2 c_i}{\partial y^2} \,. \tag{24}$$

This equation is restricted to two-dimensional flow past an electrode, with x measured along the electrode from its upstream end and y measured perpendicularly from the surface into the solution.

Due to the thinness of the diffusion layer compared to the region of variation of the velocity, it is permissible to approximate the velocity components by their first terms in Taylor's expansions in the distance y from the wall:

$$v_x = y\beta(x) \quad \text{and} \quad v_y = -\tfrac{1}{2}\, y^2 \beta'(x) \,, \tag{25}$$

where $\beta(x)$ is the velocity derivative $\partial v_x/\partial y$ evaluated at the wall ($y=0$). These expressions for the velocity thus satisfy the applicable form of equation (6):

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 \,, \tag{26}$$

as well as the boundary conditions $v_x = v_y = 0$ at $y = 0$. With this approximation, equation (24) becomes

$$y\beta \frac{\partial c_i}{\partial x} - \tfrac{1}{2}\, y^2 \beta' \frac{\partial c_i}{\partial y} = D_i \frac{\partial^2 c_i}{\partial y^2} \,. \tag{27}$$

If the concentration at the surface is a constant $c_o$, then the concentration profiles at different values of x are similar and depend only on the combined variable

$$\xi = y\sqrt{\beta} \Big/ \left[ 9D_i \int_0^x \sqrt{\beta}\, dx \right]^{1/3} . \tag{28}$$

In terms of this similarity variable, the concentration profile is given by

$$\Theta = \frac{c_i - c_o}{c_\infty - c_o} = \frac{1}{\Gamma(4/3)} \int_0^\xi e^{-\xi^3}\, d\xi \,, \tag{29}$$

where $\Gamma(4/3) = 0.89298$. This function is plotted in figure 1 and has been tabulated[24].

The limiting current density (for $c_o = 0$) is thus

$$i_n = \frac{nF\, D_i\, c_\infty \sqrt{\beta}}{s_i \Gamma(4/3)} \Bigg/ \left[9D_i \int_0^x \sqrt{\beta}\, dx\right]^{1/3} . \tag{30}$$

Equation (19) for flow between two plates is a special case of equation (30) for which β is independent of x and has the value $6 \langle v \rangle /h$. Equation (30) gives the rate of mass transfer if β is already known.

Axisymmetric diffusion layers in laminar forced convection

Equation (24) also applies to steady mass transfer in axisymmetric diffusion layers, that is, where the electrode forms part of a body of revolution. Examples would be the annulus considered earlier, a sphere, and a disk electrode. The coördinates x and y have the same meaning; x is measured along the electrode from its upstream end and y is measured perpendicularly from the surface into the solution. It is also necessary to specify the normal distance r(x) of the surface from the axis of symmetry.

The applicable form of equation (6) now is (see Schlichting[9], p. 185)

$$\frac{\partial(rv_x)}{\partial x} + r\frac{\partial v_y}{\partial y} = 0 . \tag{31}$$

Due to the thinness of the diffusion layer it is still permissible to approximate the velocity components by their first terms in Taylor's expansions in y. However, in view of equation (31), these now take the form

$$v_x = y\beta(x) \quad \text{and} \quad v_y = -\tfrac{1}{2}\, y^2 (r\beta)'/r , \tag{32}$$

and equation (24) becomes

$$y\beta \frac{\partial c_i}{\partial x} - \tfrac{1}{2}\, y^2 \frac{(r\beta)'}{r} \frac{\partial c_i}{\partial y} = D_i \frac{\partial^2 c_i}{\partial y^2} . \tag{33}$$

The concentration profile is again given by equation (29) in terms of the similarity variable

$$\xi = y\sqrt{r\beta} \Bigg/ \left[9D_i \int_0^x r\sqrt{r\beta}\, dx\right]^{1/3} , \qquad (34)$$

and the limiting current density is

$$i_n = \frac{nF\, D_i\, c_\infty \sqrt{r\beta}}{s_i \Gamma(4/3)} \Bigg/ \left[9D_i \int_0^x r\sqrt{r\beta}\, dx\right]^{1/3} . \qquad (35)$$

Equation (13) for the annulus is a special case of equation (35) in which r and $\beta$ are independent of x.

A flat plate in a free stream

The steady, laminar hydrodynamic flow parallel to a flat plate beginning at x = 0 and extending along the positive x-axis has been treated extensively. The value of the velocity derivative at the surface is (see Schlichting[9], p. 120)

$$\beta = 0.33206\, v_\infty \sqrt{v_\infty/\nu x} , \qquad (36)$$

where $v_\infty$ is the value of $v_x$ far from the plate. Substitution into equation (30) yields

$$i_n = 0.3387 \frac{nF\, D_i\, c_\infty}{s_i} \left(\frac{v_\infty}{\nu x}\right)^{1/2} \left(\frac{\nu}{D_i}\right)^{1/3} . \qquad (37)$$

The average Nusselt number for an electrode of length L is

$$Nu_{avg} = \frac{s_i\, L\, i_{avg}}{nF\, D_i\, c_\infty} = 0.6774\, Re_L^{1/2}\, Sc^{1/3} , \qquad (38)$$

where $Re_L = L\, v_\infty/\nu$. These results apply to laminar flow. The flow becomes turbulent at a Reynolds number of about $10^5$.

Electrochemical systems for which these results are directly applicable are not frequently encountered. Unfortunately the analysis for a flat plate in a free stream has been applied to annular geometries and the flow between two flat plates[25,26,27], which should follow equations (13) and (19).

Rotating cylinders

Mass transfer between concentric cylinders, the inner of which is rotating with an angular speed $\Omega$, has been studied by Eisenberg, Tobias, and Wilke[28] and by Arvia and Carrozza[29]. If the flow between the electrodes is tangential and laminar, it does not contribute to the rate of mass transfer since the flow velocity is perpendicular to the mass flux. At higher rotation speeds, the flow is still laminar but no longer tangential, and so-called Taylor vortices are formed. Superimposed on the tangential motion is a radial and axial motion, outward at one point and inward at a different axial position. At still higher rotation speeds, the flow becomes turbulent. Mass transfer in this turbulent flow, which is achieved at lower rotation speeds if the inner cylinder rotates rather than the outer, has been studied in the above-mentioned works.

