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Author

Newman, John.

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University of California

Ernest O. Lawrence
Radiation Laboratory

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THE EFFECT OF MIGRATION IN LAMINAR DIFFUSION LAYERS

John Newman

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The Effect of Migration in Laminar Diffusion Layers

John Newman
Inorganic Materials Research Division,
Lawrence Radiation Laboratory, and
Department of Chemical Engineering
University of California, Berkeley

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ABSTRACT

Potential distribution problems in electrolytic cells
can be separated into two parts, the bulk medium where Laplace's
equation holds and the diffusion layer where convection, migration,
and diffusion are all important modes of mass transfer. The prob-
lems in these two domains must still be solved simultaneously
since the concentrations and the current density at the electrode
surface must adjust themselves to the available overpotential
calculated from the solution of Laplace's equation.

Specific results are obtained for the limiting current
for arbitrary, two-dimensional and axisymmetric diffusion layers.
The correction factor for the effect of migration within the
diffusion layer is shown to be exactly the same as that calculated
earlier for a rotating disk electrode.

1. Introduction

An earlier paper[1] treats the effect of ionic migration on limiting currents for four cases: the rotating disk, the growing mercury drop, penetration into a semi-infinite medium, and the stagnant Nernst diffusion layer. These earlier results would be more useful if they could be applied to a broader class of problems. Here it is shown that this is possible; in particular, the results already calculated for the rotating disk also apply to steady mass transfer in arbitrary two-dimensional and axisymmetric diffusion layers. The current density is 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. The magnitude of this effect was calculated earlier[1] 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.

Examples of other hydrodynamic systems for which the rotating-disk results would thus be applicable include flow in tubes, annular conduits, and planar channels, boundary-layer flow past flat-plate electrodes or other submerged objects suspended in a free stream, and stagnation point flows.

The justification of the above results is so involved that it is not much more work to formulate a procedure for treating the problem of current and potential distribution in electrolytic cells for currents below, but at an appreciable fraction of, the limiting current. Here it is not possible to neglect concentration variations near electrodes, the surface overpotential associated with

the electrode reaction, or the ohmic potential drop in the bulk of the solution. Most previous work neglects either the ohmic potential drop in the bulk of the solution or the concentration variations, and many works also neglect the surface overpotential.

In many electrolytic cells the concentration variations are still restricted to thin diffusion layers near the electrodes. This allows an important simplification since it allows a separate treatment of the two regions -- the diffusion layer and the bulk solution where the potential satisfies Laplace's equation. However, the two regions are still coupled through the boundary conditions. A completely analytic treatment of such a complex problem is usually not possible, but even for a numerical treatment the separation into two regions is important because of the completely different length scales and mesh sizes appropriate to the regions. It is sometimes possible[2] to solve each region in terms of series solutions, the coefficients of which must be determined by a numerical procedure.

Earlier work

Early treatments of current distribution in electrolytic cells involved the solution of Laplace's equation for the potential in the bulk of the electrolytic solution. For boundary conditions the electrodes were taken to be equipotential surfaces, thus neglecting polarization, and the normal component of the current density is zero on insulating surfaces. This defines a classical problem in mathematical physics, and for electrolytic cells the solution yields the so-called "primary current distribution." 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.

When slow electrode reaction kinetics is taken into account, the electrolytic solution near the electrode is no longer an equipotential surface. A wide variety of expressions for the electrode polarization have 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. However, the electrode polarization is still a local phenomenon in the sense that the potential difference between a point on the electrode and the adjacent solution depends on the current density only at that point but not at other points on the boundary.

There are a considerable number of analytic solutions available for primary-current-distribution problems and a fair number for secondary-current-distribution problems. For problems of more complicated geometry and boundary conditions, numerical methods and solutions have been developed, which in some cases may also be easier to use than an available analytic solution. For treatments of primary and secondary current distribution, see references 2 to 10.

On the other extreme, at very high currents the current distribution may be determined entirely by limited rates of mass transfer of a reactant from the bulk solution to the electrode surface.

Since 1942 a considerable theoretical and experimental effort has been devoted to problems of the so-called "limiting current" distribution (see references 11 through 18). The concentration of the limiting reactant is zero at the electrode surface, and the principles governing the current distribution are not essentially different from those governing mass transfer in nonelectrolytic solutions. Electrochemical systems are, in fact, occasionally used for mass-transfer studies, where they offer the experimental convenience of accurate measurement of the rate of mass transfer. Problems treated include free and forced convection with laminar or turbulent flow and the usual variety of geometries (conduits and submerged objects). The potential distribution outside the diffusion layer is of no importance as long as the local over-potential is high enough to reduce the concentration of the limiting reactant to zero at the electrode surface. (However, the potential distribution may occasionally be so non-uniform that a high local overpotential causes evolution of hydrogen on one part of the electrode before another part attains a zero concentration of the limiting reactant.)

For problems of an intermediate nature, where concentration variations near the electrode, slow electrode reaction kinetics, and the ohmic potential drop in the solution are all important, Asada, Hine, Yoshizawa, and Okada[19] use a calculation procedure similar to that proposed here to treat free convection in a rectangular cell with a vertical electrode at each end. No detailed justification is given. The present author has applied the methods outlined here to the rotating disk electrode.[2]

The author is preparing a more extensive review of these various aspects of current distribution and mass transfer in electrochemical systems.[20]

Scope of the present work

The next section of this paper shows how one should calculate current distributions taking into account both concentration polarization and surface polarization at currents below the limiting current. The hydrodynamic velocity distribution is assumed to be known; consequently, the treatment applies to systems with forced convection. Free convection is excluded since the velocity must then be calculated at the same time as the concentration.

