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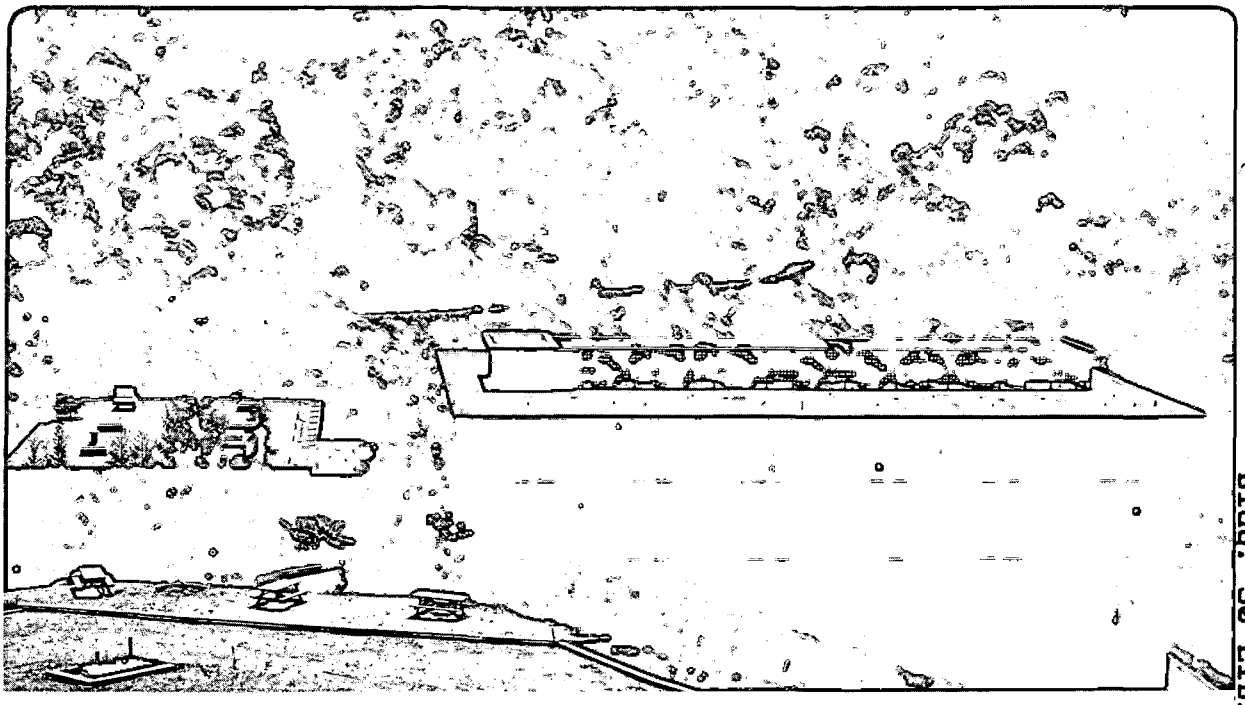

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Modeling Diffusion and Migration in Dilute Electrochemical Systems using the Quasi-potential Transformation

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Abstract

The quasi-potential transformation, based on the Kirchhoff transformation, simplifies the equations governing mass transfer in steady-state, nonconvective electrolytic systems. The major assumption is that the species concentrations can be written as single-valued functions of the electrostatic potential. Methods are developed, based on a theorem presented by Gibbs, to solve the system-specific calculations—those calculations that are dependent only on the specific chemical system used. Results are presented for the binary aqueous copper sulfate system with variable transport properties and for the acidic aqueous copper sulfate system accounting for variations in the dissociation constant of the bisulfate ions. These results are combined with solutions of Laplace's equation for some simple boundary conditions to give complete solutions for the disk and hemisphere electrodes. The effect of migration on limiting currents is discussed.

Introduction

The quasi-potential transformation, introduced by Baker *et al.* [1], transforms the set of coupled, second-order, nonlinear partial differential equations governing mass transfer by diffusion and migration in electrochemical systems into Laplace's equation for the quasi-potential and a set of coupled, first-order, nonlinear ordinary differential equations. The first part, namely Laplace's equation, is referred to as the geometry-specific part since it accounts for the geometry and is independent of the specific chemical (or electrochemical) system used. The latter part is independent of the geometry and is referred to as the system-specific part.

The resulting set of ordinary differential equations is relatively easy to solve. Furthermore, there is a vast body of literature detailing solutions to Laplace's equation subject to electrochemical-type boundary conditions. Conversely, the original set of governing equations can be difficult or impossible to solve without the introduction of restrictive conditions such as the neglect of migration as a mechanism of mass transfer. Another advantage is that the geometry-specific and system-specific parts are independent and can thus be readily combined to make the solutions for many geometries and systems easily accessible.

Certain conditions apply to the use of the quasi-potential transformation. The convective contribution to the mass transfer must be negligible. We have not been able to solve systems in which multiple independent heterogeneous reactions take place. In the problems we have

solved, it has been found necessary that all homogeneous reactions be equilibrated. The transformation applies only to steady-state or quasi-steady-state systems.

Theoretical Development

The fundamental equations governing mass transfer in a continuum are given by Newman [2]:

Material balance:

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot \mathbf{N}_i + R_i \tag{1}$$

Electroneutrality:

$$\sum_i z_i c_i = 0 \tag{2}$$

Current density:

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

Newman also shows that

$$\nabla \cdot \mathbf{i} = 0, \tag{4}$$

which is a statement of the principle of conservation of charge. According to dilute-solution theory, the molar flux of species i is given by

$$\mathbf{N}_i = -z_i u_i F c_i \nabla \Phi - D_i \nabla c_i , \tag{5}$$

where the convective contribution to the flux has been neglected.

Baker *et al.* [1] developed the quasi-potential starting from the assumption that a stagnant species satisfies a Boltzmann distribution in

the solution. Using this as their basis, they showed that the species concentrations may be written as single-valued functions of the electrostatic potential. We start with the assumption that the species concentrations may be written as single-valued functions of the electrostatic potential (or the concentration of the principal reactant in the electrode reaction). While the results obtained are identical, this basis is more general. Furthermore, starting from this basis gives us a systematic framework to develop the system-specific calculations.

We cannot use the basis given above in systems in which convection contributes to the mass transfer, since the presence of a velocity term (which is a function of the spatial variables) makes the resulting solution inconsistent with the governing equations. Applying our fundamental assumption that the concentration is a single-valued function of the electrostatic potential we get

$$\mathbf{N}_i = f_i(\Phi)\nabla\Phi, \tag{6}$$

where

$$f_i(\Phi) = -z_i u_i F c_i - D_i \frac{dc_i}{d\Phi}. \tag{7}$$

Following the Kirchhoff transformation (see Carslaw and Jaeger [3]), as used by Baker *et al.* [1], we define a new dependent variable as

$$q_i = -\int_0^{\Phi} f_i(\Phi)d\Phi. \tag{8}$$

This allows us to write simply

$$\mathbf{N}_i = f_i(\Phi)\nabla\Phi = -\nabla q_i, \tag{9}$$

or using the equation for the current density (equation 3) and the property of the differential operator ∇ that it operates linearly on sums

we write

$$\mathbf{i} = f(\Phi)\nabla\Phi = -\nabla Q, \tag{10}$$

where

$$f(\Phi) = F \sum_i z_i f_i(\Phi). \tag{11}$$

Equation 10 defines the quasi-potential. The negative sign has been included to meet with convention in the mass- (and heat-) transfer field that the flux density should be in the direction of the negative of the gradient of potential. Since the divergence of the current density is zero,

$$\nabla^2 Q = 0. \tag{12}$$

The same results could be obtained by showing that the curl of the current density is zero and applying Stokes's theorem (see Pillay [4]). This treatment shows that the simple-potential theory shown here might apply only to simply-connected regions. We see also that the value of the quasi-potential can be arbitrarily specified at a chosen position.

