The Boundary Layer in a Concentrated, Multicomponent Electrolyte

By J. A. LEWIS

We show formally how the application of boundary layer techniques to a well-stirred, concentrated, multicomponent electrolyte yields essentially the same results as those for a dilute, binary electrolyte. In particular, the coupled integral equations for the reactant concentration and the electric potential, derived by J. L. Blue for a dilute, binary electrolyte, remain valid in the general case with modified values of certain combinations of physical constants appearing in the equations.

I. INTRODUCTION

In this paper, we use the method of matched asymptotic expansions to derive boundary layer equations for a well-stirred, concentrated, multicomponent electrolyte containing a single ion reacting at the electrodes. We have two main objectives. First, we wish to show how the boundary layer approximation, up to now applied mainly to dilute, binary electrolytes or to the case of excess supporting electrolyte,[1] may be systematically generalized. Second, and more important, we show how the generalization leads to equations almost identical with those valid for a dilute, binary electrolyte, for which J. L. Blue[2] has derived an elegant and efficient method of solution.

In the general case, the singular perturbation in the boundary layer leads to a set of coupled convective diffusion (CD) equations for the concentrations or, in other words, a *vector* CD-equation in place of the single, scalar CD-equation for a dilute, binary electrolyte. The vector CD-equation is diagonalized by introducing the eigenvalues and eigenvectors of a reduced diffusivity matrix. The resulting uncoupled, scalar CD-equations can then be solved by Blue's method.

The perturbation yields linear CD-equations in the electrolyte, but the strongly nonlinear dependence of the electrode current density on the electrolyte potential and the reactant ion concentration is retained. In fact, the first approximation is simply the so-called "secondary current distribution," the potential satisfying Laplace's equation in

the electrolyte, but satisfying nonlinear boundary conditions at the electrodes. Furthermore, if, as is often the case, the current-carrying capacity of the electrode surface reaction is large compared with that due to ohmic conduction, the potential is approximately constant on the electrodes, giving the so-called "primary current distribution."

We begin in Sections II and III with a semiqualitative discussion of some of the approximations involved. Sections IV through IX contain the detailed analysis. The reader not interested in the details may skip to Sections X and XI, which contain very brief summaries of the formal perturbation solution and the equivalent boundary integral solution developed by J. L. Blue.

II. THE FIRST APPROXIMATION

A first approximation to the cathode current density serves as a convenient introduction to the general concentrated, n-component electrolyte. In a well-stirred electroplating bath, the ion concentrations are almost constant, except in thin diffusion boundary layers surrounding the electrodes. If the electrode current densities are bounded, so are the concentration gradients in the boundary layers. Thus, the changes in concentrations across the boundary layers are small when the boundary layer thicknesses are small enough. To a first approximation then, the concentrations are constant throughout the electrolyte, current being carried entirely by ohmic conduction. In the electrolyte, the dimensionless potential φ (equal to $F\Phi/RT$, for Faraday constant F, gas constant R, and absolute temperature T) satisfies Laplace's equation

$$\nabla^2 \varphi = 0.$$

On the electrodes, the current densities are determined by surface reactions producing cations (e.g., Cu^{++}) at the anode and depositing them at the cathode, the reaction rates being functions of the local concentrations and potentials. The potential φ then satisfies the boundary condition

$$k^{(0)} \partial \varphi / \partial n = k^{(0)} \mathbf{n} \cdot \nabla \varphi = \begin{cases} -j_a, & \text{on the anode,} \\ j_c, & \text{on the cathode,} \\ 0, & \text{otherwise,} \end{cases}$$

where $\mathbf{n}$ is the outward normal, $k^{(0)}$ is the dimensionless bulk conductivity, and, for $e = a, c,$

$$j_e = j_e^{*(0)}[\exp(\alpha_e|\varphi - \varphi_e|) - \exp(-\beta_e|\varphi - \varphi_e|)].$$

The dimensionless ion exchange current density $j_e^{*(0)}$, here constant, but in general a function of the concentrations, and the exponents α_e, β_e characterize the surface reaction rates. The quantity $\varphi - \varphi_e$ is the

so-called "electrode surface overpotential" for electrolyte potential φ and electrode potential φ_e.

When $j_e^{*(0)}$ is large, $|\varphi - \varphi_e|$ must be small or, to a first approximation, $\varphi = \varphi_e$ on the electrodes, giving the so-called "primary current distribution." Note, however, that the primary current distribution leads to unbounded current density at electrode edges or reentrant corners, while the secondary current distribution does not. The exponential form of the electrode current relation, however, suggests that the primary and secondary current distributions differ only in a very small neighborhood of such a boundary singularity.

Once φ has been determined, the electrode current densities can be calculated. Furthermore, the approximation does not depend on the specific electrolyte, but only on the existence of thin boundary layers across which the concentration changes are small. It thus applies to dilute, binary and concentrated, multicomponent electrolytes alike, although, of course, the various constants, e.g., the conductivities, may be vastly different in the two cases.