The Péclet number $Pe = UL/D_R$, where U is a characteristic velocity, L is a characteristic length, and D_R is a characteristic diffusion coefficient, is assumed to be large. Then the concentration variations are confined to a thin diffusion layer near the electrode surface, and the development hinges about this fact. As a consequence, the general problem can be partially separated into two parts involving the concentration distribution within the diffusion layer near the electrode and the potential distribution within the bulk medium. The concentration polarization is not a local phenomenon since the concentration at the electrode surface depends on events upstream in the diffusion layer.

The analysis thus applies to laminar boundary layers at high Reynolds numbers $Re = UL/\nu$, where ν is the kinematic viscosity. The discussion is restricted to two-dimensional and axisymmetric flow past the electrode, although the concept of a thin diffusion layer of course applies to other geometries as well. The usual boundary-layer coördinates are employed, where x denotes the distance along the electrode from the beginning of the diffusion layer and y denotes the normal distance from the electrode surface. Examples of such hydrodynamic boundary layers would include flat-plate electrodes or other submerged objects suspended in a free

stream, rotating disk electrodes, and stagnation-point flows.

In this analysis the Schmidt number $Sc = \nu/D_R$ is also taken to be large since this allows a simplification in the expression for the velocity profiles (only the derivative at the surface is needed) and since actual Schmidt numbers are on the order of 1000 for the electrolytic solutions of interest. For certain plasma systems this assumption would not be applicable. For large Schmidt numbers, the Péclet number may be large even when the Reynolds number is not so large. The analysis thus applies not only to boundary-layer flows but also to low Reynolds number flows such as the mass-transfer entry section in circular conduits and between two plates. Such geometries, as well as boundary-layer flows, have been treated in the problems of the limiting-current distribution mentioned earlier.

The present analysis, with migration effects, is intended to be applicable to the same class of hydrodynamic flows that can be and have been treated for mass transfer without migration in laminar diffusion layers in forced convection.

Outside the diffusion layer one must solve Laplace's equation for the potential with a current density at the boundary that agrees with the rate of the electrode reaction. The diffusion layer and the bulk medium must be calculated <u>simultaneously</u> since the current density and the concentration at the electrode surface must adjust themselves to balance the overpotential available after the ohmic potential drop in the bulk medium is subtracted from the potential applied to the cell.

Results can be obtained immediately for the limiting current case (section 3). By means of a similarity transformation one can calculate the current distribution on the electrode including the

effect of migration in the diffusion layer. These results are given in the section on limiting currents, both for arbitrary two-dimensional and axisymmetric diffusion layers, and apply for large values of the Schmidt number.

The following section (section 4) contains a justification of the diffusion-layer approach based on a dimensionless formulation of the problem. The limiting-current results are used to obtain the order of magnitude of the current densities. An appendix includes miscellaneous comments inserted in order to point out related ideas from the theory of transport in electrolytic solutions which might be applied in specific problems.

2. Potential distribution problems

With a known velocity profile, the concentration and potential distributions are to be determined from four equations. The first describes the flux of a species due to migration in an electric field, diffusion because of a concentration gradient, and convection with the velocity of the fluid.

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

If there are no reactions except at electrodes, a material balance for each species is described by the equation

$$\frac{\partial c_i}{\partial t} = - \nabla \cdot \underline{N}_i \,. \tag{2}$$

The current density $\underline{i}$ is due to the movement of charged species:

$$\underline{i} = F \sum_i z_i \underline{N}_i \,. \tag{3}$$

An electrolytic solution is electrically neutral,

$$\sum_i z_i c_i = 0 \,, \tag{4}$$

to a very good approximation except in a very thin region (say 10 to 100 angstroms thick) near surfaces and really a part of the interface. The validity of equation (1) is restricted to dilute solutions since, for example, it describes properly diffusion with respect to the solvent but not multicomponent diffusion. These equations, their validity and simple consequences, and the extension to concentrated solutions have been discussed at length (see, for example, reference 21).

These four equations can be combined to yield other useful equations. The concentration of each species follows the equation

$$\frac{\partial c_i}{\partial t} + \underline{v} \cdot \nabla c_i = D_i \nabla^2 c_i + z_i u_i F c_i \nabla^2 \Phi + z_i u_i F (\nabla c_i) \cdot \nabla \Phi . \qquad (5)$$

The current density can be expressed as

$$\underline{i} = -\kappa \nabla \Phi - F \sum_i z_i D_i \nabla c_i , \qquad (6)$$

where

$$\kappa = F^2 \sum_i z_i^2 u_i c_i \qquad (7)$$

is the solution conductivity. Multiplication of equation (5) by $z_i F$ and addition over i gives an equation for conservation of charge:

$$-\nabla \cdot \underline{i} = 0 = \kappa \nabla^2 \Phi + (\nabla \kappa) \cdot \nabla \Phi + F \sum_i z_i D_i \nabla^2 c_i . \qquad (8)$$

Ionic diffusion coefficients and mobilities are related, at least approximately, by the Nernst-Einstein relation

$$D_i = RTu_i . \qquad (9)$$

We take all the diffusion coefficients to be of roughly the same magnitude, but all of them to be small in the sense that

$$Pe = UL/D_R \gg 1 \ , \tag{10}$$

where D_R is one of the diffusion coefficients (taken at a later stage in this work to be that of the limiting reactant).