In all of the work that follows, we assume that the Stokes-Einstein equation

$$D_i = RTu_i \tag{13}$$

holds. We write a nondimensional potential as

$$\phi = \frac{F\Phi}{RT}. \tag{14}$$

The equation for the flux becomes

$$\mathbf{N}_i = -z_i D_i c_i \nabla\phi - D_i \nabla c_i, \tag{15}$$

or in terms of the electrostatic potential

$$N_i = f_i(\phi)\nabla\phi, \tag{16}$$

where

$$f_i(\phi) = -D_i\left[z_i c_i + \frac{dc_i}{d\phi}\right] \tag{17}$$

Also,

$$\frac{dQ}{d\phi} = -F\sum_i z_i f_i(\phi) = -f(\phi). \tag{18}$$

Central to the system-specific calculations is a theorem presented by Gibbs [5] (theorem 81, page 39):

> If throughout a certain space (which need not be continuous and which may extend to infinity)
>
> $$\nabla\cdot\nabla u = 0,$$
>
> and in all the bounding surfaces the normal component of ∇u vanishes, and at infinite distances within the space (if such there are) $r^2\frac{du}{dr} = 0$, where r denotes the distance from a fixed origin, then throughout the space
>
> $$\nabla u = 0,$$
>
> and in each continuous portion of the same
>
> $$u = \text{constant}.$$

We have shown that all species fluxes may be written as the gradient of some potential q_i (equation 9). If the species does not participate in a homogeneous reaction, then it follows, from the material balance equation 1, that this potential is governed by Laplace's equation. If, furthermore, the species does not participate in the heterogeneous reaction, then the normal component of the flux is zero at the electrode surface. If there is a counterelectrode present at a finite distance, then the normal component of the flux must be zero at the

counterelectrode to preserve the steady state in the system, since the normal component of the flux is zero at all insulating surfaces. If the counterelectrode is infinitely far from the electrode surface, then it can be shown that the condition at infinity is met as long as the normal component of the flux is zero at all finite bounding surfaces and there are no external fields acting on the system (see Pillay [4]). For a species meeting these conditions, the theorem of Gibbs holds, and the flux of this species is zero everywhere; hence, we term such a species stagnant. It follows from equations 16 and 17 that, for a stagnant species,

$$c_i = c_i^{\infty} e^{-z_i \phi}. \tag{19}$$

We have used the boundary condition that the concentration assumes its bulk value infinitely far from the electrode surface, where the electrostatic potential is set to zero.

If there are no homogeneous reactions taking place, we see from the material balance equations 1 that all the species fluxes are individually solenoidal. The only species with nonzero fluxes are those that participate in the heterogeneous reaction, which may be written

$$s_R A_R + \sum_{j \neq R} s_j A_j = n e^-. \tag{20}$$

We have designated one of the species to be the principal reactant, and for each of the other species j, participating in the heterogeneous reaction, we write a solenoidal flux defined as

$$\mathbf{N}_j - \frac{s_j}{s_R} \mathbf{N}_R. \tag{21}$$

It is evident that the normal component of this flux is zero at all

finite boundaries, and if there are no external fields imposed on the system, it follows from the theorem of Gibbs that this flux is zero everywhere. We can solve for each c_j in terms of c_R to obtain

$$\frac{dc_j}{d\phi} = -z_j c_j + \frac{s_j}{s_R}\frac{D_R}{D_j}\left(z_R c_R + \frac{dc_R}{d\phi}\right). \tag{22}$$

Combining this set of equations with the equations 19 for the stagnant species, the equation of electroneutrality, the equation of current density, and the definition of the quasi-potential, we can solve for the various concentrations, the quasi-potential, and the current density as functions of the electrostatic potential as an initial-value problem using straightforward numerical methods. The initial conditions are normally specified infinitely far from the electrode surface, where the electrostatic- and quasi-potentials are set to zero and the concentrations assume their bulk values. This constitutes the system-specific part of the calculations.

If there are homogeneous reactions taking place, the method remains essentially the same; however, we combine the material balance equations to eliminate the reaction terms. The eliminated material balance equations are replaced by the applicable equilibrium relationships. If any of the species involved in the homogeneous reactions participate in the heterogeneous reaction, then we define a solenoidal flux vector as above using the combined material balance. This procedure can get involved, especially if the species chosen to be the principal reactant participates in homogeneous reactions. In any event, the system-specific part of the problem still reduces to an initial-value problem for the concentration and the electrostatic potential as functions of the quasi-

potential Q.

We have shown that the assumption that the species concentrations can be written as single-valued functions of the electrostatic potential is consistent with the governing equations. In some systems, for example nonelectrolytic systems or binary systems where the electrostatic potential becomes infinite at the electrode surface at limiting-current conditions, it is more useful to write the species concentrations as functions of a principal reactant. It can be shown that this is also consistent with the governing equations.

Binary Systems: we derive general equations for binary electrolyte systems having one stagnant species. Since there can be no homogeneous reactions and it is often the case that only one species participates in the electrode reaction, one of the species is often stagnant. We designate the reactant ion to be species 1 and the stagnant ion to be species 2. From equation 19 and electroneutrality

$$c_2 = c_2^{\infty} e^{-z_2 \phi} \tag{23}$$

and

$$c_1 = c_1^{\infty} e^{-z_2 \phi}; \tag{24}$$

hence

$$\phi = -\frac{1}{z_2} \ln\left(\frac{c_1}{c_1^{\infty}}\right). \tag{25}$$

Since we are using the reactant concentration as the independent variable, we write the flux as

$$N_i = h_i(c_i)\nabla c_i, \tag{26}$$

and from equation 15

$$h_i(c_i) = -D_i\left[z_i c_i \frac{d\phi}{dc_i} + 1\right]. \tag{27}$$

In this particular case, since N_2 is zero,

$$i = -\nabla Q = F \sum_i z_i N_i = F z_1 h_1(c_1)\nabla c_1; \tag{28}$$

therefore

$$\frac{dQ}{dc_1} = z_1 F \frac{D}{(1 - t_1)}, \tag{29}$$

where we have substituted for the diffusion coefficient of species 1 in terms of the salt diffusion coefficient and the transference number, which are the commonly tabulated properties (see Newman [2]). If the transport properties can be considered constant, then we can integrate this equation to obtain

$$Q = z_1 F \frac{D}{(1 - t_1)}\left[c_1 - c_1^{\infty}\right], \tag{30}$$

where we have arbitrarily specified the quasi-potential to be zero at infinity.

Binary Copper Sulfate

The mechanism of the copper deposition reaction has been given by Mattsson and Bockris [6] and has been confirmed by various authors including Bertocci [7] and Brown and Thirsk [8]

$$Cu^{2+} + e^- \longrightarrow Cu^+ \quad \text{(slow)}$$

$$Cu^{+} + e^{-} \longrightarrow Cu \quad \text{(fast)}.$$

All of these authors investigated the mechanism in dilute sulfuric acid solutions. We are unaware of a study of the deposition reaction in nonacidic solutions, but since there is no obvious reason to suspect that there should be any difference in the mechanism in the absence of acid, we accept this as being the mechanism in the binary aqueous copper sulfate system, as well as in the acidic aqueous copper sulfate system.

As previously indicated we have been unable to use the quasi-potential in systems that have multiple independent heterogeneous reactions taking place at the same time. We assume, therefore, that the reaction of the cuprous ion to form metallic copper occurs rapidly, and that there is no diffusion of cuprous ions away from the electrode surface. The mechanism can then be written as

$$Cu^{2+} + 2e^{-} \longrightarrow Cu.$$

Since the second reaction in the sequence has been measured as being much faster than the first reaction, it is a fairly good assumption to write the deposition mechanism in this form, and we shall use it in the two systems studied here.

The first system we discuss is the binary copper sulfate solution, with the copper depositing on a copper electrode. We assume that the copper sulfate salt is completely dissociated into cupric and sulfate ions; there are no cuprous ions present in the solution. The equations derived above for binary electrolytes are directly applicable here, with the cupric ions being species 1 and the sulfate ions species 2.

Correlations for the salt diffusion coefficient as a function of the salt concentration are taken from the critical review of Miller *et al.* [9], and the transference-number data are taken from Pikal and Miller [10]. In some of the results we present, the bulk concentration is indicated as being 1.40 $mol \cdot dm^{-3}$, which is above the range of applicability of the diffusion-coefficient correlations. The error in the diffusion coefficient obtained by using the correlations at these concentrations is estimated by Miller *et al.* [9] to be less than 0.3%. The transference-number data are correlated (like the diffusion-coefficient data) as a quadratic in the square root of concentration. For the constant-transport properties case, we averaged the values of the diffusion coefficient and transference number over the entire range from the limit of solubility (1.4083 $mol \cdot dm^{-3}$) to zero concentration. It is believed that it is more realistic to use these average values in the model, rather than those at infinite dilution. The resulting equation for the quasi-potential, from equation 30, is

$$Q = 0.12054c_1 - 0.16876 \text{ (A/m)}, \tag{31}$$

where c_1 is in $mol \cdot dm^{-3}$. For the variable-transport properties case, we inserted the correlations for the transport properties into equation 29 and integrated using a fourth-order Runge-Kutta algorithm.