By the nature of the geometric arrangement, the current distribution is uniform. The results have been correlated by the equation

$$i_n = 0.0791 \frac{nF\, D_i\, c_\infty}{s_i d_R} \left(\frac{\Omega d_R^3}{2\nu d_L}\right)^{0.70} \left(\frac{\nu}{D_i}\right)^{0.356} , \tag{39}$$

or, in dimensionless form,

$$\mathrm{Nu} = 0.0791\ (\mathrm{Re}\ d_R/d_L)^{0.70}\ \mathrm{Sc}^{0.356} , \tag{40}$$

where $d_R$ is the diameter of the inner, rotating cylinder, $d_L$ is the diameter of the cylinder with the limiting current, $\mathrm{Nu} = i_n s_i d_R/nF\, D_i\, c_\infty$ is the Nusselt number, and $\mathrm{Re} = \Omega d_R^2/2\nu$ is the Reynolds number.

In the work of Eisenberg, Tobias, and Wilke the limiting electrode was the inner, rotating electrode, and $d_R = d_L$. The results, for which the

Reynolds number ranged from 112 to 162,000 and the Schmidt number from 2230 to 3650, agree with equations (39) and (40) within 8.3 percent. Arvia and Carrozza measured the limiting rates of mass transfer at the stationary, outer electrode.

Growing mercury drops

Limiting diffusion currents to a dropping mercury electrode find important applications in the quantitative analysis of electrolytic solutions. Let the mercury flow at a constant rate from the capillary tube to the drop growing at the tip, so that the radius increases as

$$r_o = \gamma t^{1/3} . \tag{41}$$

The diffusion layer on the drop has a thickness proportional to $\sqrt{t}$. Ilkovič[30,31] and also Mac Gillavry and Rideal[32] treated the problem with the assumption that the diffusion layer is thin compared to the radius of the drop.

For radial growth of the drop, without tangential surface motion, the limiting current density is

$$i_n = \frac{nF\ c_\infty}{s_i} \sqrt{\frac{7D_i}{3\pi t}}\ [1 + 1.0302\ D_i^{1/2}\ t^{1/6}/\gamma] . \tag{42}$$

This equation, without the correction term, was first derived by Ilkovič. The correction term, which accounts for the greater thickness of the diffusion layer and for which at least three different values of the coefficient can be found in the literature, was first derived correctly by Koutecký[33]. (We have carried this slightly further[84] to express the coefficient in terms of gamma functions:

$$1.0302 = \sqrt{3/7}\ 16\Gamma(15/14)/11\Gamma(11/7).)$$

The total current to the drop, averaged over the life time T of the drop, then takes the form

$$I_{avg} = 3.5723 \frac{nF\ c_\infty}{s_i} D_i^{1/2} m^{2/3} T^{1/6} \left[1+1.4530(D_i^3 T/m^2)^{1/6}\right] , \qquad (43)$$

where m is the volumetric flow rate of the mercury ($cm^3/sec$).

Since, in the absence of tangential surface motion, the convective flow is well defined, the dropping mercury electrode has frequently been used for the determination of diffusion coefficients.

The rotating disk

When a circular disk is rotated with an angular velocity $\Omega$ about its axis in a fluid, the centrifugal force causes the fluid to move radially outward near the disk and to be replenished by an axial motion toward the disk. Levich[21] has analyzed the mass transfer in such a fluid motion. Since the axial component of the velocity is uniform and depends only on the normal distance from the disk surface, the mass-transfer rate to the disk is also uniform.

For the disk, r = x, and the value of the velocity derivative at the surface is (see Schlichting[9], p. 87, or Sparrow and Gregg[34])

$$\beta = a\Omega x \sqrt{\Omega/\nu} , \qquad (44)$$

where a = 0.51023. Substitution into equation (35) yields

$$i_n = 0.62048 \frac{nF\ c_\infty}{s_i} \sqrt{\Omega\nu} \left(\frac{D_i}{\nu}\right)^{2/3} . \qquad (45)$$

This expression uses the approximations (32) of the velocity components near the disk and is valid for large Schmidt numbers. The correction for the fact that the Schmidt number is not infinite has also been treated[35,36] for this system.

Because of the well-defined fluid motion, the rotating disk electrode has been used extensively for the determination of diffusion coefficients and the parameters of electrode kinetics. The application of the rotating disk system has recently been reviewed by Riddiford[37].

Free convection

Free convection is a hydrodynamic flow which results from density variations in the solution produced, in the cases of interest here, by concentration variations near the electrode. Free convection at a vertical plate electrode has been studied extensively. For deposition of a metal the solution density is lower near the electrode than in the bulk, and an upward flow near the electrode occurs. This upward flow provides convective transport of the reactant to the electrode diffusion layer. Ibl[38] has reviewed the experimental work on this problem and reports the limiting current density to an electrode of length L.

$$i_{avg} = 0.66 \frac{nF D_i c_\infty}{s_i} \left[\frac{g(\rho_\infty - \rho_o)}{\rho_\infty D_i \nu L}\right]^{1/4} \tag{46}$$

or

$$Nu_{avg} = \frac{s_i L i_{avg}}{nF D_i c_\infty} = 0.66 (Sc\ Gr)^{1/4} , \tag{47}$$

where

$$Gr = \frac{g(\rho_\infty - \rho_o)L^3}{\rho_\infty \nu^2} \tag{48}$$

is the Grashof number. These results apply to values of Sc Gr between $10^4$ and $10^{12}$.

Free convection in solutions with an excess of supporting electrolyte is complicated by the fact that the concentration of the supporting electrolyte also varies in the diffusion layer and therefore contributes to the variation of the density. Approximate methods of estimating the interfacial density difference in the Grashof number have consequently been introduced, a popular method being that of Wilke, Eisenberg, and Tobias[39].

For turbulent natural convection at a vertical plate Fouad and Ibl[40] obtained the relation

$$Nu_{avg} = 0.31\ (Sc\ Gr)^{0.28}\ , \tag{49}$$

applicable in the range $4 \times 10^{13} < Sc\ Gr < 10^{15}$ .

Schütz[41] investigated experimentally free convection mass transfer to spheres and horizontal cylinders and obtained for the average Nusselt number for spheres

$$Nu_{avg} = 2 + 0.59\ (Sc\ Gr)^{1/4} \tag{50}$$

in the range $2 \times 10^{8} < Sc\ Gr < 2 \times 10^{10}$ and for cylinders

$$Nu_{avg} = 0.53\ (Sc\ Gr)^{1/4} \tag{51}$$

for $Sc\ Gr < 10^{9}$. In forming these dimensionless groups, $L = d$, the diameter of the sphere or cylinder. Schütz also measured local Nusselt numbers using a sectioned electrode technique.