The bulk medium

It is widely known that when the Péclet number Pe is large, mass transfer by convection predominates over diffusion except in a thin region, known as the diffusion layer, near the reaction surface (the electrode in this case). This has the consequence that outside the diffusion layer equation (5) reduces to

$$\frac{\partial c_1}{\partial t} + \underline{v} \cdot \nabla c_1 = 0 \ , \tag{11}$$

that is, the concentration of a fluid element is constant as it moves through the solution. In most cases the appropriate solution to equation (11) is

$$c_1 = c_{1\infty} \ , \tag{12}$$

and all concentrations have their bulk values.

For the region outside the diffusion layer, equation (12) expresses the solution for the concentrations. It is still necessary to solve for the potential by means of equation (8), which in the bulk solution reduces to Laplace's equation

$$\nabla^2 \Phi = 0 \ . \tag{13}$$

The diffusion layer

On the other hand, diffusion cannot be neglected in the diffusion layer, but other simplifications are still possible. On account of the thinness of the diffusion region, effects of curvature can be neglected, and we adopt the usual boundary-layer coördinates: x measured along the surface from its upstream end

and y, the normal distance from the surface. In the diffusion layer, equation (5) simplifies to

$$\frac{\partial c_i}{\partial t} + v_x \frac{\partial c_i}{\partial x} + v_y \frac{\partial c_i}{\partial y} = D_i \frac{\partial^2 c_i}{\partial y^2} + z_i u_i F \left(c_i \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial c_i}{\partial y} \frac{\partial \Phi}{\partial y} \right) .$$

(14)

On the right side derivatives with respect to x have been ignored compared to the derivatives with respect to y.

One more simplification is possible. We assume that

$$Sc = \nu/D_R \gg 1 ,$$

(15)

where ν is the kinematic viscosity of the fluid. The Schmidt number Sc is on the order of 1000 for the electrolytic systems of interest here. With the assumption (15) that the Schmidt number is large, the diffusion layer is thin even when compared with any hydrodynamic boundary layer which may be present, and within a two-dimensional diffusion layer the velocity components can be represented as

$$v_x = y\beta(x) \qquad \text{and} \qquad v_y = -\frac{1}{2} y^2 \beta'(x) ,$$

(16)

where $\beta(x)$ is the velocity derivative at the solid wall, $\beta = \partial v_x/\partial y$ at y = 0, and the prime denotes the derivative with respect to x. These are the first terms in expansions of the velocity in y and satisfy the continuity equation

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0 .$$

(17)

With this approximation, the diffusion-layer equation for the concentrations is

$$\frac{\partial c_i}{\partial t} + y\beta \frac{\partial c_i}{\partial x} - \frac{1}{2} y^2 \beta' \frac{\partial c_i}{\partial y} = D_i \frac{\partial^2 c_i}{\partial y^2} + z_i u_i F \left[c_i \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial c_i}{\partial y} \frac{\partial \Phi}{\partial y} \right] .$$

(18)

These equations (one for each species) are to be solved along with the equation of electroneutrality (4) and certain boundary conditions which are yet to be discussed.

Boundary conditions and matching

Boundary conditions involve the reaction rate at the electrode, which we may characterize by the current density i_y ($y = 0$), as well as the concentrations at the electrode surface and the electrode overpotential. Equation (8) can be written as

$$\frac{\partial i_x}{\partial x} + \frac{\partial i_y}{\partial y} = 0 \qquad \text{or} \qquad i_y = i_y \, (y = 0) \, - \int_0^y \frac{\partial i_x}{\partial x} \, dy \ .$$

$$(19)$$

Since the diffusion layer is thin, i_y is approximately constant throughout the diffusion layer, and this value can be used as a boundary condition on the solution of Laplace's equation in the form

$$\frac{\partial \tilde{\Phi}}{\partial y} = - \frac{i_y \, (y = 0)}{\kappa_\infty} \qquad \text{at } y = 0 \ , \qquad (20)$$

where κ_∞ is the conductivity of the bulk solution and the tilda denotes quantities pertaining to the problem outside the diffusion layer. The current density $i_y(y = 0)$ is, of course, zero on insulators.

Let the electrode reaction be expressed as

$$\sum_i s_i M_i^{z_i} \longrightarrow n e^- \ , \qquad (21)$$
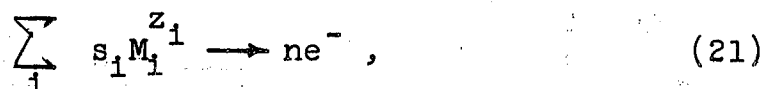
where s_i is the stoichiometric coefficient of species i and M_i is a symbol for the chemical formula of species i. Then the boundary conditions for the concentrations in the diffusion layer are

$$c_i \longrightarrow c_{i\infty} \qquad \text{as} \qquad y \longrightarrow \infty \; . \qquad (22)$$

$$N_{iy} = -\frac{s_i i_y}{nF} = \frac{s_i}{s_R} N_{Ry} \quad \text{at } y = 0 \; , \qquad (23)$$

where R denotes a reactant for which $s_R \neq 0$. (Later it will be useful to relate the flux of species i to the flux of the limiting reactant, instead of relating it to the current density.)