Figures 1 and 2 show the results of the system-specific calculation for the binary copper sulfate system. Figure 1 shows the concentration and electrostatic potential as functions of the quasi-potential. For the limiting-current and uniform-potential distributions, we are interested in the maximum current that can be passed. Figure 2 shows the variation of the value of the quasi-potential on the electrode

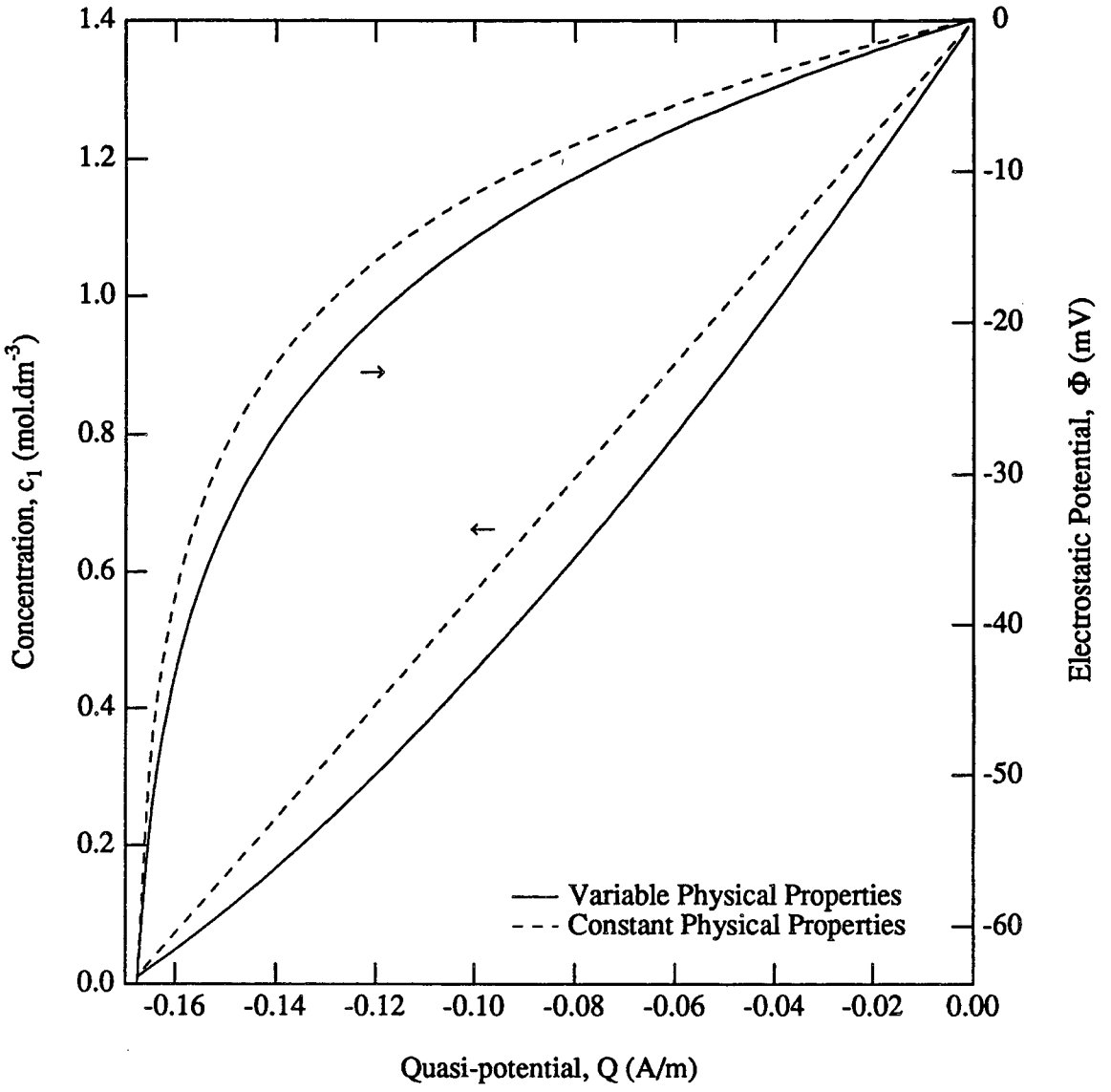

Figure 1. Electrostatic potential and concentration as functions of the quasi-potential in binary $CuSO_4$ solution. The bulk concentration of $CuSO_4$ is 1.40 mol.dm^{-3}.

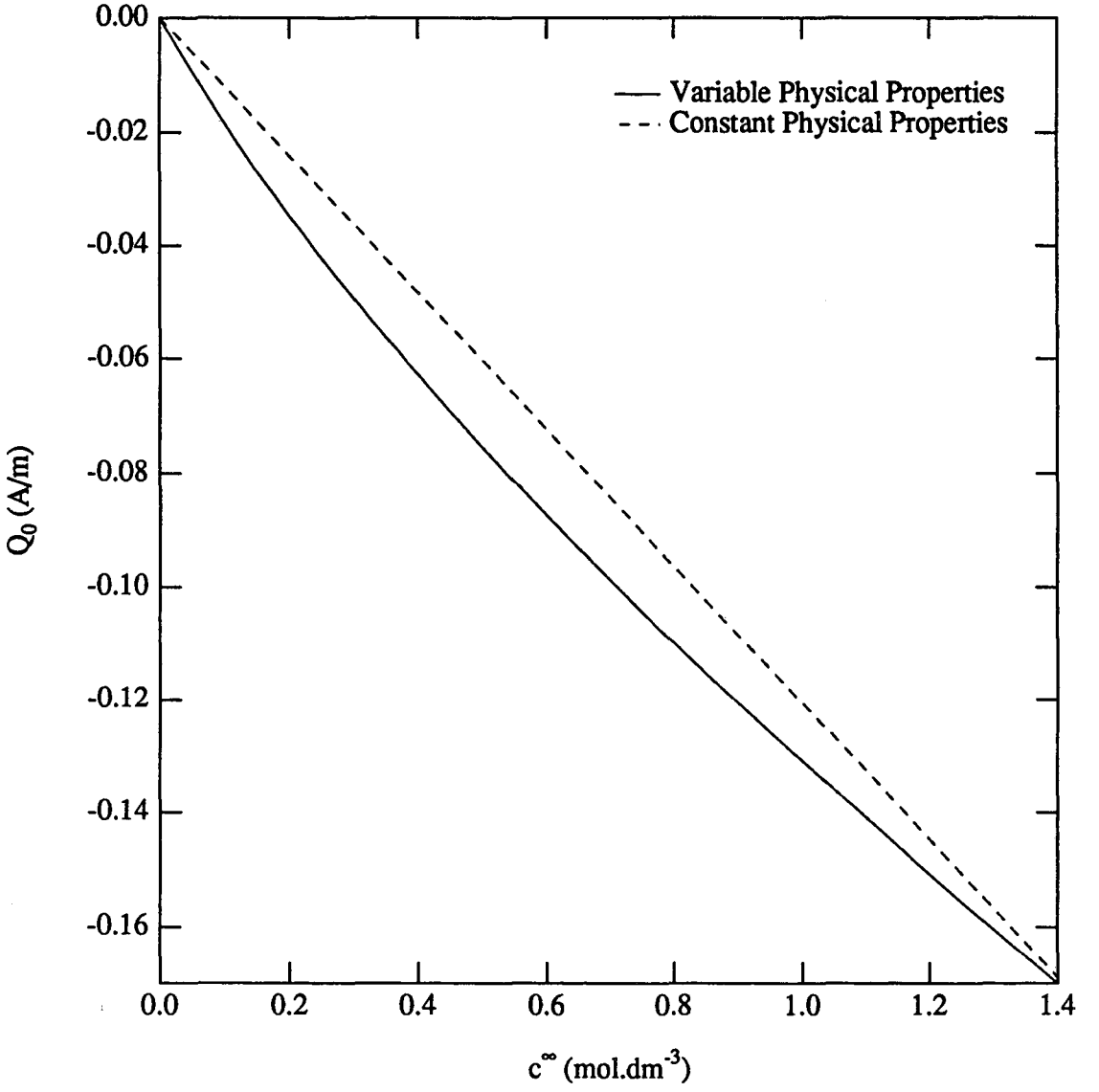

Figure 2. Quasi-potential at the surface of the electrode as a function of the concentration of $CuSO_4$ in the bulk of the solution, in binary $CuSO_4$ solution at limiting-current conditions. $i_{avg} = 4Q_0/\pi a$ for the disk, and $i_{avg} = Q_0/a$ for the hemisphere, where a denotes the radius of the electrode.

surface with changes in the value of the bulk concentration of copper sulfate. The value of the average current density depends only on the system-specific part of the calculation through Q_0 and depends on the geometry through the coefficient of Q_0 as indicated in the figure caption. These values of Q_0 also are one boundary condition in the limiting-current and uniform-potential distributions.

