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THE EFFECT OF VARIABLE TRANSPORT PROPERTIES ON MASS TRANSFER TO A ROTATING DISK

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The Effect of Variable Transport Properties on Mass Transfer to a Rotating Disk

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Abstract

It is shown how one can calculate velocity and concentration profiles near a rotating disk taking into account variable transport properties, non-zero interfacial velocity, and finite Schmidt number. It is found that the surface is uniformly accessible for mass transfer and that the limiting current, in particular, and heat and mass transfer rates, in general, are proportional to the square root of the rotation speed, other conditions being the same. Specific results are given for deposition of copper from aqueous $CuSO_4$ solutions, where it is found that the correction to Levich's classical equation due to variable properties is considerably greater than that due to either a non-zero interfacial velocity or a finite Schmidt number alone. Concentration overpotentials are defined and calculated for copper deposition.

Mathematical Formulation

A rotating disk provides a uniformly accessible surface. This means that if a heterogeneous reaction is carried out at the surface, the mass transfer rate is uniform to all parts of the surface. This is important if one wants to study the heterogeneous reaction uncomplicated by mass transfer effects.

The rotating disk was shown[1] to be uniformly accessible for mass transfer with constant fluid properties, but it seems reasonable to suppose that this characteristic is not peculiar to the constant property case.

Let us use cylindrical coördinates where z is the normal distance from the surface of the disk. Assume steady, laminar flow of a Newtonian fluid where the viscosity μ depends on composition, and let the gravitational acceleration be perpendicular to the disk. We shall further assume, and verify later, that the normal velocity component and the composition depend only on z, so that the surface is uniformly accessible. It follows from this assumption that the viscosity, density, diffusion coefficient, and other transport properties depend only on z.

The transformation of von Kármán[2] suggests that we express the velocity components and the pressure as follows:

$$\left.\begin{aligned} v_r = r\Omega F(\xi), \quad v_\theta = r\Omega G(\xi), \quad v_z = \sqrt{\Omega\nu_\infty}\, H(\xi), \\ p = \mu_\infty \Omega P(\xi) + g_z \int_0^z \rho\, dz, \end{aligned}\right\} \tag{1}$$

where

$$\xi = z\sqrt{\Omega/\nu_\infty}, \tag{2}$$

r is the radial position coördinate, ρ is the fluid density, Ω is the rotation speed of the disk (radians/sec), g_z is the z-component of the gravitational acceleration, μ_∞, ν_∞, and ρ_∞ are the viscosity, kinematic

viscosity, and density in the bulk of the solution far from the disk. Equations (1) define dimensionless functions F, G, H, and P and show how the velocity components and the pressure depend on r and Ω as well as the dimensionless normal coördinate ξ.

In order to obtain differential equations for F, G, H, and P it is necessary to substitute equations (1) into the equations of motion and continuity of the fluid:

$$\rho \frac{\partial \underline{v}}{\partial t} + \rho \underline{v} \cdot \nabla \underline{v} = - \nabla p - \nabla \cdot \underline{\tau} + \rho \underline{g} \ . \tag{3}$$

$$\frac{\partial \rho}{\partial t} + \underline{v} \cdot \nabla \rho = - \rho \nabla \cdot \underline{v} . \tag{4}$$

The viscous stress for a Newtonian fluid is

$$\underline{\tau} = - \mu [\nabla \underline{v} + (\nabla \underline{v})^T] + \frac{2}{3} \mu \underline{I} \nabla \cdot \underline{v} \ , \tag{5}$$

where $(\nabla \underline{v})^T$ denotes the transpose of the velocity gradient and $\underline{I}$ denotes the unit tensor.

We make explicit reference to the text of Bird, Stewart, and Lightfoot[3] because these equations are displayed there in cylindrical coördinates in a form appropriate to a fluid with varying density and viscosity.

With the assumptions already stated, the components of the viscous stress are found to be (ref. 3, p. 89)

$$\left.\begin{aligned} &\tau_{rr} = \tau_{\theta\theta} = - \frac{1}{2} \tau_{zz} = - \frac{2}{3} \mu \Omega (F - H'), \\ &\tau_{r\theta} = 0, \quad \tau_{\theta z} = - \frac{\mu r \Omega^{3/2}}{\sqrt{\nu_\infty}} G', \quad \tau_{rz} = - \frac{\mu r \Omega^{3/2}}{\sqrt{\nu_\infty}} F', \end{aligned}\right\} \tag{6}$$

where primes denote differentiation with respect to ξ.