The potential variation within the diffusion layer is described by equation (6). Let us denote by $\widetilde{\Phi}(x)$ the potential at the electrode calculated from Laplace's equation with boundary condition (20). This can be regarded as representing the effect of the ohmic drop in the bulk solution, extrapolated to the electrode surface using the bulk conductivity. If V_{met} is the potential of the electrode metal and Φ in the bulk solution is that measured by a reference electrode of the same kind as the working electrode, then the overpotential is

$$\eta = V_{met}(x) - \widetilde{\Phi}(x) \; . \qquad (24)$$

This is the sum of the concentration overpotential η_c, associated with concentration changes in the diffusion layer, and the surface overpotential η_s, associated with the heterogeneous electrode reaction

$$\eta = \eta_c + \eta_s \; , \qquad (25)$$

but η does not include any other ohmic overpotential since $\widetilde{\Phi}(x)$ is extrapolated to the electrode surface.

The concentration and surface overpotentials can be defined with the aid of two reference electrodes, one outside the diffusion layer and one very near the electrode surface. These reference electrodes, which may be imaginary, follow the same electrode reaction (21) as the working electrode. The surface overpotential

is defined to be the potential of the working electrode minus the potential of the reference electrode very near the electrode. For the concentration overpotential, first let ΔV_1 be the potential of the reference electrode near the surface minus the potential of the reference electrode outside the diffusion layer, and let ΔV_{ohm} be the potential difference between these electrodes when there is the same current distribution but no concentration variations near the electrode. Then

$$\eta_c = \Delta V_1 - \Delta V_{ohm} \, . \tag{26}$$

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

$$\sum_i s_i \nabla \mu_i = - nF \nabla V_r \, , \tag{27}$$

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

$$\nabla \mu_i = RT \nabla \ln c_i + z_i F \nabla \Phi \, . \tag{28}$$

Since $\sum_i s_i z_i = -n$, equation (27) becomes

$$\nabla V_r = \nabla \Phi - \sum_i \frac{s_i RT}{nF} \nabla \ln c_i \, , \tag{29}$$

where $\nabla \Phi$ is given by equation (6). 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

$$\eta_c = i_y(y=0) \int_0^\infty \left(\frac{1}{\kappa} - \frac{1}{\kappa_\infty} \right) dy + \sum_i \frac{s_i RT}{nF} \ln \frac{c_{i\infty}}{c_{io}} + F \int_0^\infty \left[\sum_i \frac{z_i D_i}{\kappa} \frac{\partial c_i}{\partial y} \right] dy , \tag{30}$$

where $c_{io}(x)$ is the concentration of species i at the electrode surface. According to equation (30), the concentration over-potential is the potential difference of a concentration cell plus an ohmic contribution due to the variation of conductivity in the diffusion layer.

The surface overpotential as defined above should depend only on the reaction rate and the concentrations at the electrode surface,

$$\eta_s = g \left[c_{io}, \ i_y(y=0) \right] , \tag{31}$$

but not on events at a distance from the surface. Equation (31) implies a steady state since the capacity of the double layer is not included. For unsteady processes one might write

$$i_y(y=0) = f(c_{io}, \ \eta_s) + C \ \frac{d\eta_s}{dt} , \tag{32}$$

where C is the capacity of the interface and f is the inverse of g in equation (31). The discussion of the particular form of f and g lies in the realm of electrode kinetics and outside the scope of this paper.

One more point remains to be brought out here. In the equations (18) for mass transfer in the diffusion layer only derivatives of potential with respect to y appear and not Φ itself. In fact, these derivatives could be eliminated in favor of the current density by appropriate use of equations (6) and (8). Consequently, let us introduce a new potential φ in the diffusion layer defined as

$$\varphi = \Phi(x,y) - \widetilde{\Phi}(x) . \tag{33}$$

Then $\widetilde{\Phi}(x)$ is important only in the determination of the total overpotential.

Summary of the calculation procedure

Let us now summarize the calculation procedure for the two parts of the problem, the bulk medium and the diffusion layer. If we know the reaction rate $i_y(y=0)$ on all boundaries, then we can solve Laplace's equation (13) for the potential in the bulk medium. On the other hand, if we know the reaction rate $i_y(y=0)$ on all boundaries, we can solve for the concentrations and the potential variation in the diffusion layer from equations (4) and (18) subject to boundary conditions (22) and (23).

From the solution of the problem for the diffusion layer one can calculate η_s and η_c according to equations (30) and (31) and hence can calculate $\widetilde{\Phi}(x)$ from equation (24). Thus it is clear that both parts of the problem can be calculated from a knowledge of $i_y(y=0)$, but these may yield different values for $\widetilde{\Phi}(x)$. In general, it is not possible to calculate the two parts separately; they remain coupled through the boundary conditions, and it is necessary to determine $i_y(y=0)$ by some method of successive approximation. It may be helpful to modify the order of calculation so that the diffusion layer is calculated from an assumed $i_y(y=0)$, which gives $\widetilde{\Phi}(x)$ as a boundary condition for Laplace's equation. The solution of Laplace's equation then gives values of $i_y(y=0)$ which can be compared with the assumed values. (See also reference 2.)

3. Limiting Currents

Two-dimensional diffusion layers

When the reaction rate is limited because the concentration of one of the reactants falls to zero at the electrode surface, the current distribution is determined by mass transfer in the

diffusion layer, and it is possible to obtain a solution. Here it is not necessary to specify $i_y(y = 0)$ in advance; instead the boundary condition

$$c_R = 0 \qquad \text{at} \qquad y = 0 \qquad (34)$$

applies.