Methods of solution of Laplace's equation were taken directly from the literature and combined with the system-specific calculations to give the concentration and potential distributions as functions of the spatial variables. Figures 3 and 4 show the distributions of concentration (or equivalently potential) over a disk and hemisphere electrode at limiting-current conditions. The solution for the disk is taken from Newman [11]. The values of η in figure 3 indicate the fractions of the total current passing between the corresponding current-lines and the insulating plane. The solution for the hemisphere is obtained by integrating twice Laplace's equation written in spherical coordinates. The limiting-current condition is very similar to the uniform-potential distribution when the quasi-potential transformation is used, since the boundary condition on the electrode surface has the same form (Q_0 = constant). The solution for the hemisphere electrode incorporates the solution for uniform-current-density distribution on the electrode surface, since the hemisphere electrode is uniformly accessible to mass transfer. The method of solution of Laplace's equation for a disk electrode subjected to a uniform-current-density distribution is taken from Nanis and Kesselman [12]. Figure 5 shows the variation of electrostatic potential adjacent to a disk electrode at uniform-current-density-

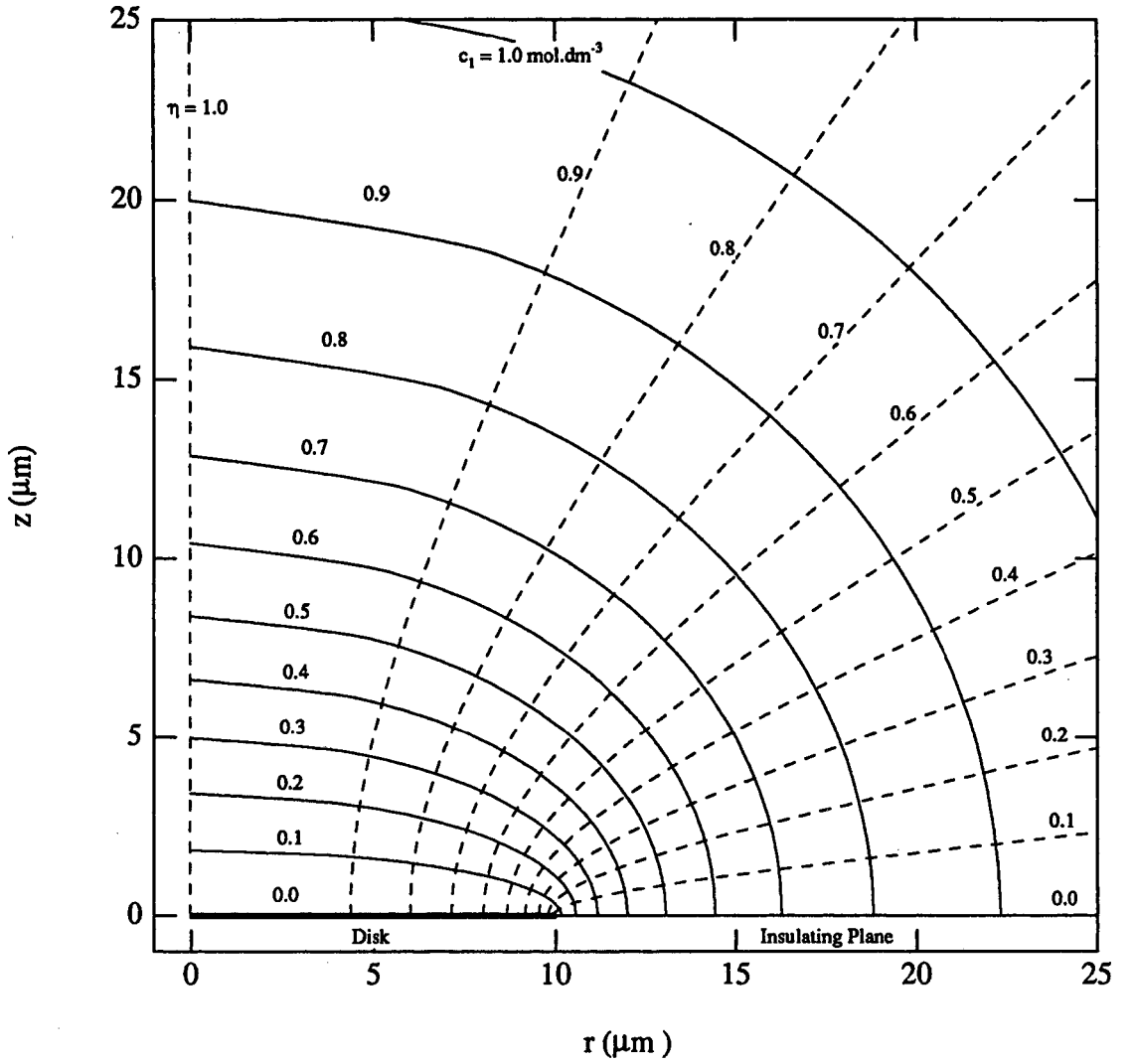

Figure 3. Equi-concentration lines and current-lines in binary $CuSO_4$ solution at limiting-current conditions, over a disk electrode of radius 10 μm. The equi-concentration lines are also lines of constant electrostatic potential and quasi-potential. The bulk concentration of $CuSO_4$ is 1.40 mol.dm^{-3}.

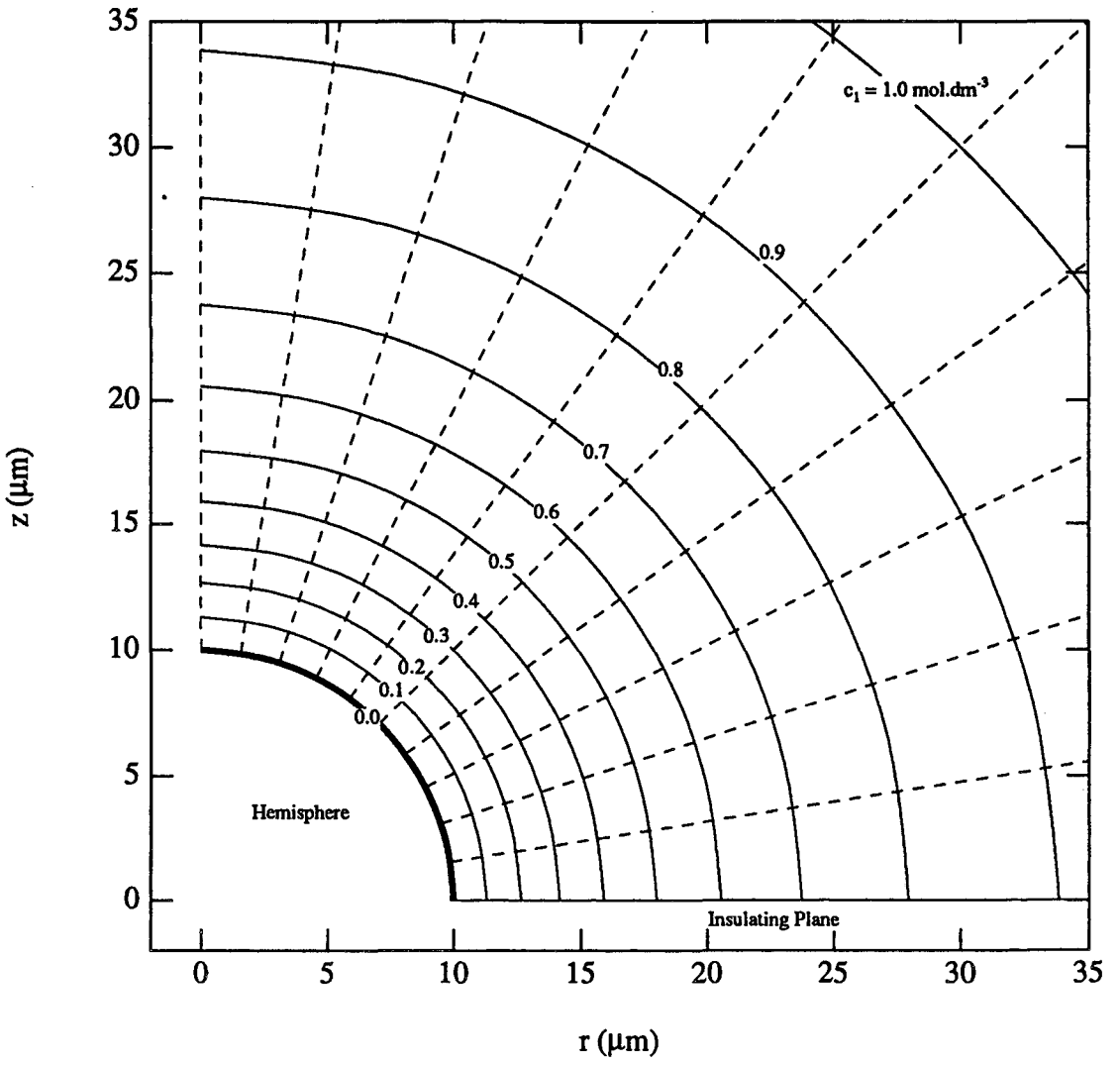

Figure 4. Equi-concentration lines and current-lines in binary $CuSO_4$ solution at limiting-current conditions, over a hemisphere electrode of radius 10 μm. The equi-concentration lines are also lines of constant electrostatic potential and quasi-potential. The bulk concentration of $CuSO_4$ is 1.40 mol.dm^{-3}.