To obtain a better approximation, we must include the effect of concentration variation across the boundary layers. Before doing so, however, let us consider a method of practical solution for φ, the method of boundary integrals widely used for the numerical solution of potential problems. Since φ is harmonic, it satisfies Green's third identity, which in the plane has the form

$$2\pi\varphi(P) = \int_\Gamma \left[\frac{\partial\varphi}{\partial n}(Q)G(P, Q) - \varphi(Q)\frac{\partial G}{\partial n}(P, Q) \right] ds(Q),$$

where Γ is the curve bounding the electrolyte and $G(P, Q) \sim \ln(1/|PQ|)$, as the point $P \to Q$, and is harmonic otherwise. When P lies on Γ, the identity becomes an integral equation for φ, nonlinear because $\partial\varphi/\partial n$ is a nonlinear function of φ. Very efficient numerical methods for solving this equation have been developed.

III. THE BINARY ELECTROLYTE

For the dilute, binary electrolyte, J. L. Blue[2] has extended the above boundary integral method to include the effect of concentration changes across the boundary layers. He derived a relation giving the concentration changes across the boundary layers in terms of integrals of the product of electrode current density and a kernel function whose form depends upon the local velocity distribution. These concentration changes affect the electrode current density in two ways. First, as we have already noted, the ion exchange current density is a function of concentration. Second, the potentials at the electrodes differ from those at the boundary layer edge, where the previous φ is actually

evaluated, by the so-called "concentration overpotentials" $\Delta \varphi_e$, $e = a$, c. These overpotentials are due to the net current carried by ions diffusing at different rates through the boundary layers. To the present degree of approximation, they are linear functions of the concentration changes across the boundary layers.

In a binary electrolyte, in which the two ion concentrations must be proportional, since the electrolyte is electrically neutral, $\Delta \varphi_e$ is proportional to the integral giving the concentration change. This constant of proportionality, the constant giving the concentration to be inserted into the ion exchange current density, and the bulk conductivity are the only constants containing material properties in the final relations. They thus characterize the electrolyte completely in this case and may thus be used in place of the individual diffusivities and mobilities.

In the above, we did not qualify the term "binary electrolyte" with the term "dilute." The discussion of the previous paragraph applies as well to concentrated binary electrolytes, provided that the boundary layer concentration changes are small. In this case, in the boundary layers, the equations are linearized around a state of constant bulk concentrations, so that the diffusivities, in general forming a 2×2 matrix, and the mobilities, both functions of the concentrations, are constants, evaluated at the constant values of the bulk concentrations. Using the charge neutrality condition, the potential and one concentration are eliminated from the two boundary layer equations governing the ion fluxes. The resulting equation has exactly the same form as that for a dilute, binary electrolyte, so that the solution has the same form, except that the proportionality constants have different values.

In the following, we extend this result to concentrated, multicomponent electrolytes, the case of the ternary $(n = 3)$ electrolyte being of particular interest. As above, we linearize the equations around a state of constant bulk concentrations, using the boundary layer approximation (*not* the assumption of excess supporting electrolyte). We eliminate the potential and one concentration to obtain a set of $(n - 1)$ boundary layer equations for the concentrations, coupled by a reduced $(n - 1) \times (n - 1)$ diffusivity matrix. This system is solved by diagonalization, using the principal values and vectors of the reduced matrix. Finally, these solutions are combined to calculate the electrode concentrations and concentration overpotentials. We find that both of these quantities are proportional to a single integral as before, so that the electrolyte can be characterized by specifying the two constants of proportionality, instead of n^2 diffusivities and n mobilities.

IV. THE COMPLETE BOUNDARY VALUE PROBLEM

The steady flow of ions in a nonreacting, concentrated, n-component electrolyte is governed by the n conservation laws[*]

$$\nabla \cdot \mathbf{N}_i = 0, \tag{1}$$

for $i = 1, \cdots, n$, where the ion flux $\mathbf{N}_i$ is given in terms of the ion concentrations $C_1, \cdots, C_n$ and the potential Φ by

$$\mathbf{N}_i = C_i \mathbf{V} - \sum_{j=1}^{n} D_{ij} \nabla C_j - F z_i U_i C_i \nabla \Phi. \tag{2}$$

In these n relations, $\mathbf{V}$ is the circulation velocity of the electrolyte due to stirring, F is the Faraday constant, z_i the charge number of the ith ion, and the diffusivities D_{ij} and mobilities U_i are functions of $C_1, \cdots, C_n$.[†] We shall not impose any restrictions on the form of the D_{ij}'s, although it seems reasonable to require, for example, that for $i \neq j$, $D_{ij} \to 0$, as $C_i \to 0$. This makes the ith ion flux $\mathbf{N}_i$ vanish, when the ith ion is absent, and gives the correct form for a dilute electrolyte. With

$$\nabla \cdot \mathbf{V} = 0, \tag{3}$$

as is appropriate for a liquid electrolyte, eqs. (1) and (2) yield the set of n nonlinear, second-order, partial differential equations

$$\nabla \cdot \left(\sum_{j=1}^{n} D_{ij} \nabla C_j + F z_i U_i C_i \nabla \Phi \right) = \mathbf{V} \cdot \nabla C_i. \tag{4}$$

The set of equations is completed by the charge neutrality condition

$$\sum_{i=1}^{n} z_i C_i = 0, \tag{5}$$

which implies that the current density

$$\mathbf{J} = \sum_{i=1}^{n} F z_i \mathbf{N}_i = -K \nabla \Phi - \sum_{i=1}^{n} \sum_{j=1}^{n} F z_i D_{ij} \nabla C_j, \tag{6}$$

with the conductivity

$$K = \sum_{i=1}^{n} F^2 z_i^2 U_i C_i, \tag{7}$$

satisfies

$$\nabla \cdot \mathbf{J} = 0. \tag{8}$$

---

[*] Capital letters denote dimensional quantities; lower case letters denote dimensionless quantities.