Acrivos[22] realized that the Lighthill transformation[23] is applicable to a wide range of problems involving nonelectrolytic mass transfer at high Schmidt numbers and heat transfer at large Prandtl numbers. By means of the Lighthill similarity transformation

$$\xi = y\sqrt{\beta(x)} \left/ \left[9D_R \int_0^x \sqrt{\beta} \, dx \right]^{1/3} \right. , \qquad (35)$$

the mass-transfer, diffusion-layer equations (18) can be reduced to ordinary differential equations for a steady-state problem

$$(D_i/D_R)c_i'' + 3\xi^2 c_i' + (z_i u_i F/D_R)(c_i \varphi'' + c_i' \varphi') = 0 , \qquad (36)$$

where primes denote differentiation with respect to ξ and where φ of equation (33) replaces Φ. Equations (36) are supposed to be solved with equation (4) subject to the boundary conditions

$$c_R = 0 \qquad \text{at} \qquad \xi = 0 , \qquad (37)$$

$$z_i u_i F c_i \varphi' + D_i c_i' = (s_i/s_R)(z_R u_R F c_R \varphi' + D_R c_R') \quad \text{at} \ \xi = 0 , \qquad (38)$$

$$c_i \longrightarrow c_{i\infty} \qquad \text{as} \qquad \xi \longrightarrow \infty . \qquad (39)$$

In addition the value of φ must be specified at some point, but this is not really relevant for the solution of the problem.

The problem outlined in equations (36) through (39) plus (4) is exactly the same as that treated earlier[1] for the effect of ionic migration on the limiting current to a rotating disk.

Hence we can immediately draw upon those results. Let us define a dimensionless current density at the electrode as

$$I = \left[c_R'(0) + (z_R u_R F c_R / D_R) \, \varphi'(0) \right] / c_{R\infty} \, . \tag{40}$$

Then the actual current density is

$$i_y(y=0) = I n F c_{R\infty} \sqrt{\beta(x)} \, D_R^{2/3} \Bigg/ s_R \left[9 \int_0^x \sqrt{\beta} \, dx \right]^{1/3} . \tag{41}$$

This shows how the reaction rate is distributed along the electrode, since I is independent of x.

When there is an excess of supporting electrolyte, migration is not important in the diffusion layer, and the corresponding limiting "diffusion current" can be expressed by

$$I_D = 1 / \Gamma(4/3) = 1.1198 \, . \tag{42}$$

When there is not an excess of supporting electrolyte, the limiting current is augmented or diminished by the effect of migration, and this effect can conveniently be expressed as I_L/I_D, the ratio of the limiting current to the limiting diffusion current. Specific calculations of the effect of migration on limiting currents, expressed as I_L/I_D, have already been given[1] 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 stagnant diffusion layer and unsteady mass transfer to growing mercury drops and from a semi-infinite stagnant medium to a plane electrode have been treated[1] in addition to the rotating disk. It is interesting that the correction factor for the effect of migration is exactly the same for the two unsteady processes,[1] while the correction factor for two-dimensional diffusion layers

discussed in this work is exactly the same as that for steady
transfer to the rotating disk. The correction factor for these
steady processes is, in principle, different from that for the
unsteady processes, but in the earlier work[1] the difference was
striking only for the discharge of hydrogen ions where the
diffusion coefficient of H^+ is greatly different from the diffu-
sion coefficients of the other ions in the system.

The results for the limiting-current case show, incidentally,
that the concentration distribution of the non-limiting species in
the diffusion layer is exactly similar to that for a rotating disk.
This gives quantitative support to the supposition that integral
diffusion coefficients appropriate for mass-transfer experiments
can be obtained from limiting-current measurements at a rotating
disk even though they have no obvious significance in terms of the
fundamental properties of the electrolytic solution. On the other
hand, integral diffusion coefficients obtained from unsteady mass
transfer to an electrode at the end of a stagnant capillary may
be slightly different.

Axisymmetric diffusion layers

Axisymmetric flow systems are also popular. We have seen
already that the results for limiting currents in two-dimensional
diffusion layers are similar to those for the rotating disk, an
axisymmetric system. It is also obvious that these results apply
to the diffusion layers on electrodes in the walls of tubes and
annular conduits, where β is a constant.

In general, an axisymmetric body must be characterized by
the normal distance $r(x)$ of the surface from the axis of symmetry.
In the diffusion layer near such an axisymmetric surface, the

continuity equation reads (see, for example, Schlichting,[24] p. 185)

$$\frac{\partial(rv_x)}{\partial x} + r \frac{\partial v_y}{\partial y} = 0 .$$ (43)

Hence the appropriate expansions of the velocity components near the solid wall are

$$v_x = y\beta(x) \qquad \text{and} \qquad v_y = -\frac{1}{2} y^2 (r\beta)' / r$$ (44)

where the primes denote differentiation with respect to x.