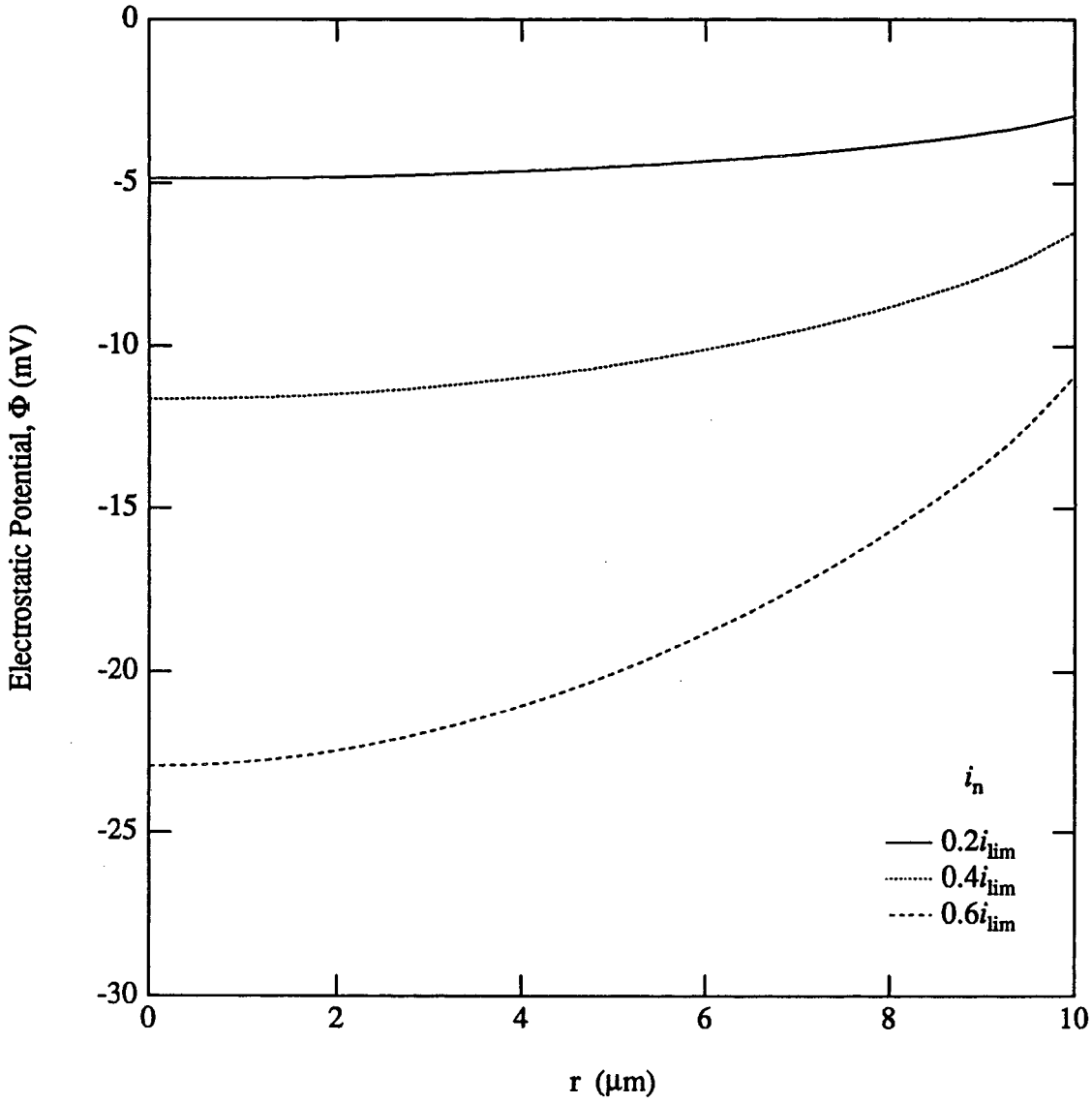

Figure 5. Variation of electrostatic potential adjacent to the surface of a disk electrode of radius 10 μm, in binary $CuSO_4$ solution at uniform-current-density conditions. The limiting current density is -2.1630 A/cm^2. The bulk concentration of $CuSO_4$ is 1.40 mol.dm^{-3}.

distribution conditions.

Acidic Copper Sulfate

The homogeneous reaction to be considered here is the incomplete dissociation of bisulfate ions

$$HSO_4^- \rightleftarrows H^+ + SO_4^{2-},$$

and we assume that this reaction is at equilibrium. Young *et al.* [13] used Raman spectroscopy to measure the equilibria present in, among others, aqueous solutions of H_2SO_4. From their measurements, it would appear safe to assume that, for solutions more dilute than 10 M, all of the H_2SO_4 is completely dissociated into H^+, HSO_4^-, and SO_4^{2-} ions. In keeping with the assumptions implicit in dilute-solution theory, we ignore the interactions between the ions in the solution and assume that the behavior of the H_2SO_4 is the same when $CuSO_4$ is present.

The mass transfer in this system has been investigated previously for the rotating-disk and the stagnant diffusion-cell configurations by Hsueh and Newman [14]. For the relationship between the apparent dissociation constant

$$K' = \frac{c_{H^+} c_{SO_4^{2-}}}{c_{HSO_4^-}} \tag{32}$$

and the thermodynamic dissociation constant

$$K = K' \frac{f_{H^+} f_{SO_4^{2-}}}{f_{HSO_4^-}}, \tag{33}$$

they used the formula

$$\ln(K'/K) = \frac{5.29\ I_r^{1/2}}{1 + 0.56\ I_r^{1/2}}, \tag{34}$$

where $K = 0.0104\ \mathrm{mol \cdot dm^{-3}}$ and I_r is the true ionic strength,

$$I_r = \frac{1}{2} \sum_i z_i^2 c_i .$$

Hsueh and Newman assumed that K' remained constant at its value infinitely far from the electrode. In this work, we allow K' to vary with ionic strength, which varies with position. We shall show the effect of assuming K' to be constant with respect to position.

In this system we ignore the variation of transport properties with concentration, as there is no straightforward way to correlate the transport properties as there is in the binary system. The diffusion coefficients used are those at infinite dilution and are taken from Newman [2]. The solubility data of Goodwin and Horsch [15] indicate that the solubility of $CuSO_4$ is at least 0.9 $\mathrm{mol \cdot dm^{-3}}$ at a H_2SO_4 concentration of 1.50 $\mathrm{mol \cdot dm^{-3}}$ and goes up to 1.4083 $\mathrm{mol \cdot dm^{-3}}$ at zero H_2SO_4 concentration at 25°C. In this work, the results we show are for a $CuSO_4$ bulk concentration of 0.50 $\mathrm{mol \cdot dm^{-3}}$ and a H_2SO_4 bulk concentration of 1.50 $\mathrm{mol \cdot dm^{-3}}$.

If species 1 is the Cu^{2+} ion, species 2 is the SO_4^{2-} ion, species 3 is the H^+ ion, and species 4 is the HSO_4^- ion, then the material balances for species 2, 3, and 4 are

$$-\nabla \cdot \mathbf{N}_2 + R = 0, \tag{35}$$

$$-\nabla\cdot N_3 + R = 0, \tag{36}$$

and

$$-\nabla\cdot N_4 - R = 0, \tag{37}$$

where R is the molar rate of the dissociation reaction. Adding and combining, we get

$$\nabla\cdot(N_2 + N_4) = 0 \tag{38}$$

and

$$\nabla\cdot(N_3 + N_4) = 0, \tag{39}$$

and by the theorem of Gibbs, since the normal components of N_2, N_3, and N_4 are zero at all finite boundaries,

$$N_2 + N_4 = 0 \tag{40}$$

and

$$N_3 + N_4 = 0, \tag{41}$$

everywhere. These two equations (after substituting equations 16 and 17), together with the equation of electroneutrality and the equilibrium condition, relate the species concentrations to the electrostatic potential. The quasi-potential is related to the electrostatic potential by equation 18. These five equations constitute the system-specific calculations and were solved using a fourth-order Runge-Kutta algorithm.