The continuity equation (4) becomes (ref. 3, p.83, eq. (B))

$$2F + H' = - H \frac{d \ln \rho}{d\xi} \ . \tag{7}$$

Substitution of the viscous stress given by equations (6) into the equation of motion (3) (ref. 3, p. 85, eq. (A),(B),and (C)) yields

$$\left.\begin{aligned} F^2 - G^2 + HF' &= \frac{\rho_\infty}{\rho}\frac{d}{d\xi}\left(\frac{\mu F'}{\mu_\infty}\right) . \\ 2FG + HG' &= \frac{\rho_\infty}{\rho}\frac{d}{d\xi}\left(\frac{\mu G'}{\mu_\infty}\right) . \end{aligned}\right\} \quad (8)$$

$$\frac{\rho}{\rho_\infty} HH' + P' = \frac{4}{3}\frac{d}{d\xi}\left[\frac{\mu}{\mu_\infty}(H'-F)\right] + \frac{2\mu}{\mu_\infty} F' . \quad (9)$$

The boundary conditions include

$$\left.\begin{aligned} F = 0,\ G = 1 \quad &\text{at } \xi = 0 . \\ F = G = 0 \quad &\text{at } \xi = \infty . \end{aligned}\right\} \quad (10)$$

In addition, the normal velocity component is related to the rate of interfacial mass transfer. When the viscosity and density are constant, equations (8) and (9) reduce to those of von Kármán[2], and these have been solved numerically by Cochran[4] when the interfacial velocity is zero, that is, $H = 0$ at $\xi = 0$.

For an electrolytic solution of a single salt in a single solvent, the concentration distribution is governed by the equation[13,14]

$$\rho\frac{\partial\omega_s}{\partial t} + \rho\underline{v}\cdot\nabla\omega_s + \frac{M_s\underline{i}\cdot\nabla t_+}{z_+\nu_+F} = \nabla\cdot(\rho D\nabla\omega_s) , \quad (11)$$

where ω_s is the mass fraction of the salt in the solution, M_s is the molecular weight of the salt, $\underline{i}$ is the current density, D is the diffusion coefficient of the salt, t_+ is the cation transference number with respect to the mass-average velocity, z_+ is the charge number of the cation, ν_+ is the number of cations per molecule of salt, and F is Faraday's constant. The transference number t_+ is related to the transference number t_+^o with respect to the solvent velocity by the relation

$$t_+ = \omega_- + (1-\omega_s)\, t_+^o \,, \tag{12}$$

where ω_- is the mass fraction of the anion in the solution. It is t_+^o which is measured and reported in the literature.

Equation (11) reduces to the equation describing diffusion in a binary mixture of non-electrolytes if the current density is zero or if the transference number is constant. If we take the current density to be constant and to lie in the z-direction, then we can write equation (11) as an ordinary differential equation:

$$\left(\frac{\rho}{\rho_\infty} H + I \frac{dt_+}{d\omega_s}\right) \omega_s' = \frac{d}{d\xi}\left(\frac{\rho D \omega_s'}{\mu_\infty}\right), \tag{13}$$

where

$$I = \frac{M_s i_z}{z_+ \nu_+ F \sqrt{\Omega \mu_\infty \rho_\infty}} \,. \tag{14}$$

For boundary conditions we take

$$\omega_s = \omega_o \text{ at } \xi = 0; \qquad \omega_s = \omega_\infty \text{ at } \xi = \infty \,. \tag{15}$$

It is still necessary to show how the mass transfer rate, the current density, the concentration gradient, and the normal component of the velocity are related at the disk surface. For metal deposition or dissolution the normal fluxes of solvent and of the anion are zero at the interface. Hence the mass-average velocity is simply related to the mass flux of the cation, which is in turn related to the current density.

$$\rho v_z = n_{+z} = \frac{M_+ i_z}{z_+ F} \text{ at } z = 0.$$

The mass flux of the cation is

$$\underline{n}_+ = -\frac{\nu_+ M_+}{M_s} \rho D \nabla \omega_s + \frac{M_+ t_+}{z_+ F} \underline{i} + \rho \omega_+ \underline{v} \,. \tag{16}$$

The concentration gradient at the disk can then be obtained from

equation (16):

$$\rho v_z \, (t_- - \omega_+) = - \frac{\nu_+ M_+}{M_s} \rho D \frac{d\omega_s}{dz} \text{ at } z = 0 \tag{17}$$

or, in dimensionless form,

$$I = \frac{\rho}{\rho_\infty} \frac{M_s}{\nu_+ M_+} H = \frac{1}{\omega_+ - t_-} \frac{\rho D}{\mu_\infty} \frac{d\omega_s}{d\xi} \text{ at } \xi = 0 \, . \tag{18}$$

The mathematical problem for the determination of the concentration and velocity distributions is defined by the differential equations (7), (8), (9), and (13) and the boundary conditions (10), (15), and (18). The assumptions underlying this mathematical formulation are the same as in the classical work of von Kármán[2] and of Levich[1] in that edge effects are neglected and the flow is assumed to be steady and laminar. The assumptions of constant properties and zero interfacial velocity are removed in the present work, and the solutions for F, G, H, P, and ω_s constitute an exact solution of the hydrodynamic and mass-transfer equations.

If the pressure dependence of the fluid properties is ignored, there is no need to solve equation (9) for the pressure. This approximation will be made in the present work.