Acrivos[42] has obtained a solution of the laminar free-convection boundary-layer equations for arbitrary two-dimensional and axisymmetric surfaces in the asymptotic limit $Sc \rightarrow \infty$. These results should be of some interest here since the Schmidt number is large for electrolytic solutions. The local limiting current density for two-dimensional surfaces is predicted to be

$$i_n = 0.5029\ \frac{nF\ D_i\ c_\infty}{s_i} \left[\frac{g(\rho_\infty - \rho_o)}{\rho_\infty\ D_i\ \nu}\right]^{1/4} \frac{(\sin\epsilon)^{1/3}}{\left[\int_0^x (\sin\epsilon)^{1/3} dx\right]^{1/4}}\ , \tag{52}$$

and the average limiting current from $x = 0$ to $x = L$ is

$$i_{avg} = 0.6705\ \frac{nF\ D_i\ c_\infty}{L\ s_i}\ (Sc\ Gr)^{1/4} \left[\frac{1}{L} \int_0^x (\sin\epsilon)^{1/3} dx\right]^{3/4}\ , \tag{53}$$

where $\epsilon(x)$ is the angle between the normal to the surface and the vertical. For a vertical electrode, $\sin\epsilon = 1$, and the coefficient 0.6705 of equation (53) can be compared directly with the experimental coefficient of equation (46).

For an axisymmetric surface, where $r(x)$ is again the distance of the surface from the axis of symmetry, the local limiting current density is

$$i_n = 0.5029 \frac{nF\, D_i\, c_\infty}{s_i} \left[\frac{g(\rho_\infty-\rho_o)}{\rho_\infty D_i\, \nu}\right]^{1/4} \frac{(r \sin\epsilon)^{1/3}}{\left[\int_0^x (r^4 \sin\epsilon)^{1/3} dx\right]^{1/4}} . \qquad (54)$$

From the results of Acrivos, the predicted coefficients of $(\mathrm{Sc\,Gr})^{1/4}$ in the expressions for the average Nusselt number for the sphere and the horizontal cylinder are 0.58 and 0.50, respectively, which can be compared with the experimental coefficients in equations (50) and (51).

Free convection at a horizontal plate is essentially different from that discussed above since there is no chance for a laminar boundary layer to form and sweep fresh solution past the plate. At a horizontal electrode with a small density gradient, the solution at first remains stratified. With a higher density difference, a cellular flow pattern results, and for still higher density differences, the flow is turbulent. In the turbulent region, Fenech and Tobias[43] propose the relation

$$i_n = 0.19 \frac{nF\, D_i\, c_\infty}{s_i} \left[\frac{g(\rho_\infty-\rho_o)}{\rho_\infty\, \nu\, D_i}\right]^{1/3} , \qquad (55)$$

for electrodes wider than 2 cm.

### Combined free and forced convection

When there is the possibility of effects of free convection superimposed on forced convection, the situation becomes essentially more complicated.

Fortunately it appears that one effect or the other predominates in the mass transfer process, depending upon the values of the Reynolds and Grashof numbers. At horizontal electrodes Tobias and Hickman[17] find that free convection predominates and the average rate of mass transfer is given by equation (55) if

$$\frac{L\, d_e\, g(\rho_\infty - \rho_o)}{\langle v \rangle\, \nu\, \rho_\infty} > 923, \qquad (56)$$

where L is the electrode length and $d_e$ is the equivalent diameter of the channel. Otherwise forced convection predominates and the average rate of mass transfer is given by equation (21). These results apply to laminar flow ($Re < 2100$). For turbulent flow, Tobias and Hickman find that forced convection predominates.

Acrivos[44] has analyzed the combined effect of free and forced convection for surfaces which are not horizontal and also finds that the transition region between predominance of free convection and predominance of forced convection is usually narrow.

## Limitations of surface reactions

The work described above is restricted to processes at the limiting current where the concentration of the reactant at the surface has a constant value of zero. Most industrial processes are operated below the limiting current, and the kinetics of the surface reaction then influence the distribution of current. In this section on convective-transport problems, the ohmic potential drop is not considered. Thus we must assume here that the ohmic potential drop is either negligible or constant for all parts of the electrode in question. The sum of the surface overpotential and the concentration overpotential is then constant, and the current distribution is determined by a balance of these overpotentials. The concentration and the current density at the surface vary with position on the electrode and must adjust themselves so that the total overpotential is constant. The more general problem involving the ohmic potential drop will be discussed in a later section.

Under these conditions the reaction rate at the electrode can be expressed in terms of the concentration at the surface, and the problem is similar to nonelectrolytic catalytic problems[45-48]. The convective-transport problem can then be reduced to an integral equation relating the reaction rate to an integral over the surface concentration at points upstream in the diffusion layer. Other approximate methods have also been developed for calculating the surface concentration and reaction rate as a function of position on the electrode. These methods, including the integral equation method, should also provide a useful starting point for attacking the more general problem involving the ohmic potential drop.

## Applications of Potential Theory

When concentration gradients in the solution can be ignored, substitution of equation (1) into equation (4) yields

$$\underline{i} = -\kappa \nabla \Phi \ , \tag{57}$$

where

$$\kappa = F^2 \sum_i z_i^2 u_i c_i \tag{58}$$

is the conductivity of the solution and where the convective transport terms sum to zero by the electroneutrality relation (3). Equation (2) when multiplied by $z_i$ and summed over i yields

$$\nabla^2 \Phi = 0 \ , \tag{59}$$

that is, the potential satisfies Laplace's equation.

The boundary conditions are determined with equation (57). On insulators

$$\partial\Phi/\partial y = 0 , \qquad (60)$$

where y is the normal distance from the surface. On electrodes, equation (57) relates this potential derivative to the surface overpotential through equation (9) or (10). If the potential $\Phi$ in the solution is measured with a reference electrode of the same kind as the working electrode, then the surface overpotential can be eliminated with the relation

$$\eta_s = V - \Phi \quad \text{at} \quad y = 0 , \qquad (61)$$

where V is the potential of the metal electrode. The resulting boundary condition is a nonlinear relationship between the potential and the potential derivative and is not commonly encountered in other applications of potential theory.

As formulated above, the potential-distribution problem is similar to the problem of the steady temperature distribution in solids, with the potential playing the role of the temperature, the current density that of the heat flux, and the electrical conductivity that of the thermal conductivity. Consequently, it is useful to be familiar with treatises on heat conduction, such as that of Carslaw and Jaeger[49]. A knowledge of electrostatics[85] and of the flow of inviscid fluids[50] is helpful since they are also involved with the solution of Laplace's equation.