Mass transfer in the diffusion layer still follows equation (14), but for large Schmidt numbers one should use the expansions (44) instead of (16). Equation (14) becomes

$$\frac{\partial c_1}{\partial t} + y\beta \frac{\partial c_1}{\partial x} - \frac{1}{2} y^2 \frac{(r\beta)'}{r} \frac{\partial c_1}{\partial y} = D_1 \frac{\partial^2 c_1}{\partial y^2} + z_1 u_1 F \left[c_1 \frac{\partial^2 \Phi}{\partial y^2} + \frac{\partial c_1}{\partial y} \frac{\partial \Phi}{\partial y} \right] .$$ (45)

For the limiting-current case,

$$c_R = 0 \qquad \text{at} \qquad y = 0 ,$$ (46)

and for steady problems the similarity transformation

$$\xi = y\sqrt{r\beta} \Big/ \left[9D_R \int_0^x r\sqrt{r\beta}\, dx \right]^{\frac{1}{3}}$$ (47)

reduces equation (45) to equation (36), and the results for steady mass transfer to the rotating disk can be applied to axisymmetric diffusion layers as well. In particular, the current distribution is given by

$$I = \frac{s_R i_y(y=0)}{nFc_{R\infty} \sqrt{r\beta}\, D_R^{\frac{2}{3}}} \left[9 \int_0^x r\sqrt{r\beta}\, dx \right]^{\frac{1}{3}} ,$$ (48)

the limiting diffusion current is given by equation (42), and the correction factors for the effect of migration I_L/I_D are exactly

the same as those calculated earlier[1] for the rotating disk.

.For tubes and annular conduits, r is independent of x and cancels out of equation (47). For a rotating disk r = x and $\beta = a\Omega x \sqrt{\Omega/\nu}$ where a = 0.51023 and Ω is the rotation speed of the disk. Equation (47) then yields

$$\xi = y(a\nu/3D_R)^{\frac{1}{3}} \sqrt{\Omega/\nu} \; . \tag{49}$$

4. Dimensionless formulation

The justification for separating the diffusion layer from the bulk medium is that the Péclet number is large. However, it is difficult to see just what simplifications are justified unless the problem is stated in a dimensionless form. For this purpose, and as a check on the preceding analysis, let us go back and make a careful estimate of the order of magnitude of the various terms. Due to the singular nature of the problem it is necessary to make these estimates both in the diffusion layer and in the bulk medium.

Channel flows

We have taken both Pe and Sc to be large, but we simplify the discussion by regarding the Péclet number, which is the product of the Reynolds number Re = UL/ν and the Schmidt number, to be large because the Schmidt number is large. Thus we regard the Reynolds number to be of order unity (that is, constant in the limit process Pe $\longrightarrow \infty$; the numerical value of Re may be as large as 2000), and consequently

$$\beta = \bigcirc(U/L) \; . \tag{50}$$

This is particularly appropriate for flow in tubes and channels.

We shall take the current to be an appreciable fraction of the limiting current. From equation (41) all current densities,

inside and outside the diffusion layer, have the order

$$i = \bigcirc(Pe^{1/3} FD_R c_{R\infty} / L) . \tag{51}$$

From equations (7) and (9)

$$\kappa = \bigcirc(F^2 D_R c_{R\infty} / RT) . \tag{52}$$

Consequently, in the bulk,

$$\nabla\Phi = \bigcirc(i/\kappa) = \bigcirc(Pe^{1/3} RT / LF) . \tag{53}$$

In the diffusion layer $x = \bigcirc(L)$, and from equation (35)

$$y = \bigcirc(L / Pe^{1/3}) . \tag{54}$$

Generally, in the diffusion layer,

$$\left. \begin{array}{ll} \partial c_i/\partial x = \bigcirc(c_{R\infty}/L) & \text{and} \quad \partial c_i/\partial y = \bigcirc(c_{R\infty} Pe^{1/3}/L) \\ \partial^2 c_i/\partial x^2 = \bigcirc(c_{R\infty}/L^2) & \text{and} \quad \partial^2 c_i/\partial y^2 = \bigcirc(c_{R\infty} Pe^{2/3}/L^2) . \end{array} \right\} \tag{55}$$

From equation (6)

$$\bigcirc\left(\frac{\partial\Phi}{\partial y}\right) = \bigcirc\left(\frac{\partial\Phi}{\partial x}\right) = \bigcirc(Pe^{1/3} RT / LF) . \tag{56}$$

By differentiating equation (6) with respect to x, we find

$$\partial^2\Phi/\partial x^2 = \bigcirc(Pe^{1/3} RT / L^2 F) , \tag{57}$$

but from differentiation of equation (6) with respect to y,

$$\partial^2\Phi/\partial y^2 = \bigcirc(Pe^{2/3} RT / L^2 F) . \tag{58}$$

On the basis of these estimates, it is appropriate to define dimensionless concentrations, current density, and electric field:

$$\left. \begin{array}{ll} \theta_i = c_i/c_{R\infty}, & \underline{i}^* = \underline{i}L / Pe^{1/3} FD_R c_{R\infty} , \\ \multicolumn{2}{c}{\underline{E}^* = - LF \nabla\Phi / Pe^{1/3} RT .} \end{array} \right\} \tag{59}$$

Further let

$$\underline{v}^* = \underline{v}/U, \qquad \beta^* = \beta L/U, \qquad \kappa^* = \kappa RT/F^2 D_R c_{R\infty} . \qquad (60)$$

In the bulk medium, the appropriate dimensionless coördinates are

$$\tilde{t} = tU/L, \quad \tilde{x} = x/L, \quad \text{and} \quad \tilde{y} = y/L , \qquad (61)$$

where x and y are cartesian coördinates. In the diffusion layer the appropriate dimensionless coördinates are

$$t^* = tU/Pe^{1/3}L, \quad x^* = x/L, \quad \text{and} \quad y^* = yPe^{1/3}/L, \qquad (62)$$

where x and y are boundary-layer coördinates (refer to the text above equation (14)).