Numerical Solution Method

The problem consists of a group of coupled, non-linear differential equations with boundary conditions at zero and infinity. Equations (7) and (8) were linearized about a trial solution producing a series of coupled, linear differential equations in which the concentration distribution is assumed to be known. In finite difference form these give coupled, tri-diagonal matrices which can be solved readily on a high-speed, digital computer. With a known velocity distribution, equation (13) can be solved

for the concentration. The non-linear problem can then be solved by iteration. A total of one thousand mesh points was used.

It probably would have been more efficient in the numerical solution to linearize simultaneously equations (7), (8), and (13), but the method used can be applied directly for calculating the velocity profiles in a multicomponent solution if the concentration distributions are known.

Results

a) Dependence on the Rotation Speed

The mathematical formulation, and in particular equation (14), makes it clear that the current density is proportional to the square root of the rotation speed Ω, since i_z and Ω appear only in the parameter I and nowhere else in the dimensionless formulation of the problem. The parameter I is then determined in the course of solving this problem and can itself depend on ω_o and ω_∞ and how the fluid properties vary with concentration.

This dependence of i_z on Ω is exact for any Schmidt number and for any variation of the fluid properties with concentration, and it should also apply to multicomponent systems. Hence the many experimental verifications of the linear dependence of the limiting current density upon the square root of the rotation speed confirm the applicability of the present analysis but would not serve to justify any approximations for large Schmidt numbers or for constant physical properties.

b) Effect of a Non-zero Interfacial Velocity

Actual mass-transfer rates may deviate from the classical result of Levich[1] because the Schmidt number is not infinite, because the interfacial velocity is not zero, or because the fluid properties vary with

concentration. Corrections for finite Schmidt numbers have been discussed by Gregory and Riddiford[5] and by Newman[6]. Sparrow and Gregg[7] give results for the analogous heat-transfer problem corresponding to Schmidt numbers of 0.01, 0.1, 1, 10, and 100, whereas the Schmdit number is closer to 1000 for mass tansfer in liquids. For electrolytic solutions the Schmidt-number correction to Levich's formula amounts to about 3 percent.

Olander[8] has obtained numerical solutions for the effect of the interfacial velocity for non-electrolytic solutions of constant properties. These results are applicable to electrolytic solutions if one accounts for the contribution of migration to the mass transfer. For deposition of a metal cation, figure 1 shows the correction factor for mass-transfer rates

$$\theta = \frac{1-\omega_o}{\omega_o-\omega_\infty} I\, t_-^o \Big/ \lim_{H(o)\to 0}\left[\frac{1-\omega_o}{\omega_o-\omega_\infty} I\, t_-^o\right] \tag{19}$$

plotted against the "flux ratio"

$$R = \frac{\nu_+ M_+}{t_-^o M_s}\,\frac{\omega_o-\omega_\infty}{1-\omega_o}\,. \tag{20}$$

The limit in the denominator of equation (19) means the limit of low rates of mass transfer where the interfacial velocity is negligible. Curves are shown for Sc = ∞ and for Sc = 1. The curve for Sc = ∞ is the same as that for two-dimensional, boundary-layer flows (see Acrivos[9,p.341]) and is given by

$$\theta = \Gamma(4/3) \Big/ \int_0^\infty e^{-x^3} \exp\{xR\theta/\Gamma(4/3)\}\, dx. \tag{21}$$

The calculated points for Sc = 1000 and for Sc = 100 deviate from this curve for Sc = ∞ by less than 0.3 and 1 percent, respectively. It is interesting that the curves for Sc = 1000 and for Sc = 100 do not lie between the curves for Sc = 1 and for Sc = ∞.