[†] In Appendix C, we show how D_{ij} and U_i can be expressed in terms of the electrochemical potential.

We assume that there is no flux through the surface bounding the electrolyte, except that flux due to the production of cation 1 (e.g., Cu^{++}) at the anode and deposition of the same cation at the cathode. Thus, for outward normal $\mathbf{n}$,

$$\mathbf{V} \cdot \mathbf{n} = \mathbf{N}_i \cdot \mathbf{n} = 0 \tag{9}$$

for $i = 2, \cdots, n$, while

$$\mathbf{N}_1 \cdot \mathbf{n} = \mathbf{J} \cdot \mathbf{n}/Fz_1 \tag{10}$$

on the boundary, where

$$\mathbf{J} \cdot \mathbf{n} = \begin{cases} -J_a, & \text{on the anode,} \\ J_c, & \text{on the cathode,} \\ 0, & \text{otherwise.} \end{cases} \tag{11}$$

We shall assume that the electrode current densities determined by the surface reaction rates have the form

$$J_e = J_e^*(C_1/C_e^*)^{\gamma_e}[\exp(\alpha_e F|\Phi - \Phi_e|/RT) \\ - \exp(-\beta_e F|\Phi - \Phi_e|/RT)], \tag{12}$$

for $e = a, c$, where the ion exchange current density $J_e^*(C_1/C_e^*)^{\gamma_e}$ is assumed to be a function only of the concentration of the cation participating in the surface reactions, R is the gas constant, T the absolute temperature, Φ the electrolyte potential, Φ_e the electrode potential, and $|\Phi - \Phi_e|$ the surface overpotential. These conditions complete the boundary value problem.

Now let L, V, C, RT/F, D, D/RT, and FDC/L be some typical length, velocity, concentration, potential, diffusivity, mobility, and current density and set

$$(x, y, z) = (X, Y, Z)/L,$$
$$c_i = C_i/C,$$
$$\varphi = F\Phi/RT,$$
$$\mathbf{v} = \mathbf{V}/V,$$
$$\mathbf{j} = L\mathbf{J}/FDC,$$
$$d_{ij} = D_{ij}/D,$$
$$u_i = RTU_i/D.$$

The equations and boundary conditions then take the dimensionless form

$$\nabla \cdot \left(\sum_{j=1}^{n} d_{ij}\nabla c_j + z_i u_i c_i \nabla \varphi \right) = \text{Pe } \mathbf{v} \cdot \nabla c_i, \tag{13}$$

for $i = 1, \cdots, n$, where the Peclet number $\text{Pe} = VL/D$,

$$\sum_{i=1}^{n} z_i c_i = 0, \tag{14}$$

$$\nabla \cdot \left(k \nabla \varphi + \sum_{i=1}^{n} \sum_{j=1}^{n} z_i d_{ij} \nabla c_j \right) = 0, \tag{15}$$

where

$$k = \sum_{i=1}^{n} z_i^2 u_i c_i. \tag{16}$$

With $\mathbf{v} \cdot \mathbf{n} = 0$ on the boundary,

$$\sum_{j=1}^{n} d_{ij} \partial c_j / \partial n + z_i u_i c_i \partial \varphi / \partial n = \begin{cases} -\mathbf{j} \cdot \mathbf{n} / z_1, & \text{for} \quad i = 1, \\ 0, & \text{for} \quad i = 2, \cdots, n, \end{cases} \tag{17}$$

where

$$-\mathbf{j} \cdot \mathbf{n} = k \partial \varphi / \partial n + \sum_{i=1}^{n} \sum_{j=1}^{n} z_i d_{ij} \partial c_j / \partial n$$

$$= \begin{cases} j_a, & \text{on the anode,} \\ -j_c, & \text{on the cathode,} \\ 0, & \text{otherwise,} \end{cases} \tag{18}$$

and, for $e = a, c$,

$$j_e = j_e^* c_1^{\gamma_e} [\exp(\alpha_e | \varphi - \varphi_e |) - \exp(-\beta_e | \varphi - \varphi_e |)], \tag{19}$$

$$j_e^* = (L J_e^* / F D C)(C / C_e^*)^{\gamma_e}. \tag{20}$$

V. THE BOUNDARY LAYER APPROXIMATION

To obtain explicit results, we consider a plane, rectangular region with a cathode at $Y = y = 0$ and an anode at $Y = L$, $y = 1$. We assume that the electrolyte is well stirred, with Pe $\gg 1$, so that the concentrations are nearly constant, except in thin boundary layers, of thickness of order ϵL, $\epsilon = (\text{Pe})^{-\frac{1}{3}}$, balancing diffusion and convection near the electrodes. Far from the electrodes, we introduce the outer expansions

$$\begin{aligned} c_i &= \bar{c}_i(x, y, \epsilon) = c_i^{(0)} + O(\epsilon^3), \\ \varphi &= \bar{\varphi}(x, y, \epsilon) = \bar{\varphi}^{(0)}(x, y) + \epsilon \bar{\varphi}^{(1)}(x, y) + \cdots, \end{aligned} \tag{21}$$

since eq. (13) implies that $\mathbf{v} \cdot \nabla \bar{c}_i = O(\epsilon^3)$, where the $c_i^{(0)}$'s are the constant bulk concentrations and $\bar{\varphi}^{(0)}$, $\bar{\varphi}^{(1)}$ are harmonic functions; i.e.,

$$\bar{\varphi}_{xx}^{(0)} + \bar{\varphi}_{yy}^{(0)} = \bar{\varphi}_{xx}^{(1)} + \bar{\varphi}_{yy}^{(1)} = 0. \tag{22}$$