Rousselot[51] presents an interesting discussion of potential distribution problems. Kronsbein[52] has given an historical account of the literature of current distribution, and Fleck[53] has recently reviewed the available analytic solutions of such problems.

### Primary current distribution

In so-called primary-current-distribution problems the surface overpotential is neglected altogether, and the solution adjacent to the electrode is taken to be an equipotential surface. This defines a classical problem in mathematical physics. The primary current density is always infinite or zero at the edge of an electrode unless the electrode is perpendicular to an insulating surface at its edge. Generally, the primary current distribution shows that the more inaccessible parts of an electrode receive a lower current density.

Moulton[54] gave a classical solution for the primary current distribution for two electrodes placed arbitrarily on the boundary of a rectangle. This is an example of one way to solve Laplace's equation, that of conformal mapping[55] using in this case the Schwarz-Christoffel transformation. A special case of this geometry is the primary current distribution for two plane electrodes placed opposite each other in the flow channel considered earlier. This is shown in figure 3 for L = 2h and can be contrasted with the distribution determined by convection and diffusion. The distribution is symmetric since convection is not important. The current density is infinite at the ends of the electrodes since the current can flow through the solution beyond the ends of the electrodes. The current distribution in this case is given by

$$\frac{i_n}{i_{avg}} = \frac{\epsilon \cosh \epsilon / K(\tanh^2 \epsilon)}{\sqrt{\sinh^2 \epsilon - \sinh^2 (2x\epsilon/L)}} , \qquad (62)$$

where $\epsilon = \pi L/2h$, x is measured from the center of the electrode, and K(m) is the complete elliptic integral of the first kind, tabulated in reference 24, p. 608. This illustrates the fact that the primary current distribution depends only on the geometric ratios of the cell, in this case the parameter $\epsilon$. The conductivity of the solution does not enter into the relation.

Kasper[56] gives the primary current distribution for a point electrode and a plane electrode, line electrodes parallel to plane electrodes and plane insulators, and for cylindrical electrodes in various configurations. These systems illustrate the application of the method of images. According to Newman[57], the primary current distribution on a disk electrode of radius $r_o$ embedded in an infinite insulating plane is

$$\frac{i_n}{i_{avg}} = \frac{0.5}{\sqrt{1-(r/r_o)^2}} \quad . \tag{63}$$

This is a simple example of the application of the method of separation of variables and Fourier series and integrals[58,59].

Hine, Yoshizawa, and Okada[60] have described the primary current distribution for two plane electrodes of infinite length and finite width confined between two infinite insulating planes perpendicular to, but not touching, the electrodes. Wagner[61] has given the primary current distribution for a two-dimensional rectangular slot in a plane electrode. These are further examples of the Schwarz-Christoffel transformation.

Kojima[62] has collected various expressions for the resistance between two electrodes in various configurations. Analogous collections should be found for the resistance for heat conduction in solids[63] and for the capacitance of two electrodes. The resistance for a disk electrode embedded in an infinite insulating plane with the counter electrode in the form of a hemisphere at infinity is[57]

$$R = 1/4\kappa r_o \; . \tag{64}$$

The resistance for two plane electrodes of length L in the walls of a flow channel separated by a distance h, where the primary current distribution is given by equation (62) is

$$R = \frac{1}{\kappa W}\,\frac{K(1/\cosh^2\epsilon)}{K(\tanh^2\epsilon)}, \tag{65}$$

where W is the width of the electrodes perpendicular to the length of the channel.

## Secondary current distribution

When slow electrode reaction kinetics are taken into account, the electrolytic solution near the electrode is no longer an equipotential surface. A wide variety of expressions for the electrode polarization has been used, which reflects the variety of electrode kinetics as well as a variety of approximations. The result of such a calculation is the so-called "secondary current distribution." The general effect of electrode polarization is to make the secondary current distribution more nearly uniform than the primary current distribution, and an infinite current density at the edge of electrodes is eliminated. The mathematical problem now involves the solution of Laplace's equation subject to a more complicated, perhaps even nonlinear, boundary condition.

For sufficiently small surface overpotentials, equation (10) can be linearized to read

$$i_n = \left.\frac{di_n}{d\eta_s}\right|_{\eta_s=0} \eta_s = \frac{i_o nF}{RT} \eta_s \,. \qquad (66)$$

This provides a linear boundary condition for Laplace's equation and has been popular in the literature since there is some hope of solving the resulting linear problem. Furthermore, if the range of current densities at the electrode is sufficiently narrow, as one wants to achieve in electroplating, it is, of course, justified to linearize the polarization equation about some other, nonzero value of the surface overpotential. Finally, with linear polarization one achieves an economy of parameters needed to determine the current distribution,and the calculation of a family of curves representing the current distribution for a particular geometry is justified.

The secondary current distribution $i_n/i_{avg}$ depends upon the same geometric ratios as the primary current distribution and, in addition, for linear polarization depends on the parameter $(L/\kappa)di_n/d\eta_s$, where L is a length characteristic of the system. This parameter has been identified by Hoar and Agar[64] for the characterization of the influence of electrolytic resistance, polarization, and cell size on current distribution. When both electrodes are polarized, there are two such parameters involving the slope of the polarization curve on both the anode and the cathode. For linear polarization, the current distribution $i_n/i_{avg}$ is still independent of the magnitude of the current.

The Tafel polarization law, where one of the exponential terms in equation (10) is negligible, is also popular in the literature. For a cathodic reaction we have

$$\eta_s = - \frac{RT}{(1-\alpha)nF} [\ln(-i_n) - \ln i_o] \ . \qquad (67)$$

This is popular because, while being a fairly realistic polarization law, Tafel's equation introduces a minimum of additional parameters into the problem. In addition to depending on the same geometric ratios as the primary current distribution, the current distribution $i_n/i_{avg}$ now depends on the parameter $|i_{avg}|(1-\alpha)nFL/RT\kappa$. The current distribution now depends on the magnitude of the current, but it is independent of the value of the exchange current density $i_o$, insofar as Tafel polarization is applicable only for current densities appreciably above the exchange current density.

Newman[65] has treated the secondary current distribution for a disk electrode embedded in an infinite insulating plane. For both a linear and a Tafel polarization law, the current distribution approaches the primary current distribution as the electrode becomes large at a constant average current density. This is a general effect of the change of size in an electrochemical system. Kasper[56] has treated the effect of linear polarization on some line-plane systems and for cylindrical electrodes.