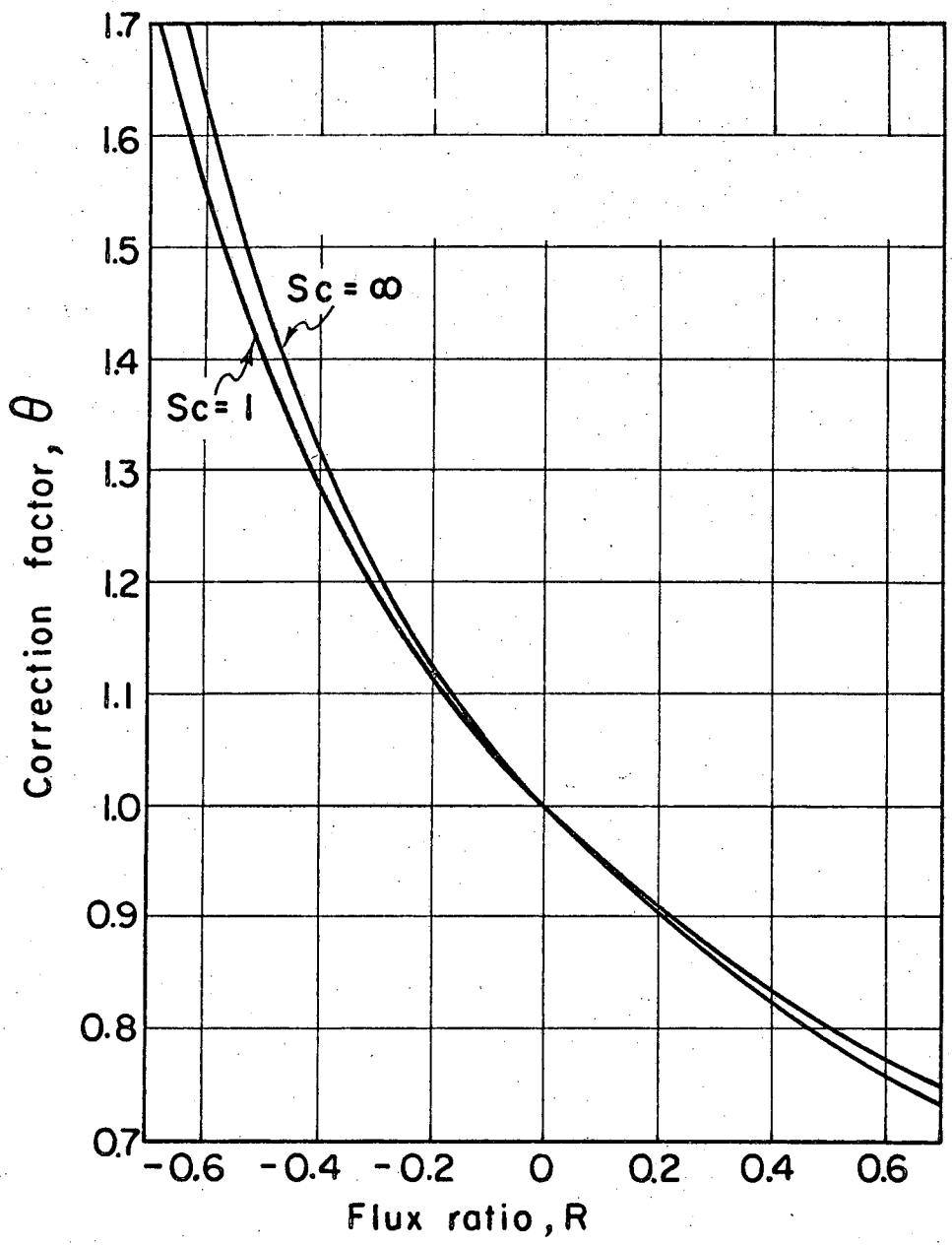

Figure 1. The effect of an interfacial velocity on mass transfer rates.

The constant-property case is of interest if we want to assess the relative importance of non-constant properties and of a non-zero interfacial velocity in leading to deviations from the results of dilute-solution theory. In gases the properties are quite constant, but the interfacial velocity can be significant. In liquids, on the other hand, the solutions may be fairly dilute because of the solubility limit, but the diffusion coefficient can be a strong function of position. (Compare Spalding[10].)

For metal deposition at the limiting current from a 0.5 M solution of copper sulfate in water, R = -0.0469 which corresponds to a correction factor of $\theta = 1.027$. In this case the correction is in the opposite direction from the Schmidt-number correction.

c) Deposition of Copper

Mass-transfer rates calculated for the deposition of copper from aqueous cupric sulfate solutions at 25°C are shown in figure 2 in the form of the limiting current density divided by the square root of the rotation speed plotted against the bulk concentration of $CuSO_4$. The curve labeled "exact" is calculated as outlined earlier so as to account for property variations, non-zero interfacial velocity, and non-infinite Schmidt number. For comparison, the equation of Levich[1] has been evaluated with the bulk values of the physical properties. Figure 2 also shows the results when the Levich equation is corrected[5,6] for the fact that the Schmidt number is not infinite. The fourth curve shows the results when the Levich equation is corrected for the effect of a non-zero interfacial velocity according to figure 1. In this case all properties were evaluated at the bulk concentrations except the transference number in R (equation (20)), which was evaluated at the surface concentration since it arises from the boundary condition (18).

Figure 2 shows that corrections for finite Schmidt number and non-zero interfacial velocity are small compared to the effect of property variations. The constant-property solutions would, of course, give better agreement with the exact analysis if appropriate average values of the physical properties were used. Figure 3 shows "integral" diffusion coefficients appropriate for