The straightforward procedure for finding what approximations are justified for large Pe is to substitute the appropriate dimensionless variables into the original statement of the problem and then let the Péclet number approach infinity. This procedure applied to equation (5) justifies equation (11) for the bulk medium and equation (18) for the diffusion layer.

On the basis of the estimates of magnitude given above, equation (30) shows that

$$\eta_c = \bigcirc(RT/F) \qquad (63)$$

and that all the terms in equation (30) are of the same order.

On the other hand, the ohmic drop across the cell is, from equation (53),

$$\Delta\Phi_{ohm} = \bigcirc(Pe^{1/3} RT/F) . \qquad (64)$$

Thus, if one increases the stirring while operating at roughly the same fraction of the limiting current, the ohmic drop should become more important relative to the concentration polarization in determining the current distribution. At the same time the surface overpotential in equation (31) should increase (see

equation (51)), but not as fast as the ohmic drop if the surface overpotential is of a Tafel (logarithmic) type. Then

$$\eta_s = O\left[(RT/F) \ln Pe\right] .$$ (65)

These relations (63), (64), and (65) may have important engineering consequences in the design of electrochemical cells.

Boundary-layer flows

If, on the other hand, one is dealing with boundary-layer flows at high Reynolds numbers on bodies submerged in a free stream or on a rotating disk, the order of magnitude of β becomes

$$\beta = O(U \sqrt{Re}/L)$$ (66)

and all the other magnitude estimates must be changed accordingly.

$$i = O(Re^{\frac{1}{2}}Sc^{\frac{1}{3}} FD_R c_{R\infty}/L). \qquad \nabla\Phi = O(Re^{\frac{1}{2}}Sc^{\frac{1}{3}} RT/LF) .$$ (67)

Within the diffusion layer

$$y = O(L/Re^{\frac{1}{2}}Sc^{\frac{1}{3}}), \qquad etc.$$ (68)

There is really no difference in the justification of the separation of the current-distribution problem into two parts, but the dependence on the Reynolds number is shown explicitly.

5. Discussion and Conclusions

Current and potential distribution problems in electrolytic cells where neither ohmic potential drop in the bulk solution nor mass-transfer limitations near the electrodes can be neglected are treated most conveniently by separate calculations for the two regions, the bulk medium and the diffusion layer. The two regions remain coupled through the boundary conditions. For example, in purely numerical calculations it would be unwise to try to use the

same grid mesh in the two regions. It would either be too coarse for the diffusion layer or require too many mesh points for the bulk medium.

The analysis here has been restricted to laminar forced convection. A similar separation into two regions would also be possible for other situations where the concept of a thin diffusion layer applies, for example, turbulent flow, free convection, and growing mercury drops as used in polarographic analysis. For turbulent flow it would be necessary to include turbulent transport terms $\partial \overline{c_i' v_y'} / \partial y$ in equation (14). For free convection, the principle of a thin diffusion layer and of the separation of the problem into two parts still applies, but two differences should be noted. The fluid velocity in free convection depends upon variations of density within the diffusion layer. Consequently, one cannot assume that the velocity is known in advance. Instead he must calculate the velocity at the same time as the mass-transfer rate. Furthermore, the hydrodynamic boundary layer is of roughly the same thickness as the diffusion layer, and it is not possible to use only the velocity derivative at the wall as in equation (18), even for very large Schmidt numbers.

For current distribution problems at the limiting current, where the ohmic potential drop in the bulk solution can be neglected, the current is distributed along the electrode in a manner exactly similar to that which would be predicted by diffusion theory in the absence of ionic migration. The correction factor for the effect of migration in the diffusion layer depends on the composition of the bulk solution, but it is independent of the geometry of the electrode. These conclusions are shown to

apply for large Schmidt numbers and for arbitrary two-dimensional and axisymmetric diffusion layers.

6. Appendix

Even though no specific problems are treated in this paper at currents below the limiting current, the additional simplifications possible in certain special cases should be pointed out.

Binary electrolyte

For the solution of a single salt, the requirement of electroneutrality (4) restricts the concentrations of anions and cations so that the potential can be eliminated from the two mass-transfer, boundary-layer equations (18) to yield

$$\frac{\partial c}{\partial t} + y\beta \frac{\partial c}{\partial x} - \frac{1}{2} y^2 \beta' \frac{\partial c}{\partial y} = D \frac{\partial^2 c}{\partial y^2} \tag{69}$$

where

$$c = c_+/\nu_+ = c_-/\nu_- \tag{70}$$

and

$$D = \frac{z_+ u_+ D_- - z_- u_- D_+}{z_+ u_+ - z_- u_-} . \tag{71}$$

The number of cations and anions per molecule of salt is ν_+ and ν_-, respectively. The boundary conditions (22) and (23) become

$$c \longrightarrow c_\infty \quad \text{as} \quad y \longrightarrow \infty . \tag{72}$$

$$\left(\frac{D_+}{z_+ u_+} - \frac{D_-}{z_- u_-} \right)\frac{\partial c}{\partial y} = \left(\frac{s_+}{u_+} + \frac{s_-}{u_-} \right)\frac{i_y}{nFz_+ \nu_+} \quad \text{at } y = 0 . \tag{73}$$