In the boundary layers, we set

$$\begin{aligned} c_i &= \tilde{c}_i(x, \tilde{y}, \epsilon) = c_i^{(0)} + \epsilon \tilde{c}_i^{(1)}(x, \tilde{y}) + \cdots, \\ \varphi &= \tilde{\varphi}(x, \tilde{y}, \epsilon) = \tilde{\varphi}^{(0)}(x, \tilde{y}) + \epsilon \tilde{\varphi}^{(1)}(x, \tilde{y}) + \cdots, \end{aligned}$$

where the stretched variable $\tilde{y} = y/\epsilon$ in the cathode boundary layer and $\tilde{y} = (1 - y)/\epsilon$ in the anode boundary layer. The assumption that the electrode current densities are bounded has already been introduced by choosing the leading term in the expansion of $\tilde{c}_i$ to be constant. In the boundary layer eqs. (13) and (15) become

$$\left(\sum_{j=1}^{n} \tilde{d}_{ij} \tilde{c}_{j\tilde{y}} + z_i \tilde{u}_i \tilde{c}_i \tilde{\varphi}_{\tilde{y}} \right)_{\tilde{y}} - (\tilde{\psi}_{\tilde{y}} \tilde{c}_{ix} - \tilde{\psi}_x \tilde{c}_{i\tilde{y}})$$

$$= -\epsilon^2 \left(\sum_{j=1}^{n} \tilde{d}_{ij} \tilde{c}_{jx} + z_i \tilde{u}_i \tilde{c}_i \tilde{\varphi}_x \right)_x, \quad (23)$$

$$\left(\tilde{k} \tilde{\varphi}_{\tilde{y}} + \sum_{i=1}^{n} \sum_{j=1}^{n} z_i \tilde{d}_{ij} \tilde{c}_{j\tilde{y}} \right)_{\tilde{y}} = -\epsilon^2 \left(\tilde{k} \tilde{\varphi}_x + \sum_{i=1}^{n} \sum_{j=1}^{n} z_i \tilde{d}_{ij} \tilde{c}_{jx} \right)_x, \quad (24)$$

where we have introduced the reduced stream function

$$\tilde{\psi}(x, \tilde{y}, \epsilon) = \epsilon^{-2} \psi(x, \epsilon \tilde{y}),$$

with the x and y components of $\mathbf{v}$ given by

$$u = \psi_y, \qquad v = -\psi_x,$$

vanishing on the electrodes. The tildes on d_{ij}, etc., mean $\tilde{d}_{ij} = d_{ij}(\tilde{c}_1, \cdots, \tilde{c}_n)$, etc. Note that the $\tilde{d}$'s, $\tilde{u}$'s, $\tilde{k}$, and $\tilde{\psi}$ must all be expanded around $\epsilon = 0$ to obtain the equations satisfied by $\tilde{c}_i^{(1)}$, $\tilde{\varphi}^{(0)}$, $\tilde{\varphi}^{(1)}$, $\cdots$. The boundary conditions, for example at the cathode $y = \tilde{y} = 0$, have the form

$$\sum_{j=1}^{n} \tilde{d}_{ij} \tilde{c}_{j\tilde{y}} + z_i \tilde{u}_i \tilde{c}_i \tilde{\varphi}_{\tilde{y}} = \begin{cases} \epsilon \tilde{j}_c/z_1, & \text{for} \quad i = 1, \\ 0, & \text{for} \quad i = 2, \cdots, n, \end{cases} \quad (25)$$

where

$$\tilde{j}_c = \tilde{j}_c^*(\tilde{c}_1)^{\gamma_c}[\exp(\alpha_c \tilde{\varphi}) - \exp(-\beta_c \tilde{\varphi})], \quad (26)$$

$\tilde{c}_1$ and $\tilde{\varphi} > 0$ being evaluated at $\tilde{y} = 0$ and the cathode assumed to be grounded, so that $\varphi_c = 0$. Obviously $\tilde{j}_c$ must also be expanded in powers of ϵ. Finally, multiplying eq. (25) by z_i and summing yields

$$\tilde{k} \tilde{\varphi}_{\tilde{y}} + \sum_{i=1}^{n} \sum_{j=1}^{n} z_i \tilde{d}_{ij} \tilde{c}_{j\tilde{y}} = \epsilon \tilde{j}_c. \quad (27)$$