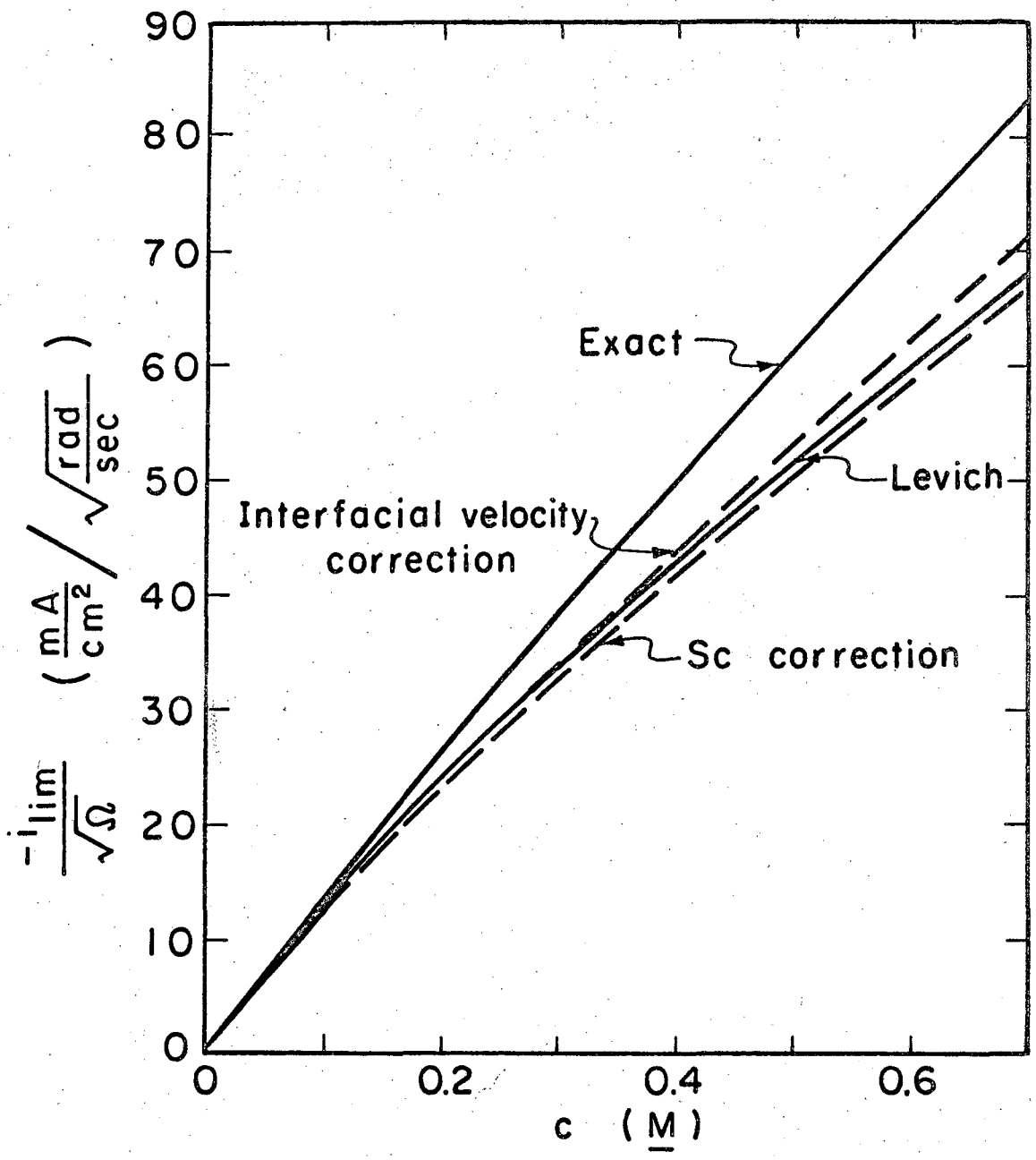

Figure 2. Limiting currents for copper deposition.

the rotating disk plotted against the square root of the mass fraction of $CuSO_4$. These were calculated from the equation of Levich[1] in the form

$$D_{in} = \nu_\infty \left[\frac{-i_{lim}}{z_+ \nu_+ F c_\infty \sqrt{\Omega \nu_\infty}} \frac{1-t_+}{0.62048} \right]^{3/2} = \nu_\infty \left(\frac{-I_{lim}}{\omega_\infty} \frac{1-t_+}{0.62048} \right)^{3/2}, \tag{22}$$

where the limiting current was calculated according to the rigorous analysis. Also shown are the differential diffusion coefficients of Eversole[11] and of Emanuel and Olander[12], which were used in the rotating disk calculations, and the integral diffusion coefficients appropriate to a diaphragm cell and defined as

$$D_{in} = \frac{1}{\omega_\infty} \int_0^{\omega_\infty} D \, d\omega \, . \tag{23}$$

Figure 3 shows that the integral diffusion coefficient appropriate to a rotating disk is not the same as that appropriate to a diaphragm cell. Since no way has been developed for resolving the rotating disk data into the differential diffusion coefficient data, the rotating disk is not very useful for measuring the concentration dependence of the diffusion coefficient in a binary electrolyte.