Wagner has treated the secondary current distribution for a plane electrode with a two-dimensional slot[61], two cases of plane electrodes in the walls of an insulating channel, and a nonplanar electrode with a triangular profile[66]. One of the cases treated by Wagner for linear polarization, that of a plane electrode of finite width embedded in an insulating plane and with the counter electrode at infinity, has been treated by Gnusin, Poddubnyĭ, Rudenko, and Fomin[67] for Tafel polarization. Some of these cases illustrate the use of current sources distributed along the electrode surface as a method of reducing the problem to an integral equation. This integral equation, which may be linear or nonlinear depending on the polarization law used, frequently requires a numerical solution.

### Numerical solution by finite differences

Analytic solutions of current-distribution problems are usually restricted to simple geometric arrangements and to no polarization or linear polarization. The use of some analytic solutions is facilitated by computer evaluation of certain integrals and infinite series. Some methods, like Wagner's integral-equation method or solutions in infinite series with undetermined coefficients, require numerical evaluation of the current distribution on the electrodes or of the coefficients. When such methods can be used, the labor is less and the results more accurate than a numerical solution of Laplace's equation by finite-difference methods. Nevertheless, finite-difference methods have been developed for solving Laplace's equation for heat-conduction problems, for example. The applicability of this procedure is much less restricted than analytic or partial analytic solutions.

Klingert, Lynn, and Tobias[68] have used a finite-difference method for the solution of Laplace's equation in an L-shaped region where the anode forms a right angle one side of which is opposite the cathode and the other side of which is opposite an insulating surface. Fleck[53] has developed a general computer program for solving Laplace's equation by successive overrelaxation in arbitrarily-shaped, two-dimensional regions, including those with curved boundaries, and for arbitrary polarization laws.

This review of the applications of potential theory has not been exhaustive. Other interesting sources can be found in the references already cited.

## Intermediate Problems

We have discussed at length two extreme cases of current distribution problems: convective-transport problems mostly at the limiting current and applications of potential theory to cases where concentration variations near the electrodes can be ignored.

A relatively simple problem of an intermediate nature results if the current is maintained at a limiting value, but the concentration of supporting electrolyte is reduced relative to the concentration of the reacting ions. Since the current is at its limiting value, the ohmic potential drop in the bulk of the solution is still negligible, and the current distribution is determined by mass transfer in the diffusion layer. However, the presence of an electric field in the diffusion layer can lead to an increase or a decrease in the limiting current due to migration of the reacting ions.

At currents below but at an appreciable fraction of the limiting current, concentration variations cannot be ignored. As indicated in the subsection on "limitations of surface reactions," it may occasionally be possible to treat the problem like one involving non-electrochemical catalysis. More frequently, however, the variations in the ohmic potential drop in the solution cannot be ignored.

As mentioned in the introduction, porous electrodes will not be discussed here.

Effect of migration on limiting currents

Because of the electroneutrality condition (3), solutions of only two ions also satisfy the equation of convective diffusion (12) but with $D_i$ replaced by the diffusion coefficient of the electrolyte

$$D = \frac{z_+u_+D_- - z_-u_-D_+}{z_+u_+ - z_-u_-} . \tag{68}$$

Consequently it is relatively simple to solve convective-transport problems at the limiting current for these solutions. For example, Levich originally treated the rotating disk for such a binary electrolyte[21]. The Ilkovič equation for a growing mercury drop has been extended to a binary electrolyte by Lingane and Kolthoff[69]. These results indicate an enhancement of the limiting current compared to the same discharging ion in a solution with excess inert electrolyte, and this can be attributed to the effect of migration in the diffusion layer.

There is some interest in calculating the limiting current for intermediate cases where there is some inert electrolyte but not a large excess. Eucken[70] gave the solution for three ion types in systems which could be represented by a stagnant Nernst diffusion layer. Because experimental data[71] for the discharge of hydrogen ions on growing mercury drops did not agree with Eucken's formula, Heyrovský[30] rejected his method and introduced a correction factor involving the transference number of the discharging ion. This transference number correction is not based on quantitative arguments, but it has become entrenched in the electrochemical literature.

Gordon, Newman, and Tobias[72] have considered the effect of ionic migration on limiting currents for a rotating disk electrode. Newman[73] has treated the effect for four cases: the rotating disk, the growing mercury drop, penetration into a semi-infinite medium, and the stagnant Nernst diffusion layer. The ratio $I_L/I_D$ of the limiting current to the limiting diffusion current, calculated as in the section on convective-transport problems, is a convenient measure of the effect of migration and depends on the ratios of concentrations in the bulk solution. It is found that this correction factor is exactly the same for the two transient processes, the growing mercury drop and penetration into a stagnant medium. Numerical values of the correction factor were calculated for redox reactions in a ferro-ferricyanide system, discharge of hydrogen ions from KCl solutions, deposition of copper from $H_2SO_4$ and $MgSO_4$ solutions, and deposition of silver from $HNO_3$ solutions. The difference between the results for the disk and the drop was striking only for the discharge of hydrogen ions, the same system that bothered Heyrovský. In a later work Newman[74] showed that the correction factor for steady transfer in arbitrary two-dimensional and axisymmetric diffusion layers is exactly the same as that already calculated for the rotating disk.

The effect of migration on limiting currents is a simple example of a phenomenon which does not occur in nonelectrolytic systems, in contrast to the convective-transport problems which have direct analogues in heat transfer and nonelectrolytic mass transfer.

### Currents below the limiting current

Problems involving consideration of concentration variations near electrodes, ohmic potential drop in the bulk of the solution, and electrode kinetics are inherently of greater complexity than either the convective-transport problems or the potential-theory problems. For geometric and hydrodynamic conditions where it is possible to solve both of the extreme cases, there is some hope that the intermediate problem can also be treated. Problems of poorly defined stirring or geometry so complicated that even numerical solution of Laplace's equation is not feasible would not be expected to be amenable to analysis at intermediate current levels.

Fortunately the concentration variations are usually restricted to thin layers adjacent to the surfaces of the electrodes, and Laplace's equation still applies in the bulk of the solution outside these diffusion layers. This means that one can devote separate attention to these different regions. Since the diffusion layers are thin, the bulk region essentially fills the region of the electrolytic solution bounded by the walls of the cell and the electrodes. In this region the potential is determined so as to satisfy Laplace's equation and agree with the current density distribution on the boundaries of the region. In the diffusion layers the concentrations are determined so as to satisfy the appropriate form of the transport equations, with a mass flux at the wall appropriate to the current density on the electrodes and approaching the bulk concentrations far from the electrode. The current distribution and concentrations at the electrode surface must adjust themselves so as to agree with the overpotential variation determined from the calculation of the potential in the bulk region.