The set of relations from which the boundary layer equations are obtained is completed by matching $\tilde{c}_i(x, \tilde{y}, \epsilon)$ with $\bar{c}_i(x, y, \epsilon)$ and $\tilde{\varphi}(x, \tilde{y}, \epsilon)$ with $\bar{\varphi}(x, y, \epsilon)$ for small y and large $\tilde{y}$. Specifically, we use intermediate matching, setting

$$y = \epsilon^\alpha y^*, \qquad \tilde{y} = \epsilon^{\alpha-1} y^*,$$

for fixed y^* and $0 < \alpha < 1$, and considering the limit $\epsilon \to 0$. Matching

$$\tilde{c}_i(x, \epsilon^{\alpha-1}y^*, \epsilon) = c_i^{(0)} + \epsilon \tilde{c}_i^{(1)}(x, \epsilon^{\alpha-1}y^*)$$

with

$$\bar{c}_i(x, \epsilon^\alpha y^*, \epsilon) = c_i^{(0)} + O(\epsilon^3)$$

trivially yields the boundary conditions

$$\tilde{c}_i^{(1)}(x, \infty) = 0,$$

for $i = 1, \cdots, n$. Similarly, matching $\bar{\varphi}^{(0)}$ and $\bar{\varphi}^{(0)}$ gives

$$\tilde{\varphi}^{(0)}(x, \infty) = \bar{\varphi}^{(0)}(x, 0).$$

The differential equation (24) and the boundary condition (27) imply that $\tilde{\varphi}_{\bar{y}\bar{y}}^{(0)} = \tilde{\varphi}_{\bar{y}}^{(0)} = 0$, so that

$$\tilde{\varphi}^{(0)}(x, \bar{y}) \equiv \bar{\varphi}^{(0)}(x, 0).$$

To a first approximation, the outer potential $\bar{\varphi}^{(0)}$, as yet undetermined, simply penetrates the boundary layer.

VI. FIRST-ORDER MATCHING: THE SECONDARY CURRENT DISTRIBUTION

Boundary conditions on $\bar{\varphi}^{(0)}$ are found by matching

$$\bar{\varphi} = \bar{\varphi}^{(0)} + \epsilon \bar{\varphi}^{(1)}$$

with

$$\tilde{\varphi} = \tilde{\varphi}^{(0)} + \epsilon \tilde{\varphi}^{(1)}.$$

The zero-order inner potential $\tilde{\varphi}^{(0)}$ has already been determined. The first-order potential $\tilde{\varphi}^{(1)}$ satisfies the differential equation

$$\left[k^{(0)} \tilde{\varphi}_{\bar{y}}^{(1)} + \sum_{i=1}^{n} \sum_{j=1}^{n} z_i d_{ij}^{(0)} \tilde{c}_{j\bar{y}}^{(1)} \right]_{\bar{y}} = 0,$$

and the boundary condition

$$k^{(0)} \tilde{\varphi}_{\bar{y}}^{(1)} + \sum_{i=1}^{n} \sum_{j=1}^{n} z_i d_{ij}^{(0)} \tilde{c}_{j\bar{y}}^{(1)} = j_c^{(0)},$$

at $\bar{y} = 0$, where $d_{ij}^{(0)}$, $k^{(0)}$ are evaluated at $c_1^{(0)}, \cdots, c_n^{(0)}$ and $j_c^{(0)}$ at $c_1^{(0)}$, $\bar{\varphi}^{(0)}(x, 0) = \bar{\varphi}^{(0)}(x, 0)$, so that

$$j_c^{(0)}(x) = j_c^*[c_1^{(0)}]^{\gamma_c}\{\exp[\alpha_c \bar{\varphi}^{(0)}(x, 0)] - \exp[-\beta_c \bar{\varphi}^{(0)}(x, 0)]\}.$$

Two integrations yield

$$\tilde{\varphi}^{(1)}(x, \bar{y}) = \hat{\varphi}^{(1)}(x) + \left[\bar{y} j_c^{(0)}(x) - \sum_{i=1}^{n} \sum_{j=1}^{n} z_i d_{ij}^{(0)} \tilde{c}_j^{(1)}(x, \bar{y}) \right] \Big/ k^{(0)}, \quad (28)$$

where $\hat{\varphi}^{(1)}(x)$ is an arbitrary function of x. The last term can be identified as the concentration overpotential. Since, for large $\bar{y}$, $\tilde{c}_i^{(1)} \to 0$,

$$\tilde{\varphi} \sim \bar{\varphi}^{(0)}(x, 0) + \epsilon[\hat{\varphi}^{(1)}(x) + \epsilon^{\alpha-1} y^* j_c^{(0)}(x)/k^{(0)}],$$

for $\tilde{y} = \epsilon^{\alpha-1} y^*$ and $\epsilon \to 0$. On the other hand, expanding in Taylor series gives

$$\bar{\varphi} \sim \bar{\varphi}^{(0)}(x, 0) + \epsilon^{\alpha} y^* \bar{\varphi}_y^{(0)}(x, 0) + \epsilon \bar{\varphi}^{(1)}(x, 0) + \cdots,$$

for $y = \epsilon^{\alpha} y^*$. First-order matching then yields the zero-order boundary condition

$$\bar{\varphi}_y^{(0)}(x, 0) = j_c^{(0)}(x)/k^{(0)}$$

and

$$\hat{\varphi}^{(1)}(x) = \bar{\varphi}^{(1)}(x, 0),$$

another penetration condition. A similar analysis produces the boundary condition

$$\bar{\varphi}_y^{(0)}(x, 1) = j_a^{(0)}(x)/k^{(0)}$$

at the anode $y = 1$. Since $j_c^{(0)}$ and $j_a^{(0)}$ depend only on $\bar{\varphi}^{(0)}$, we now have a complete boundary value problem for $\bar{\varphi}^{(0)}$. To a first approximation then, the potential φ satisfies Laplace's equation

$$\varphi_{xx} + \varphi_{yy} = 0, \qquad (29)$$

in the electrolyte, and the nonlinear boundary condition

$$k^{(0)} \partial \varphi / \partial n = \begin{cases} j_a, & \text{on the anode,} \\ -j_c, & \text{on the cathode,} \\ 0, & \text{otherwise,} \end{cases} \qquad (30)$$

where, for $e = a, c$,

$$j_e = j_c^* [c_1^{(0)}]^{\gamma_e} [\exp(\alpha_e |\varphi - \varphi_e|) - \exp(-\beta_e |\varphi - \varphi_e|)], \qquad (31)$$

yielding the so-called "secondary current distribution."