Other useful by-products of the mass-transfer calculations are the surface concentration and the concentration overpotential. Figure 4 shows how the surface concentration varies from the bulk value at zero current to zero at the limiting current for several values of bulk concentration. The straight, diagonal line corresponds to the results for constant properties.

d) Concentration Overpotential

We define here the concentration overpotential for this particular, copper system in terms of two copper reference electrodes, one in the bulk

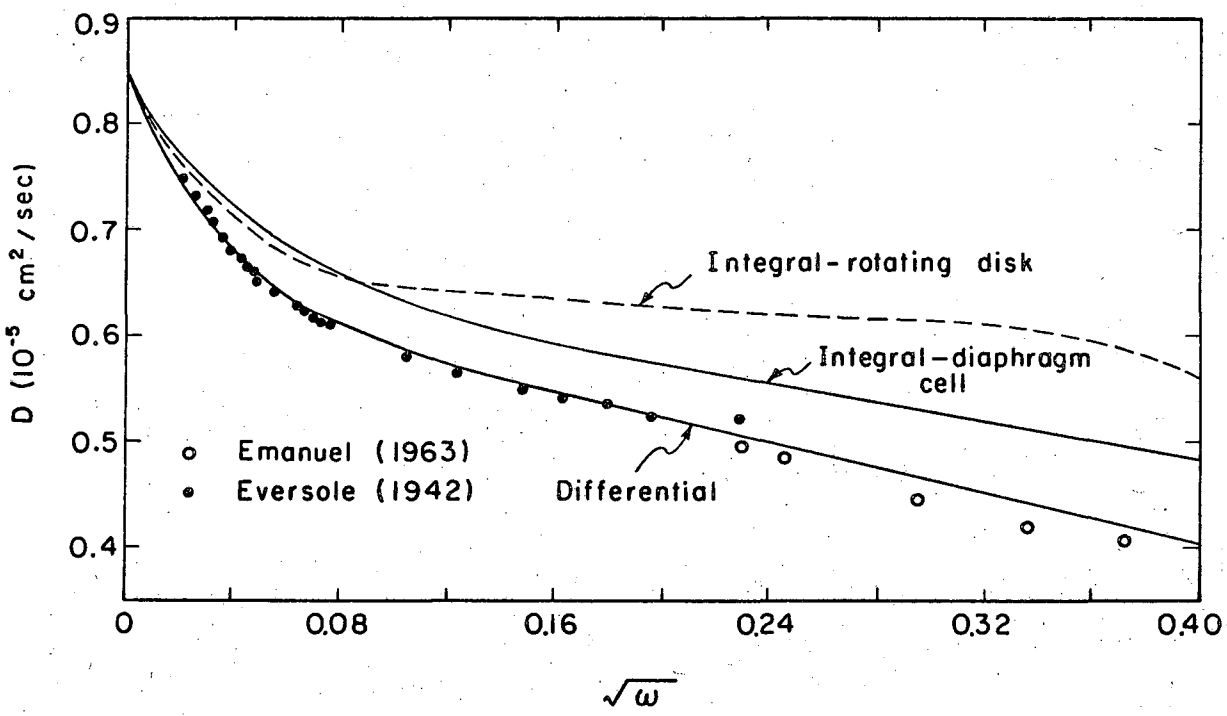

Figure 3. Diffusion coefficients for $CuSO_4$ in water.