The thinness of the diffusion layers also allows one to separate the irreversible part of the cell potential into the sum of the surface overpotentials, the concentration overpotentials, and the ohmic potential drop in the solution. The surface overpotential has already been defined and is related to the concentrations and current density at the electrode surface by the polarization equation (9). The surface overpotential varies with position on the electrode unless the concentrations and current density are uniform on the electrode.

For the concentration overpotential, first let $\Delta V_1$ be the potential of the reference electrode near the surface of the working electrode minus the potential of a reference electrode outside the diffusion layer, and let $\Delta V_{ohm}$ be the potential difference between these electrodes when there is the same current distribution but no concentration variations near the electrode. Then the concentration overpotential $\eta_s$ is

$$\eta_c = \Delta V_1 - \Delta V_{ohm} . \tag{69}$$

This general definition is applicable even for concentrated solutions where the transport equation (1) is not applicable.[75] By subtracting $\Delta V_{ohm}$ as defined above, the concentration overpotential becomes independent of the placement of the second reference electrode in the bulk of the solution.

The manner in which the potential $V_r$ of a movable reference electrode (relative to a fixed reference electrode) varies with position can be expressed as

$$\sum_i s_i \nabla \mu_i = -nF\nabla V_r , \tag{70}$$

where $\mu_i$ is the electrochemical potential of species i. In the dilute-solution approximation used here, these can be written

$$\nabla \mu_i = RT \, \nabla \, ln \, c_i + z_i F \nabla \Phi . \tag{71}$$

Since $\sum_i s_i z_i = -n$, equation (70) becomes

$$\nabla V_r = \nabla \Phi - \sum_i \frac{s_i RT}{nF} \nabla \, ln \, c_i , \tag{72}$$

where $\nabla\Phi$ is obtained by substituting equation (1) into equation (4) with the result

$$\underline{i} = -\kappa\nabla\Phi - F\sum_i z_i D_i \nabla c_i \; . \tag{73}$$

If we subtract the ohmic drop which would exist in the absence of concentration variations and integrate across the diffusion layer, we obtain the concentration overpotential as defined above

$$\eta_c = i_n \int_0^\infty \left(\frac{1}{\kappa} - \frac{1}{\kappa_\infty}\right) dy + \sum_i \frac{s_i RT}{nF} \ln \frac{c_{i\infty}}{c_{io}} + F\int_0^\infty \left[\sum_i \frac{z_i D_i}{\kappa} \frac{\partial c_i}{\partial y}\right] dy, \tag{74}$$

where y is the normal distance from the electrode surface, $\kappa_\infty$ is the conductivity of the bulk solution, $c_{io}(x)$ is the concentration of species i at the electrode surface, and $c_{i\infty}$ is the concentration in the bulk. According to equation (74), the concentration overpotential is the potential difference of a concentration cell plus an ohmic contribution due to the variation of conductivity in the diffusion layer. In general, the concentration overpotential also depends upon the position along the electrode surface.

For simplicity, let us restrict ourselves to systems where the anode and cathode reactions are the same. Let x and y represent cartesian coördinates appropriate to the solution of Laplace's equation in the bulk region and let $x_{cath}$, $y_{cath}$, $x_{anode}$, and $y_{anode}$ represent diffusion-layer coördinates appropriate to the cathode and the anode, as used in the section on convective-transport problems. Let $\Phi_{cath}(x_{cath})$ and $\Phi_{anode}(x_{anode})$ represent the solution of Laplace's equation in the bulk region evaluated at the surfaces of the cathode and anode. Further let $\eta_{c,cath}$, $\eta_{s,cath}$, $\eta_{c,anode}$, and $\eta_{s,anode}$ represent the concentration and surface overpotentials at the cathode and anode and let $V_{cath}$ and $V_{anode}$ be the potentials of the metal cathode and anode. Then the applied cell potential $V_{anode}-V_{cath}$ can, in view of the definitions of overpotentials, be expressed as

$$V_{anode} - V_{cath} = \eta_{s,anode}(x_{anode}) + \eta_{c,anode}(x_{anode}) + \Phi_{anode}(x_{anode})$$
$$- \eta_{s,cath}(x_{cath}) - \eta_{c,cath}(x_{cath}) - \Phi_{cath}(x_{cath}). \qquad (75)$$

If the metal anode and cathode are equipotentials, then the overpotentials and ohmic potential drop $\Phi_{anode} - \Phi_{cath}$ must add up to a constant value according to equation (75) even though individually they depend upon the position along the electrodes. The current densities and concentrations at the electrode surfaces must adjust themselves so that this condition is satisfied. According to the second law of thermodynamics, the overpotentials are always positive at an anode and negative at a cathode.

If the potential in the bulk of the solution is measured with a reference electrode of the same kind as the working electrodes, then the total overpotentials at the anode and cathode are

$$\eta_{anode} = V_{anode} - \Phi_{anode} = \eta_{s,anode} + \eta_{c,anode} , \qquad (76)$$

$$\eta_{cath} = V_{cath} - \Phi_{cath} = \eta_{s,cath} + \eta_{c,cath} . \qquad (77)$$

Asada, Hine, Yoshizawa, and Okada[76] have used a separate treatment of the diffusion layers and the bulk solution to treat free convection in a rectangular cell with a vertical electrode at each end for currents below the limiting current. Newman has given a detailed justification for such a procedure for systems with laminar, forced convection[74] and has applied the method to the rotating disk electrode[65,77].

In discussing the details of the application of these concepts, let us pick a fresh example, that of two electrodes of length L placed opposite each other at a distance h, embedded in the walls of a flow channel with steady, laminar flow. The mass-transfer-limited current distribution and the primary current distribution have already been depicted for this system in figure 3. No calculated results will be given, but it will be shown how to treat the diffusion layers and the bulk solution without the necessity for a numerical solution of partial differential equations by finite differences.

a. The diffusion layers

The determination of all the concentrations in the diffusion layer is complicated and usually not required. Let us suppose that the electrode reactions involve deposition and dissolution of copper from copper sulfate solutions with enough sulfuric acid added that the effect of ionic migration in the diffusion layers can be ignored, and equation (11) applies. Let us also assume that the solution is so dilute that supersaturation of copper sulfate at the anode is not a problem.