Although we have derived this secondary current distribution specifically for small boundary layer thickness and moderate electrode current density, it probably is valid over a much wider range. The basic assumption is simply that the concentration variations are small. Thus, it is probably still valid when the flow is turbulent and the present simple description of the flow field does not suffice or at loci of boundary singularities (sharp edges, etc.) where the gradients are not necessarily normal to the boundary, as is assumed tacitly when one introduces the stretched variable $\tilde{y}$ in the boundary layer approximation. In any event, by calculating the first-order terms $\tilde{c}_i^{(1)}$, $\bar{\varphi}^{(1)}$, we can obtain an error estimate or an improved approximation.

VII. CONCENTRATION VARIATIONS

Although we have already derived boundary conditions on the $\tilde{c}_i^{(1)}$'s, we have not yet displayed the equations which they satisfy. With

constant leading terms $c_i^{(0)}$ and $\bar{\psi}$ expanded in the form

$$\bar{\psi} = \bar{\psi}_0 + \epsilon\bar{\psi}_1 + \cdots = \bar{y}^2 f(x) + \epsilon\bar{y}^3 g(x) + \cdots,$$

where $f(x) = \psi_{yy}(x,0)/2$, $g(x) = \psi_{yyy}(x,0)/6$, $\cdots$, eq. (23) becomes, to first order,

$$\sum_{j=1}^{n} d_{ij}^{(0)}\tilde{c}_{j\bar{y}\bar{y}}^{(1)} + (k_i^{(0)}/z_i)\,\bar{\varphi}_{\bar{y}\bar{y}}^{(1)} = \bar{\psi}_{\bar{y}}^{(0)}\tilde{c}_{ix}^{(1)} - \bar{\psi}_x^{(0)}\tilde{c}_{i\bar{y}}^{(1)}, \tag{32}$$

for $i = 1, \cdots, n$, where the ith partial conductivity

$$k_i^{(0)} = z_i^2 u_i^{(0)} c_i^{(0)},$$

while the boundary condition (25) at $\bar{y} = 0$ yields

$$\sum_{j=1}^{i} d_{ij}^{(0)}\tilde{c}_{j\bar{y}}^{(1)} + (k_i^{(0)}/z_i)\,\bar{\varphi}_{\bar{y}}^{(1)} = \begin{cases} j_c^{(0)}/z_1, & \text{for} \quad i = 1, \\ 0, & \text{for} \quad i = 2, \cdots, n. \end{cases} \tag{33}$$

We can use the charge neutrality condition

$$\tilde{c}_n^{(1)} = -\sum_{j=1}^{n-1} (z_j/z_n)\tilde{c}_j^{(1)}$$

and the relation

$$k^{(0)}\bar{\varphi}_{\bar{y}}^{(1)} = j_c^{(0)} - \sum_{p=1}^{n}\sum_{j=1}^{n} z_p d_{pj}^{(0)}\tilde{c}_{j\bar{y}}^{(1)},$$

found from eq. (28), to eliminate $\tilde{c}_n^{(1)}$ and $\bar{\varphi}^{(1)}$. We obtain the reduced boundary layer equations

$$\sum_{j=1}^{n-1} d_{ij}'\tilde{c}_{j\bar{y}\bar{y}}^{(1)} = \bar{\psi}_{\bar{y}}^{(0)}\tilde{c}_{ix}^{(1)} - \bar{\psi}_x^{(0)}\tilde{c}_{i\bar{y}}^{(1)}, \tag{34}$$

for $i = 1, \cdots, n-1$, and the boundary conditions at $\bar{y} = 0$

$$\sum_{j=1}^{n-1} d_{ij}'\tilde{c}_{j\bar{y}}^{(1)} = \begin{cases} (1 - t_1^{(0)})\,j_c^{(0)}/z_1, & \text{for} \quad i = 1, \\ -t_i^{(0)}\,j_c^{(0)}/z_i, & \text{for} \quad i = 2, \cdots, n-1, \end{cases} \tag{35}$$

where $t_i^{(0)} = k_i^{(0)}/k^{(0)}$ is the ith transference number and the reduced diffusivity matrix $[d_{ij}']$ has elements

$$d_{ij}' = d_{ij}^{(0)} - (z_j/z_n)d_{in}^{(0)} - t_i^{(0)}\sum_{p=1}^{n} (z_p/z_i)[d_{pj}^{(0)} - (z_j/z_n)d_{pn}^{(0)}], \tag{36}$$

for $i = 1, \cdots, n-1$, $j = 1, \cdots, n-1$. The boundary value problem is completed by the conditions at infinity

$$\tilde{c}_i^{(1)}(x, \infty) = 0, \tag{37}$$

and the "initial condition"

$$\tilde{c}_i^{(1)}(0, \bar{y}) = 0. \tag{38}$$

As usual, the boundary layer approximation changes the equations from elliptic to parabolic type, requiring a condition at $x = 0$ in the time-like variable x. Equation (38) is equivalent to the assumption that the concentrations have their free-stream, bulk values near the leading edge $x = \bar{y} = 0$. We now have a complete set of coupled equations and boundary conditions for the first-order boundary layer concentration variations $\tilde{c}_i^{(1)}$. We note in passing that the corresponding set for the second-order variations $\tilde{c}_i^{(2)}$ would be much more complicated, containing not only $\tilde{\psi}^{(1)}$, as in the case of the dilute binary electrolyte, but also first-order terms $\tilde{d}_{ij}^{(1)}$, etc., due to the concentration dependent diffusivities and mobilities.