With the use of equation (7) for the conductivity, equation (30) becomes

$$\eta_c = \frac{i_y(y=0)}{z_+ \nu_+ F^2 (z_+ u_+ - z_- u_-)} \int_0^\infty \left(\frac{1}{c} - \frac{1}{c_\infty} \right) dy$$

$$+ \left[\frac{1}{F} \frac{D_+ - D_-}{z_+ u_+ - z_- u_-} + \frac{RT}{nF} (s_+ + s_-) \right] \ln \frac{c_\infty}{c_o} \, . \qquad (74)$$

It is tempting to try to simplify this expression for the concentration overpotential even further. For steady problems equation (69) shows that

$$\partial^2 c / \partial y^2 = 0 \quad \text{at } y = 0 \, , \qquad (75)$$

and, for the purpose of evaluating the integral in equation (74), the concentration profile could be approximated as

$$\left. \begin{array}{ll} c = c_o + (c_\infty - c_o) y / \delta & \text{for } y \leqslant \delta \\[6pt] c = c_\infty & \text{for } y > \delta \, , \end{array} \right\} \qquad (76)$$

where δ is given by

$$\frac{\partial c}{\partial y} = \frac{c_\infty - c_o}{\delta} \qquad \text{at } y = 0 \, . \qquad (77)$$

Then

$$\int_0^\infty \left(\frac{1}{c} - \frac{1}{c_\infty} \right) dy = \frac{\delta}{c_\infty - c_o} \ln \frac{c_\infty}{c_o} - \frac{\delta}{c_\infty} = \left[\ln \frac{c_\infty}{c_o} - \frac{c_\infty - c_o}{c_\infty} \right] \Bigg/ \frac{\partial c}{\partial y} \Bigg|_{y=0} \, . \qquad (78)$$

For a metal deposition reaction $(s_- = 0)$ and with the use of the Nernst-Einstein relation (9) and the approximation (78), the expression for the concentration overpotential reduces to

$$\eta_c = RT \left[(z_+ - z_-) \big/ z_+ z_- F \right] \left[\ln (c_\infty / c_o) - t_+ (1 - c_o / c_\infty) \right] \, , \qquad (79)$$

where $t_+ = z_+ u_+ / (z_+ u_+ - z_- u_-)$ is the cation transference number. Except near the limiting current the second term is not negligible compared to the logarithmic term. At the same time, the

approximation (76) is not justified by the thinness of the diffusion layer.

Equation (79) is simplified and does not require a knowledge of the concentration profile in the diffusion layer. Nevertheless, it should be emphasized that concentration polarization is not a local phenomenon. The concentration c_o at the surface depends on events upstream in the diffusion layer. If, however, one postulated a stagnant Nernst diffusion layer of thickness $\delta(x)$, then concentration polarization could be treated as a local phenomenon. This could give only a qualitative representation of the effect of concentration polarization.

Solutions with supporting electrolyte

For solutions with an excess of supporting electrolyte, one may wish to neglect the migration terms in equation (18). But even with less supporting electrolyte, it should be possible to neglect conductivity variations in the diffusion layer so that the concentration overpotential (30) becomes

$$\eta_c = \sum_i \left[\frac{s_i RT}{nF} \ln \frac{c_{i\infty}}{c_{io}} + \frac{z_i FD_i}{\kappa_\infty} (c_{i\infty} - c_{io}) \right] . \qquad (80)$$

High rates of stirring

For very vigorous stirring and currents considerably below the limiting current, the concentrations can be taken to be uniform even in the diffusion layer. Then the current distribution is found by solving Laplace's equation subject to the boundary condition

$$\widetilde{\Phi}(x) = V_{met}(x) - \eta_s = V_{met}(x) - g\left[c_{i\infty}, i_y(y=0) \right] , \qquad (81)$$

where $i_y(y=0)$ is related to the normal derivative of the potential

by equation (20). Laplace's equation and this (frequently) nonlinear boundary condition define the problem of the so-called "secondary current distribution."

Acknowledgment

Nomenclature

a   = 0.51023

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

C   - capacity of the double layer (farad/cm^2)

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

e^- - symbol for the electron

$\underline{E}$ - electric field (volt/cm)

f   - expresses dependence of reaction rate on surface overpotential

F   - Faraday's constant (96,500 coulomb/equiv.)

g   - expresses dependence of surface overpotential on current density

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

I   - dimensionless current density

L   - length characteristic of the cell (cm)

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)

Pe = UL/D_R, the Péclet number

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

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

Re = UL/ν, the Reynolds number

s_i - stoichiometric coefficient in electrode reaction

$Sc = \nu/D_R$, the Schmidt number

t — time (sec)

t_+ — cation transference number

T — temperature (deg K)

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

U — characteristic velocity (cm/sec)

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

V — potential of an electrode (volt)

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

β — velocity derivative at the solid electrode (sec^{-1})

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

δ — diffusion layer thickness (cm)

η — overpotential (volts)

θ_i — dimensionless concentration

κ — conductivity (mho/cm)

μ_i — electrochemical potential of species i (joule/mole)

ν — kinematic viscosity (cm^2/sec)

ν_+, ν_- — number of cations and anions per molecule of electrolyte

ξ — dimensionless independent variable [see equations (35) and (47)]

φ — potential appropriate to the diffusion layer (volt)

Φ — electrostatic potential (volt)

Ω — rotation speed of disk (radians/sec)

Subscripts

∞ — in the bulk medium R — limiting reactant

o — at the electrode surface $+,-$ — cation and anion, respectively

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