Application of Duhamel's theorem to the solution expressed by equation (19) yields a relation between the current density and the concentration of copper ions (indicated by the subscript R) at the surface of the electrode (see also Acrovos and Chambré[46]):

$$i_n(x) = \frac{nF}{s_i} D_i \left.\frac{\partial c_i}{\partial y}\right|_{y=0} = - \frac{nF\, D_R}{s_R \Gamma(4/3)} \left(\frac{2\langle v\rangle}{3hD_R}\right)^{1/3} \int_0^x \frac{dc_{Ro}(x')}{dx'} \frac{dx'}{(x-x')^{1/3}} \ . \quad (78)$$

This equation can be applied to either the anode or the cathode by adding appropriate subscripts to $i_n$, x, and $c_{Ro}$, but in either case it should be noted that the equation involves a Stieltjes integral. This is important only if there is an abrupt change in the surface concentration at the leading edge of the electrode, as there is at the limiting current.

b. Solution of Laplace's equation

The solution of Laplace's equation for current sources distributed along the anode and the cathode is (compare Wagner[66])

$$\Phi = \Phi_* - \frac{1}{2\pi\kappa_\infty} \int_0^L i_{n,cath}(x') \ln\left[\sinh^2\left(\frac{\pi(x-x')}{2h}\right) + \sin^2\left(\frac{\pi(y-h)}{2h}\right)\right] dx'$$

$$- \frac{1}{2\pi\kappa_\infty} \int_0^L i_{n,anode}(x') \ln\left[\sinh^2\left(\frac{\pi(x-x')}{2h}\right) + \sin^2\left(\frac{\pi y}{2h}\right)\right] dx' , \qquad (79)$$

where the cathode is at $y = h$ and the anode is at $y = 0$. From this equation, the potential in the bulk solution extrapolated to the cathode surface is

$$\Phi_{cath}(x) = \Phi_* - \frac{1}{2\pi\kappa_\infty} \int_0^L i_{n,cath}(x') \ln \sinh^2\left(\frac{\pi(x-x')}{2h}\right) dx'$$

$$- \frac{1}{2\pi\kappa_\infty} \int_0^L i_{n,anode}(x') \ln \cosh^2\left(\frac{\pi(x-x')}{2h}\right) dx' , \qquad (80)$$

and that extrapolated to the anode surface is

$$\Phi_{anode}(x) = \Phi_* - \frac{1}{2\pi\kappa_\infty} \int_0^L i_{n,cath}(x') \ln \cosh^2\left(\frac{\pi(x-x')}{2h}\right) dx'$$

$$- \frac{1}{2\pi\kappa_\infty} \int_0^L i_{n,anode}(x') \ln \sinh^2\left(\frac{\pi(x-x')}{2h}\right) dx' . \qquad (81)$$

The current density at the anode is positive and that at the cathode is negative, in accordance with equation (78). The integration constant $\Phi_*$ is to be determined from the condition that the total anode and cathode currents are equal

$$\int_0^L [i_{n,cath}(x') + i_{n,anode}(x')]\, dx' = 0 . \qquad (82)$$

Otherwise the solution (79) represents a "leakage" of current along the channel to + and - infinity.

c. Boundary conditions

The boundary conditions have, to some extent, already been incorporated into the solutions for the diffusion layers and the bulk region. The solution (79) for the potential in the bulk solution already satisfies the condition of zero current normal to the insulating walls of the channel and gives the appropriate current densities on the anode and the cathode. The solution for the concentrations in the diffusion layers, on which equation (78) is based, agrees with the value $c_{R\infty}$ in the bulk of the solution. For the determination of the unknown concentrations and current densities along the electrode surfaces it is necessary to use equations (76), (77), (74), and the polarization equation (9). In view of the assumption of an excess of supporting electrolyte, it is appropriate to simplify equation (74) to

$$\eta_c = \frac{s_R RT}{nF} \ln \frac{c_{R\infty}}{c_{Ro}} . \qquad (83)$$

This neglects the variation of the conductivity across the diffusion layers and also the diffusion potential represented by the second integral in equation (74). If this were not permissible, it would be necessary to solve for the concentration profiles of each ionic species in the diffusion layers.

d. Suggested solution procedure

The method of solving the problem even as formulated is by no means obvious or straightforward. In fact it is worthwhile to verify that there are enough equations to match the unknowns. By combining equations (9), (76), (77), and (83) it is possible to relate the current densities at the electrodes to the total overpotential and the concentrations in the bulk and at the surface:

$$i_n = f(\eta, c_{Ro}, c_{R\infty}) , \qquad (84)$$

where the total overpotentials are obtained from equations (76), (77), (80), and (81):

$$\eta = V - \Phi_* + g(i_{n,cath}; i_{n,anode})\gamma/2\pi\kappa_\infty \, , \qquad (85)$$

where g represents the integrals in equations (80) and (81). Thus there is one constant unknown $\Phi_*$ and six variable unknowns, $i_n$, $\eta$, and $c_{Ro}$ at both the cathode and the anode. There is one equation (82) for the determination of the constant, and there are two each of integral equations (78) and (85) and of equation (84), which applies at all points on the electrodes. Thus the problem is determinate.

The following, doubly iterative, calculation procedure is suggested, but convergence can hardly be guaranteed. Let $V_{cath}$ and $V_{anode}$ be given.

1. Assume values of $i_{n,cath}(x)$ and $i_{n,anode}(x)$ such that equation (82) is satisfied.

2. Guess a value of $\Phi_*$ .

3. Calculate $\eta_{cath}(x)$ and $\eta_{anode}(x)$ from equation (85).

4. Solve the integral equation (78) with equation (84) for $i_n$ and $c_{Ro}$ for both the anode and the cathode. This is an integral equation of the Volterra type, and the method of numerical solution has been outlined by Acrivos and Chambré[46], but one must take into account the fact that $\eta$ depends on x.

5. If the correct value of $\Phi_*$ was used, the values of $i_n$ will now satisfy equation (82). If not, pick a new value of $\Phi_*$, by trial and error, and go back to step 3, using the <u>old</u> values of $i_n$ to calculate $\eta_{cath}$ and $\eta_{anode}$.

6. If the correct values of $i_n$ had been used in step 3, the new values of $i_n$ will agree with the old. If not, pick new values and go back to step 2. It will probably be necessary[65] to average the new and old values in some way at this point in order to achieve convergence.

From the complexity of this example, one will perceive why so few solutions of intermediate problems are found in the literature.

## Discussion and Conclusions

Existing work on current distribution and mass transfer in electrochemical systems has been reviewed, with emphasis being placed on how each contribution is related to the limiting cases of convective-transport problems (directly analogous to problems in convective heat and nonelectrolytic mass transfer) and applications of potential theory (where concentration variations can be ignored and the electrostatic potential satisfies Laplace's equation). This framework can be compared with Wagner's discussion[78] of the scope of electrochemical engineering. Much work either fits into the extreme cases or takes into account phenomena neglected in the extreme cases.