VIII. THE VECTOR CD-EQUATION AND ITS SOLUTION

Equation (34) and boundary condition (35) can be written in the vector form

$$[d'][\tilde{c}^{(1)}]_{\bar{y}\bar{y}} = \tilde{\psi}_{\bar{y}}^{(0)}[\tilde{c}^{(1)}]_x - \tilde{\psi}_x^{(0)}[\tilde{c}^{(1)}]_{\bar{y}} \tag{39}$$

in $\bar{y} > 0$, and

$$[d'][\tilde{c}^{(1)}]_{\bar{y}} = [T^{(0)}]j_c^{(0)} \tag{40}$$

on $\bar{y} = 0$, where $[d']$ is the $(n-1) \times (n-1)$ matrix

$$[d'] = \begin{bmatrix} d'_{11} & \cdots & d'_{1(n-1)} \\ \cdots & \cdots & \cdots \\ d'_{(n-1)1} & \cdots & d'_{(n-1)(n-1)} \end{bmatrix},$$

and $[\tilde{c}^{(1)}]$ and $[T^{(0)}]$ the column vectors

$$[\tilde{c}^{(1)}] = \begin{bmatrix} \tilde{c}_1^{(1)} \\ \vdots \\ \tilde{c}_{n-1}^{(1)} \end{bmatrix}, \qquad [T^{(0)}] = \begin{bmatrix} (1-t_1)/z_1 \\ \vdots \\ -t_{n-1}/z_{n-1} \end{bmatrix}.$$

By way of comparison, for the binary electrolyte $(n = 2)$, one has

$$\tilde{c}_{\bar{y}\bar{y}}^{(1)} = \tilde{\psi}_{\bar{y}}^{(0)}\tilde{c}_x^{(1)} - \tilde{\psi}_x^{(0)}\tilde{c}_{\bar{y}}^{(1)}, \tag{41}$$

for $\bar{y} > 0$, and

$$\tilde{c}_{\bar{y}}^{(1)} = T^{(0)}j_c^{(0)}, \tag{42}$$

for $\bar{y} = 0$, where $d'_{11} = 1, \tilde{c}^{(1)} = \tilde{c}_1^{(1)}, T^{(0)} = T_1^{(0)}(1-t_1)/z_1$. The solution of this problem is given in Appendix A, together with that of the corresponding axially symmetric problem, important for jet plating and for the rotating disk electrode.

We now introduce the eigenvalues $d^{(p)}$ and the eigenvectors $[u^{(p)}]$ of $[d']$, such that[*]

$$[d'][u^{(p)}] = d^{(p)}[u^{(p)}],$$

for $p = 1, \cdots, n - 1$. If we set

$$[\tilde{c}^{(1)}] = \sum_{p=1}^{n-1} c^{(p)}[u^{(p)}],$$

$$[T^{(0)}] = \sum_{p=1}^{n-1} \tau^{(p)}[u^{(p)}],$$

eqs. (39) and (40) are satisfied if

$$d^{(p)}c_{\bar{y}\bar{y}}^{(p)} = \bar{\psi}_{\bar{y}}^{(0)}c_x^{(p)} - \bar{\psi}_x^{(0)}c_{\bar{y}}^{(p)}, \tag{43}$$

in $\bar{y} > 0$, and

$$d^{(p)}c_{\bar{y}}^{(p)} = \tau^{(p)}j_c^{(0)}, \tag{44}$$

on $\bar{y} = 0$, for $p = 1, \cdots, n - 1$.

Now, in Appendix A we show that, if $c(x, y)$ satisfies

$$c_{yy} = \psi_y c_x - \psi_x c_y,$$

with $\psi = y^2 f(x)$, and

$$c(0, y) = c(x, \infty) = 0,$$

then

$$c(x, 0) = \int_0^x c_y(x', 0)K(x, x')dx', \tag{45}$$

where the kernel

$$K(x, x') = -(\tfrac{1}{6})^{\frac{1}{3}}\left(\int_{x'}^x [f(z)]^{\frac{1}{3}}dz\right)^{-\frac{2}{3}}\Big/\Gamma(\tfrac{2}{3}). \tag{46}$$

Thus,

$$c^{(p)}(x, 0) = [d^{(p)}]^{-\frac{1}{3}}\tau^{(p)}\int_0^x j_c^{(0)}(x')K(x, x')dx', \tag{47}$$

with a factor $(d^{(p)})^{\frac{1}{3}}$, found by replacing f by $f/d^{(p)}$ in K, and a factor $(d^{(p)})^{-1}$ from the boundary conditions. Finally, to first order in ϵ, the concentrations at the cathode are given by

$$\tilde{c}_i(x, 0) = c_i^{(0)} + \epsilon\mu_i\int_0^x j_c^{(0)}(x')K_c(x, x')dx', \tag{48}$$

for $i = 1, \cdots, n - 1$, where

$$\mu_i = \sum_{p=1}^{n-1} [d^{(p)}]^{-\frac{1}{3}}\tau^{(p)}u_i^{(p)}, \tag{49}$$