Figure 6 shows the values of the concentrations and electrostatic potential as functions of the quasi-potential. Figure 7, analogous to figure 2, shows values of the quasi-potential at the limiting current evaluated at the electrode surface for various values of bulk H_2SO_4 and $CuSO_4$ concentrations. Of course, the results of the system-specific

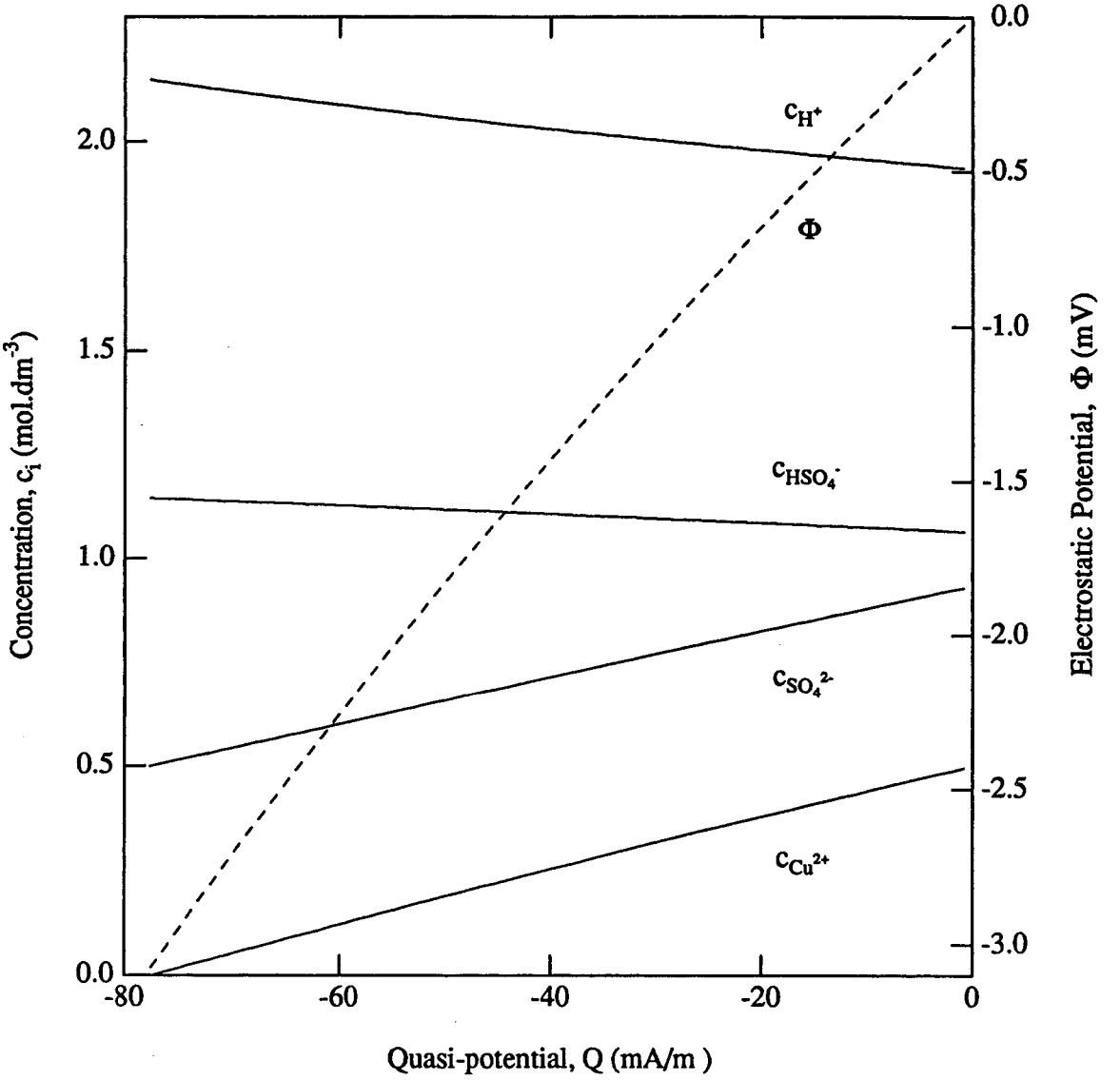

Figure 6. Electrostatic potential and ionic concentrations as functions of the quasi-potential in acidic $CuSO_4$ solution. The bulk concentration of $CuSO_4$ is 0.50 mol.dm^{-3}, and that of H_2SO_4 is 1.50 mol.dm^{-3}.

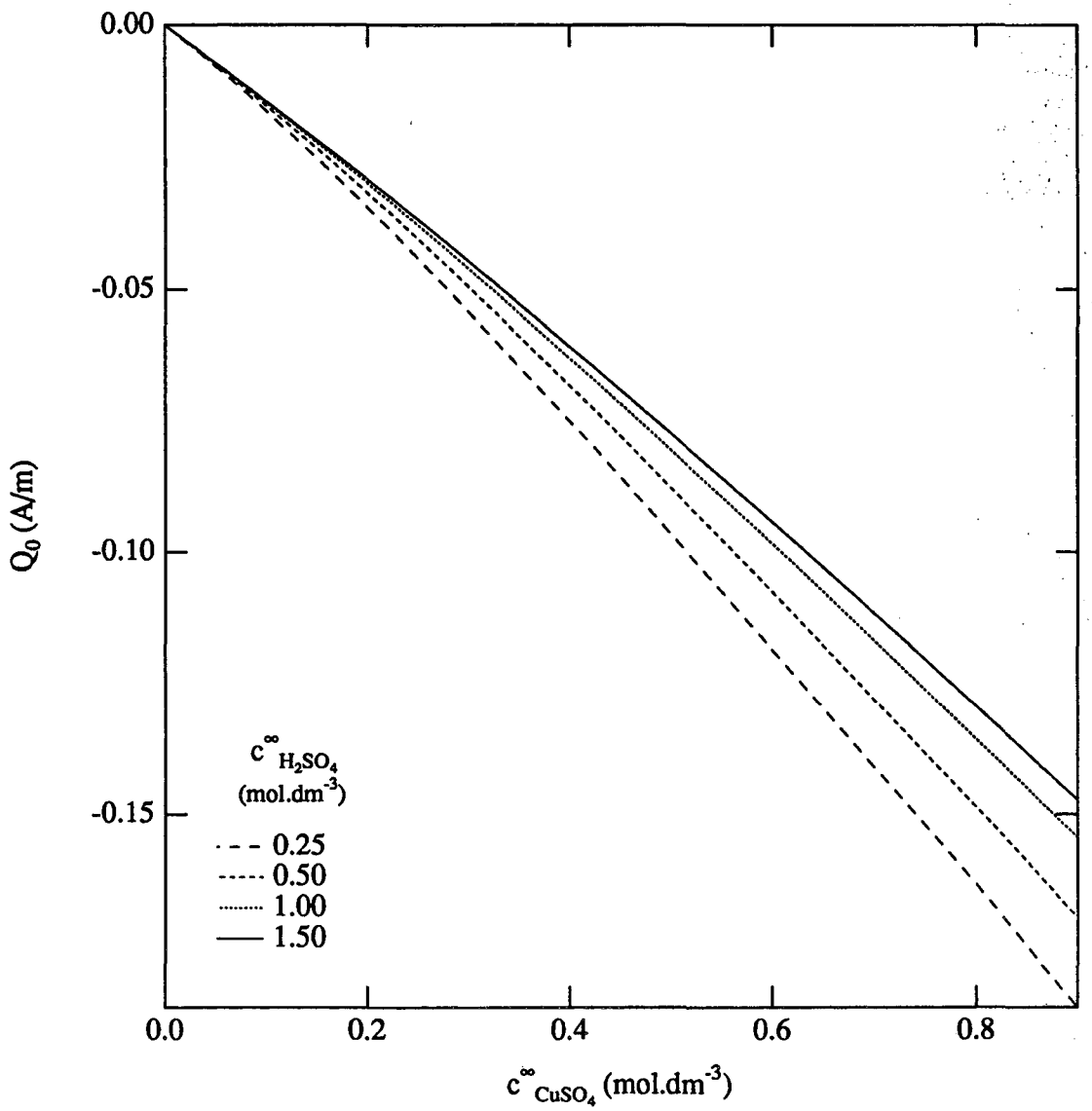

Figure 7. Quasi-potential at the surface of the electrode as a function of the concentration of $CuSO_4$ in the bulk of the solution, in acidic $CuSO_4$ solution at limiting-current conditions, for varying values of bulk H_2SO_4 concentration. $i_{avg} = 4Q_0/\pi a$ for the disk, and $i_{avg} = Q_0/a$ for the hemisphere, where a denotes the radius of the electrode.

calculations can be combined with any number of solutions of Laplace's equation to complete the solutions of the mass-transfer problem. We choose to present only the results for the disk electrode at limiting-current conditions. Figure 8 shows the species concentrations and electrostatic potential as functions of the rotational elliptic coordinate ξ. The solution is taken, as previously, from Newman [11]. The curves show a marked effect due to holding the dissociation constant invariable with respect to position.