Information regarding convective-transport problems not yet treated for electrochemical systems can be inferred from the literature of convective heat and mass transfer. Electrochemical systems provide a convenient experimental means of studying problems of wider interest, particularly at large Schmidt numbers. They can, for example, yield information about turbulent transport very close to a solid wall.

In technical electrochemical systems, the ohmic potential drop is of great importance, and potential-theory problems find application here. Nevertheless, concentration variations near electrodes frequently provide limitations on reaction rates and current efficiencies in industrial operations. In view of the complexity of treating simultaneously concentration variations and ohmic potential drop, qualitative or semi-quantitative application of these concepts may have to suffice for some time.

### Concentrated solutions

Transport theory valid for dilute solutions has been applied fruitfully to electrochemical systems. It should be pointed out that equations valid for concentrated solutions and multicomponent transport are available[2,79].

Transport theory for solutions of a single salt is moderately simple and has been applied to electrodeposition on a rotating disk electrode[75,80]. Furthermore, transport properties for such solutions are frequently available in the literature[81].

Multicomponent transport theory could be applied to certain simple geometries which would involve numerical solution of ordinary differential equations for the concentration profiles. However, in most cases data for all the necessary transport properties are incomplete[82], and a rigorous treatment is precluded. There is, however, reason to believe that integral diffusion coefficients measured, say, with a rotating disk electrode at the limiting current would also be applicable to other geometries even though there is migration in the diffusion layer[74] and the transport properties vary with the concentrations in the diffusion layer[23].

## Geometries of interest in electrode kinetic studies

The behavior of the interface, particularly the electrode kinetics, is important in determining the behavior of an electrochemical system. In selecting a system for the study of electrode kinetics care should be used to avoid complications not essential to the electrode kinetics.

The rotating disk electrode has been popular for the study of moderately fast electrode reactions because the hydrodynamic flow is well defined and concentration variations can be calculated. However, it should be realized that the primary current distribution is not uniform, and this problem becomes more serious for faster reactions, larger current densities, and larger disks.

Perhaps more attention should be devoted to the possibility of using rotating cylindrical electrodes. Here both the primary and mass-transfer-limited current distributions are uniform on the electrodes and both the ohmic potential drop and the concentration change at the electrodes can be accurately calculated even though the flow is turbulent. It might be more difficult to maintain cleanliness in such a system than with a rotating disk electrode.

Another way to avoid concentration variations in studies of the kinetics of moderately fast electrode reactions is to use a step change in current and follow the change in electrode potential in the time before the concentration can change significantly. For studies of the electrodeposition of copper by this method, Mattsson and Bockris[83] used small spherical electrodes, where the primary current distribution should be uniform. Current-step methods should not be used if the primary current distribution is not uniform.

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## Nomenclature

$a$ = 0.51023.

$c_i$ - concentration of species i (mole/cm$^3$).

$d_e$ - equivalent diameter of annulus (cm).

$D$ - diffusion coefficient of salt (cm$^2$/sec).

$D_i$ - diffusion coefficient of species i (cm$^2$/sec).

$e^-$ - symbol for the electron.

$f$ - function in expression of electrode kinetics.

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

$\underline{g}$ - gravitational acceleration (cm/sec$^2$).

Gr - Grashof number.

$h$ - distance between walls of flow channel (cm).

$\underline{i}$ - current density (amp/cm$^2$).

$i_n$ - normal component of current density at a surface (amp/cm$^2$).

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

$I$ - total current (amp).

$K$ - complete elliptic integral of the first kind.

$L$ - length of electrodes (cm).

$L$ - characteristic length (cm).

$m$ - volumetric flowrate of mercury (cm$^3$/sec).

$M_i$ - symbol for the chemical formula of species i.

$n$ - number of electrons transferred in electrode reaction.

$\underline{N}_i$ - flux of species i (mole/cm$^2$-sec).

Nu - Nusselt number.

$p$ - pressure (dyne/cm$^2$).

$r$ - radial position coördinate (cm).

$r$ - defines position of surface for an axisymmetric body (cm).

$r_o$ - radius of disk electrode or of growing mercury drop (cm).

$R$ - radius of outer cylindrical electrode (cm).

$R$ - universal gas constant (joule/mole-deg K).

$R$ - resistant (ohm).

$R_i$ - homogeneous rate of production of species i (mole/cm$^3$-sec).

Re - Reynolds number.

$s_i$ - stoichiometric coefficient of species i in electrode reaction.

Sc - Schmidt number

$t$ - time (sec).

$T$ - temperature (deg K).

$T$ - life time of drop (sec).

$u_i$ - mobility of species i (cm$^2$-mole/joule-sec).

$\underline{v}$ - fluid velocity (cm/sec).

$\langle v \rangle$ - average velocity (cm/sec).

$V$ - potential of an electrode (volt).

$W$ - width of electrodes (cm).

$x$ - distance measured along an electrode surface (also used as a cartesian coördinate in the bulk medium)(cm).

$y$ - normal distance from the surface (also used as a cartesian coördinate in the bulk medium)(cm).

$z_i$ - charge number of species i.

$\alpha$ - transfer coefficient.

$\beta$ - velocity derivative at the solid electrode (sec$^{-1}$).

$\gamma$ - constant in rate of growth of mercury drops (cm/sec$^{1/3}$).

$\Gamma(4/3) = 0.89298$, the gamma function of 4/3.

$\epsilon$ - angle between the normal to a surface and vertical (radian).

$\epsilon = \pi L/2h$.

$\eta$ - overpotential (volt).

$\eta_c$ - concentration overpotential (volt).

$\eta_s$ - surface overpotential (volt).

$\Theta$ - dimensionless concentration.

$\kappa$ - conductivity (mho/cm).

$\kappa$ - ratio of radii of inner to outer cylinder.

$\mu$ - viscosity (g/cm-sec).

$\mu_i$ - electrochemical potential of species i (joule/mole).

$\nu$ - kinematic viscosity ($cm^2$/sec).

$\xi$ - dimensionless independent variable (see equations (28) and (34)).

$\rho$ - density ($g/cm^3$).

$\phi$ - dimensionless velocity derivative at the surface.

$\Phi$ - electrostatic potential (volt).

$\Omega$ - rotation speed (radians/sec).

subscripts

anode - anode.

avg - average.

cath - cathode.

R - reactant.

o - at the electrode surface.

$\infty$ - in the bulk solution.

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