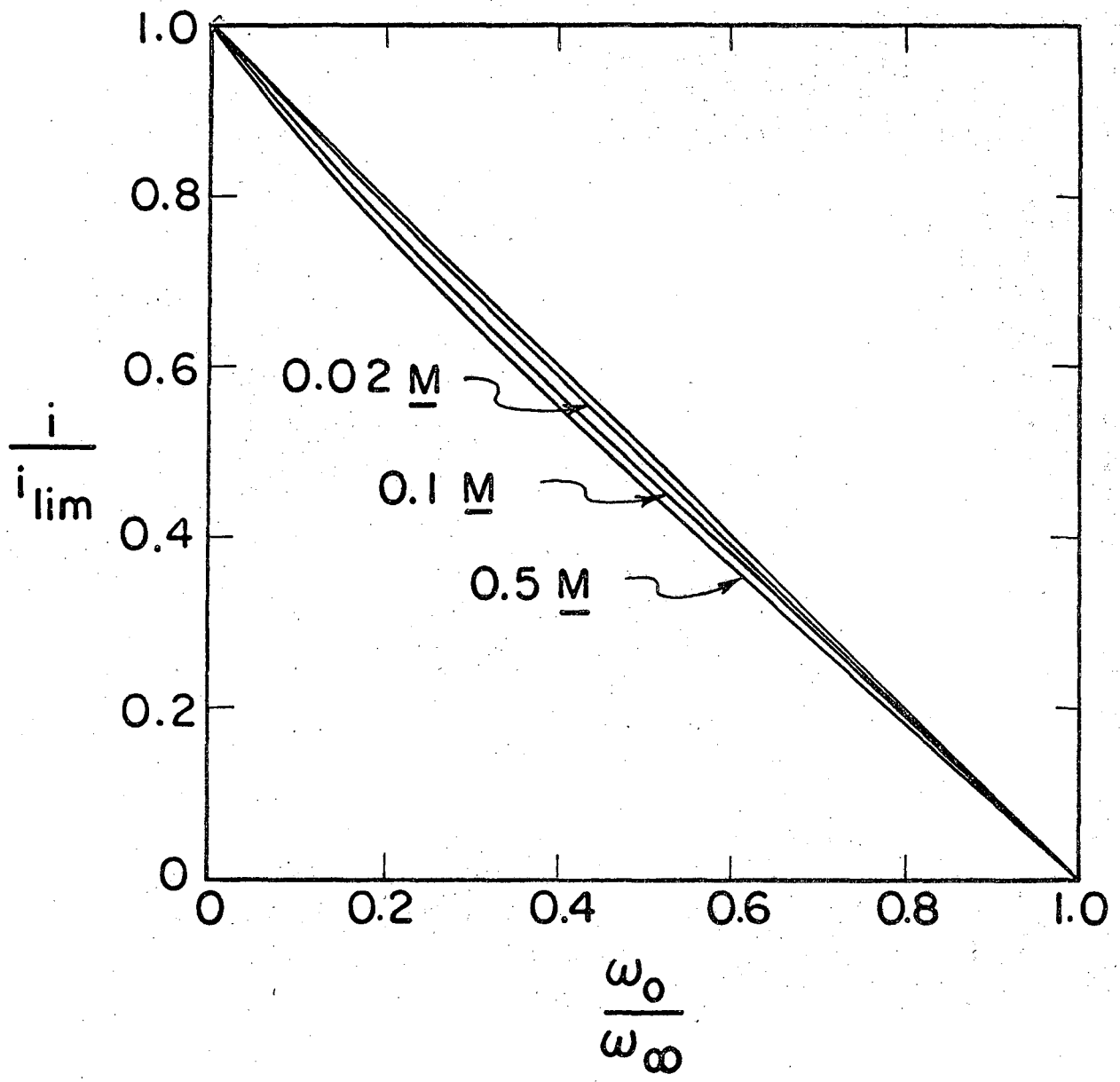

Figure 4. Concentration at the electrode surface.

solution and one located very near the disk surface. Let $\Delta\Phi_i$ be the potential of the reference electrode near the disk minus the potential of the reference electrode in the bulk, and let $\Delta\Phi_{ohm}$ be the potential difference which would exist if there were the same current distribution but no concentration variations in the diffusion layer. Then we define the concentration overpotential as

$$\eta_c = \Delta\Phi_i - \Delta\Phi_{ohm} .$$

The concentration overpotential thus defined is the potential of a concentration cell plus an ohmic contribution due to the change of resistivity in the diffusion layer.

The potential Φ of a movable, copper reference electrode varies with position according to the equation[13]

$$\nabla\Phi = - \underline{i}/\kappa + (RT/F)(1-t_+^o) \nabla \ln \gamma m . \tag{24}$$

By subtracting the current density divided by the bulk conductivity and integrating, we obtain for the concentration overpotential at the rotating disk as defined above

$$\eta_c = \int_0^\infty i_z \left(\frac{1}{\kappa} - \frac{1}{\kappa_\infty}\right) dz - \frac{RT}{F} \int_{\omega_0}^{\omega_\infty} (1-t_+^o) \frac{d \ln \gamma m}{d\omega} d\omega . \tag{25}$$

The calculated concentration overpotential is plotted against a dimensionless current density in figure 5 for various bulk concentrations of $CuSO_4$.

By defining the concentration overpotential in terms of two reference electrodes, there is no question that it is well defined, and the potential difference between the disk electrode and the reference electrode adjacent to its surface can be regarded as the "surface overpotential" associated with the electrode reaction itself. In this way the "surface overpotential" depends only on the current density and the concentration at the electrode