Effect of Migration on Limiting Currents

The effect of migration on limiting currents is often quantified by the ratio of the limiting current obtained with consideration of migration to the diffusion-limiting current, which is the limiting current obtained when diffusion is considered to be the only mechanism of mass transfer. If the quasi-potential transformation is applicable, this ratio takes on the simple, geometry-independent form

$$\frac{i_L}{i_{LD}} = \frac{Q_0}{Q_{D0}}, \tag{42}$$

where the subscript D indicates that the property is obtained with diffusion considered to be the only mechanism of mass transfer.

The quasi-potential at the electrode surface at diffusion-limiting conditions is simple to obtain if the principal reactant does not participate in homogeneous reactions. The quasi-potential is defined as previously

$$\mathbf{i}_D = -\nabla Q_D. \tag{43}$$

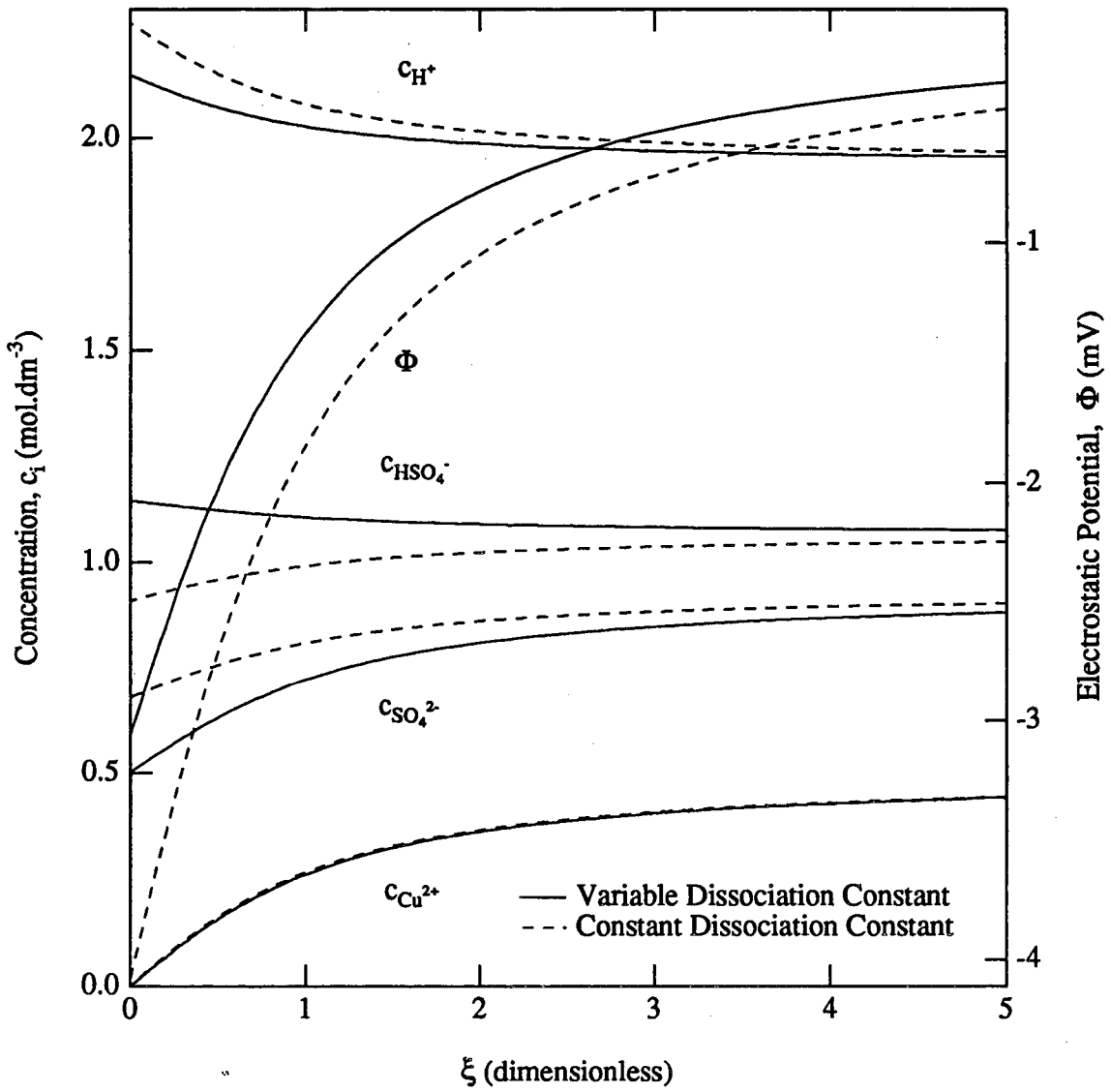

Figure 8. Electrostatic potential and ionic concentrations as functions of the rotational elliptic coordinate, ξ, in acidic $CuSO_4$ solution at limiting-current conditions, over a disk electrode, showing the effect of assuming the dissociation constant to be constant with respect to position. The bulk concentration of $CuSO_4$ is 0.50 mol.dm^{-3}, and that of H_2SO_4 is 1.50 mol.dm^{-3}.

Faraday's law states that

$$N_{Rn} = -\frac{s_R}{nF} i_n, \tag{44}$$

at the electrode surface. Since the current density and the flux of the principal reactant are individually solenoidal, it follows from the theorem of Gibbs and Faraday's law that

$$\mathbf{N}_R + \frac{s_R}{nF} \mathbf{i} = 0. \tag{45}$$

Substituting for $\mathbf{N}_{RD}$ and $\mathbf{i}_D$ and rearranging gives

$$\frac{dQ_D}{dc_R} = -\frac{nFD_R}{s_R}. \tag{46}$$

For binary-electrolyte systems, the effect of migration reduces, after integrating this equation and equation 29, to

$$\frac{i_L}{i_{LD}} = -\frac{s_R}{n} \frac{z_R(z_2 - z_R)}{z_2}. \tag{47}$$

This equation applies to both the constant- and variable- transport property cases. For the binary copper sulfate, specifically,

$$\frac{i_L}{i_{LD}} = 2. \tag{48}$$

If we assume that the transport properties are constant, then

$$Q_{D0} = \frac{nFD_R}{s_R} c_R^{\infty}. \tag{49}$$

It follows that for the acidic copper sulfate system, specifically,

$$\frac{i_L}{i_{LD}} = \frac{Q_0}{-2FD_R c_R^{\infty}}. \tag{50}$$

In figure 7 we presented values of Q_0 calculated for various values of

bulk composition of copper sulfate and sulfuric acid. In figure 9 we use these results to show the effect of migration on limiting currents in the copper sulfate system. The parameter r is that defined by Newman [2]

$$r = \frac{c^{\infty}_{H_2SO_4}}{c^{\infty}_{CuSO_4} + c^{\infty}_{H_2SO_4}}. \tag{51}$$

Newman [2] presents results (figure 19.2, page 402) showing the effect of migration on limiting currents in the Nernst stagnant diffusion layer for the acidic KCl system. Since this is one of the geometries to which the quasi-potential transformation is applicable, this curve could easily be derived using similar methods to those used for the acidic $CuSO_4$ system. Newman also presents results (figure 19.13, page 415) for the acidic $CuSO_4$ system for various values of the ratio of the bulk ionic strength at complete bisulfate dissociation to the dissociation constant evaluated at bulk conditions. Since the dissociation constant is not held constant in our system, this parameter is not really relevant. For all of the curves shown in figure 9, this parameter assumes values between 2.72 and 4.72; this gives an indication of where our system lies in the parameter space of Newman's figure.

Newman also shows the change in concentration of the supporting electrolyte between the bulk and the surface. In terms of the quasi-potential transformation, this can be interpreted as a result of the system-specific part of the problem and independent of the geometry. Thus, for all geometries satisfying the conditions of the quasi-potential transformation, Newman's results for the Nernst stagnant dif-

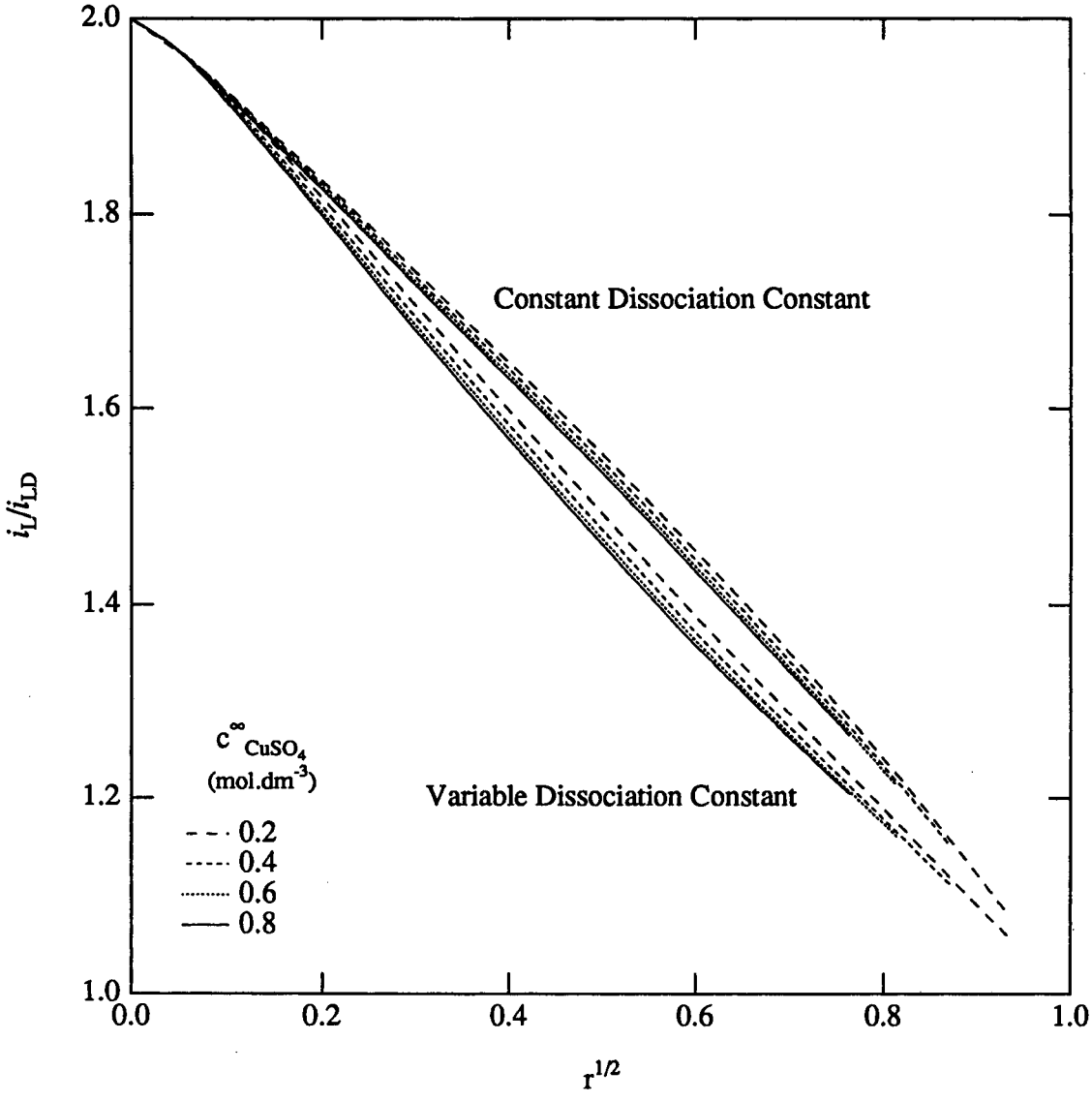

Figure 9. The effect of migration on limiting currents for the acidic $CuSO_4$ system, shown for various values of the bulk concentration of $CuSO_4$. The bulk concentration of H_2SO_4 is constrained by the limit of solubility. Also displayed is the effect of considering the dissociation constant to be constant with respect to position.

fusion layer apply and are different from those for two other classes of systems—the systems of the Lighthill transformation exemplified by the rotating-disk results and the transient systems (of the penetration model) exemplified by the results for a growing-mercury drop and for transient transport in a semi-infinite stagnant diffusion layer.

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List of Symbols

a	radius of the electrode, m or μm
c_i	concentration of species i, mol/dm^3
D	salt diffusion coefficient, cm^2/s
D_i	diffusion coefficient of species i, cm^2/s
$f(\phi)$	scalar function of dimensionless potential, A·cm^2/dm^3

$f(\Phi)$	scalar function of potential, $A \cdot cm^2/V \cdot dm^3$
$f_i(\phi)$	scalar function of dimensionless potential for species i, $cm^2 \cdot mol/dm^3 \cdot s$
$f_i(\Phi)$	scalar function of potential for species i, $cm^2 \cdot mol/V \cdot dm^3 \cdot s$
f_i	fugacity of species i, bar
F	Faraday's constant, 96487 C/equiv
$\mathbf{i}$	current density, A/cm^2 or A/m^2
I_r	true ionic strength, mol/dm^3
K	thermodynamic dissociation constant, mol/dm^3
K'	apparent dissociation constant, mol/dm^3
n	number of electrons exchanged in the heterogeneous reaction, dimensionless
N_i	flux of species i, $mol/dm^2 \cdot s$
q_i	potential governing the flux of species i, $mol/m \cdot s$
Q	quasi-potential, A/m
r	radial coordinate, m or μm
r	parameter indicating the ratio of supporting electrolyte to total amount of electrolyte, dimensionless
R	universal gas constant, 8.314 $J/mol \cdot K$
R_i	rate of generation of species i, $mol/dm^3 \cdot s$
s_i	stoichiometric coefficient of species i in the heterogeneous reaction, dimensionless
t	time, s
t_i	transference number of species i, dimensionless
T	temperature, K
u_i	mobility of species i, $cm^2 \cdot mol/J \cdot s$
z	axial distance, m or μm

z_i	charge number of species i, equiv/mol
η	rotational elliptic coordinate, dimensionless
ξ	rotational elliptic coordinate, dimensionless
ϕ	electrostatic potential, dimensionless
Φ	electrostatic potential, V or mV

Subscripts

0	evaluated at electrode surface
avg	average value
D	evaluated with consideration of diffusion only
i	species i
j	species j
L, lim	evaluated at limiting-current conditions
n	normal component
R	principal reactant

References

[1] D. R. Baker, M. W. Verbrugge, and J. Newman, "A transformation for the treatment of diffusion and migration. Application to stationary disk and hemisphere electrodes," *J. Electroanal. Chem.*, 314, 23-44 (1991).

[2] J. Newman, *Electrochemical Systems*, Prentice Hall, Englewood Cliffs, New Jersey (1991).

[3] H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Oxford University Press, New York (1959).

[4] B. Pillay, M. S. Thesis, University of California, Berkeley (1992).

[5] J. W. Gibbs, *The Scientific Papers Vol. II*, Dover Publications Inc., New York (1961).

[6] E. Mattsson and J. O'M. Bockris, "Galvanostatic Studies of the Kinetics of Deposition and Dissolution in the Copper + Copper Sulphate System," *Trans. Faraday Soc.*, 55, 1586-1601 (1959).

[7] U. Bertocci, "Application of Electrochemical Theory to the Behaviour of Copper in Cupric and Cuprous Solutions," *Electrochim. Acta*, 11, 1261-1277 (1966).

[8] O. R. Brown and H. R. Thirsk, "The Rate-Determining Step in the Electrodeposition of Copper on Copper from Aqueous Cupric Sulphate Solutions," *Electrochim. Acta*, 10, 383-393 (1965).

[9] D. G. Miller, J. Rard, L. B. Eppstein, and R. A. Robinson, "Mutual Diffusion Coefficients, Electrical Conductances, Osmotic Coefficients, and Ionic Transport Coefficients l_{ij} for Aqueous $CuSO_4$ at 25°C," *J. Solution Chem.*, 9(7), 467-496 (1980).

[10] M. J. Pikal and D. G. Miller, "Hittorf Transference Numbers in Aqueous Copper Sulfate at 25°C," *J. Chem. Eng. Data*, 16(20), 226-229 (1971).

[11] J. Newman, "Resistance for Flow of Current to a Disk," *J. Electrochem. Soc.*, 113(5), 501-502 (1966).

[12] L. Nanis and W. Kesselman, "Engineering Applications of Current and Potential Distributions in Disk Electrode Systems," *J. Electrochem. Soc.*, 118(3), 454-461 (1971).

[13] T. F. Young, L. F. Maranville, and H. M. Smith, "Raman Spectral Investigations of Ionic Equilibria in Solutions of Strong Electrolytes," Chapter 4 in *The Structure of Electrolytic Solutions*, edited by W. J. Hamer, John Wiley and Sons Inc., New York (1959).

[14] L. Hsueh and J. Newman, "The Role of Bisulfate Ions in Ionic Migration Effects," *Ind. and Eng. Chem. Fundamentals*, 10, 615-620 (1971).

[15] H. M. Goodwin and W. G. Horsch, "The Electrical Conductivity and Other Properties of Saturated Solutions of Copper Sulphate in the Presence of Sulphuric Acid," *Chem. and Metallurgical Eng.*, 21(4), 181-182 (1919).

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