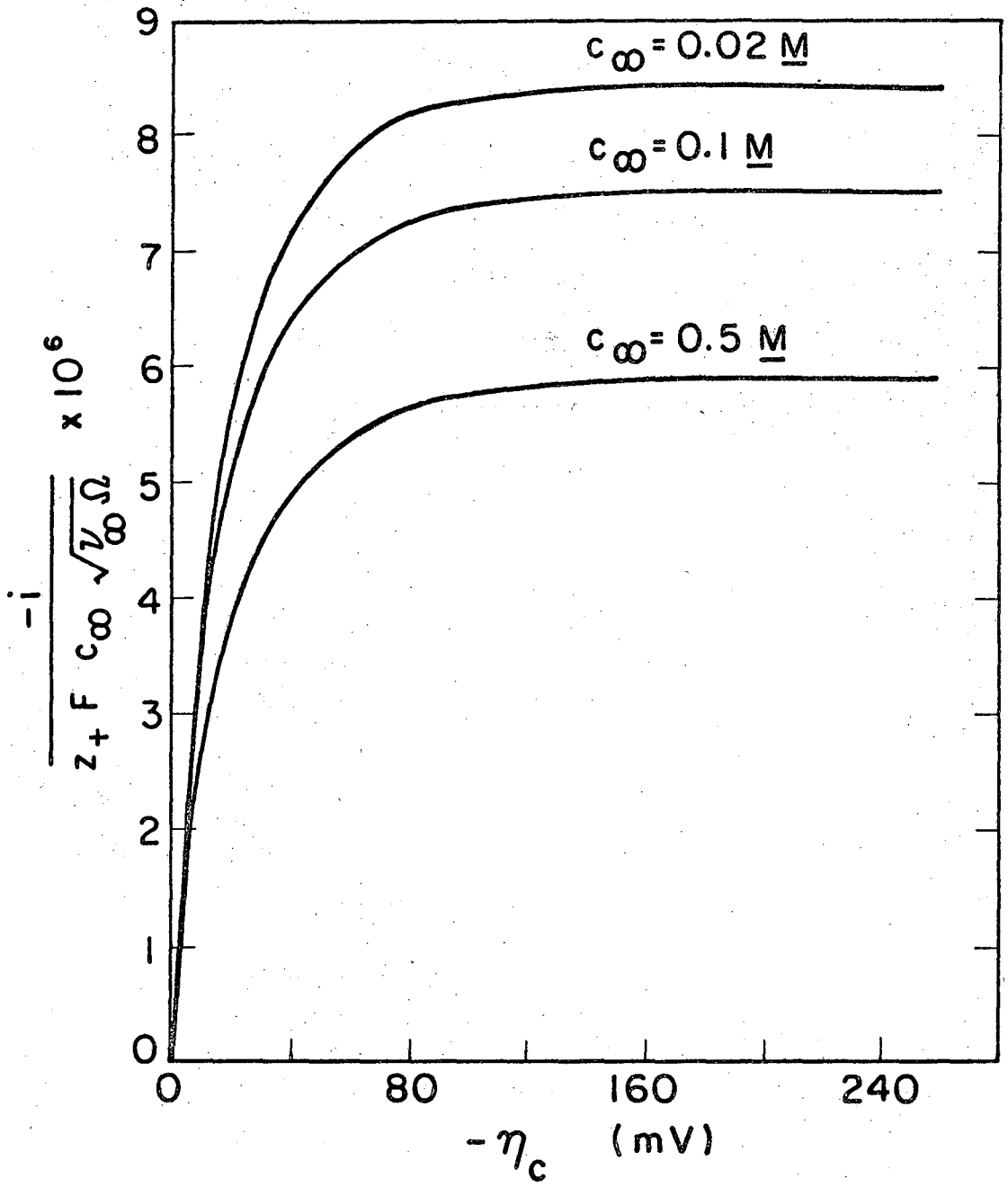

Figure 5. Concentration overpotential.

surface, as it should, and not upon any events occurring in the diffusion layer or beyond.

By subtracting the potential difference between the two reference electrodes which would exist in the absence of concentration variations, the concentration overpotential becomes independent of the position of the second reference electrode outside the diffusion layer. One can then calculate a separate "ohmic overpotential" which will depend upon the macroscopic current distribution in the cell outside the diffusion layer and on the placement of the reference electrode.

The concentration overpotential thus defined can be calculated from mass-transfer theory and requires a knowledge of all the transport properties of the solution (μ, κ, t_+^o, and D) but does not require any quantitative expressions for the electrode kinetics.

Acknowledgment

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Nomenclature

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

D_{in} - integral diffusion coefficient (cm^2/sec).

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

F - dimensionless radial velocity.

G - dimensionless tangential velocity.

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

H - dimensionless axial velocity.

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

I - dimensionless current density (see equation (14)).

m - molality (moles/kg).

M - molecular weight (g/mole).

$\underline{n}_+$ - mass flux of cations (g/cm^2-sec).

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

P - dimensionless dynamic pressure.

r - radial coördinate (cm).

R - flux ratio (see equation (20)).

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

Sc = ν/D, Schmidt number.

t - time (sec).

t_+ - cation transference number with respect to mass-average velocity.

t_+^o - cation transference number with respect to solvent velocity.

T - absolute temperature (deg K).

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

z - normal distance from disk (cm).

z_+ - charge number of cation.

γ - mean molal activity coefficient.

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

η_c - concentration overpotential (volt).

θ - angular coördinate.

θ - correction factor (see equation (19)).

κ - conductivity (mho/cm).

μ - viscosity (g/cm-sec).

ν - kinematic viscosity (cm^2/sec).

ν_+ - number of cations per molecule of salt.

ξ - dimensionless normal distance (see equation (2)).

ρ - density (g/cm^3)

$\underline{\tau}$ - viscous stress ($dyne/cm^2$).

Φ - potential of reference electrode (volt).

ω - mass fraction.

Ω - rotation speed of disk (radians/sec).

subscripts

+ - cation.

- - anion.

o - electrode surface.

∞ - bulk solution.

s - salt.

lim - limiting.

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