[*] We assume that such u's and d's exist. This must be verified in each particular case.

and we now write K_c for K to indicate that the kernel depends on the velocity distribution near the cathode. A similar expression

$$\tilde{c}_i(x, 0) = c_i^{(0)} + \epsilon \mu_i \int_0^x j_a^{(0)}(x') K_a(x, x') dx', \qquad (50)$$

with x measured from the anode leading edge and $i = 1, \cdots, n - 1$, is valid for the concentrations at the anode. The concentration of the nth ion at cathode and anode is found from the charge neutrality relation

$$\tilde{c}_n(x, 0) = - \sum_{i=1}^{n-1} (z_i/z_n) \tilde{c}_i(x, 0). \qquad (51)$$

With the $\tilde{c}_i^{(1)}$'s determined, we are almost ready to calculate the first-order corrections to the electrode current densities. For example, at the cathode we have

$$j_c = j_c^*(\tilde{c}_1)^{\gamma_c} [\exp(\alpha_c \tilde{\varphi}) - \exp(-\beta \tilde{\varphi})],$$

where

$$\tilde{c}_1 = c_1^{(0)} + \epsilon \tilde{c}_1^{(1)},$$
$$\tilde{\varphi} = \tilde{\varphi}^{(0)} + \epsilon \tilde{\varphi}^{(1)},$$

all quantities being evaluated at $\tilde{y} = 0$. With

$$j_c = j_c^{(0)} + \epsilon \tilde{j}_c^{(1)} + \cdots,$$

we find

$$j_c^{(0)} = j_c^*[c_1^{(0)}]^{\gamma_c} [\exp(\alpha_c \tilde{\varphi}^{(0)}) - \exp(-\beta_c \tilde{\varphi}^{(0)})],$$

as before, and

$$\tilde{j}_c^{(1)} = j_c^*[c_1^{(0)}]^{\gamma_c} \{ [\gamma_c \tilde{c}_1^{(1)} + \alpha_c \tilde{\varphi}^{(1)}] \exp(\alpha_c \tilde{\varphi}^{(0)}) \\ - [\gamma_c \tilde{c}_1^{(1)} - \beta_c \tilde{\varphi}^{(1)}] \exp(-\beta_c \tilde{\varphi}^{(0)}) \},$$

where

$$\tilde{\varphi}^{(1)} = \tilde{\varphi}^{(1)}(x, 0) - \sum_{i=1}^{n} \sum_{j=1}^{n} z_i d_{ij}^{(0)} \tilde{c}_j^{(1)}(x, 0)/k^{(0)}. \qquad (52)$$

We still must determine the first-order outer potential $\tilde{\varphi}^{(1)}$. It is the solution of the linear potential problem

$$\tilde{\varphi}_{xx}^{(1)} + \tilde{\varphi}_{yy}^{(1)} = 0, \qquad (53)$$

in the electrolyte,

$$k^{(0)} \partial \tilde{\varphi}^{(1)}/\partial n = \begin{cases} \tilde{j}_a^{(1)}, & \text{on the anode,} \\ -\tilde{j}_c^{(1)}, & \text{on the cathode,} \\ 0, & \text{otherwise,} \end{cases} \qquad (54)$$

where the $\tilde{j}_c^{(1)}$'s are linear functions of $\tilde{\varphi}^{(1)}$, with coefficients which

depend on $c_i^{(0)}$, $\bar{\varphi}^{(0)}$, and $\tilde{c}_i^{(1)}$. This boundary condition is found from second-order matching of $\tilde{\varphi}$ and $\bar{\varphi}$, just as the boundary condition on $\bar{\varphi}^{(0)}$ was found from first-order matching. As is usual in boundary layer problems, the complexity of matching increases rapidly with order so this rather messy matching is relegated to Appendix B. Once $\bar{\varphi}^{(1)}$ has been determined, the electrode current densities can be calculated to first order in ϵ.

IX. THE CONCENTRATION OVERPOTENTIALS

The concentration variations $\tilde{c}_i^{(1)}$ appear in the $\tilde{\jmath}_e^{(1)}$'s in two ways. First of all, there is the power law dependence of the ion exchange densities on the concentration $\tilde{c}_1$ of the "active" cation (e.g., Cu^{++}). This concentration is given by

$$\tilde{c}_1 = c_1^{(0)} + \epsilon\mu_1 \int_0^x j_e^{(0)} K_e dx' \tag{55}$$

in terms of the bulk concentration $c_1^{(0)}$ and the constant μ_1.

The second concentration dependence is contained in the so-called "concentration overpotential," the difference between the potential $\tilde{\varphi}(x, 0)$ at the electrode and the potential $\bar{\varphi}(x, 0)$ at the edge of the boundary layer. To first order in ϵ, this concentration overpotential is given by

$$\Delta\varphi_e = \epsilon(\tilde{\varphi}^{(1)} - \bar{\varphi}^{(1)}) = \epsilon\delta \int_0^x j_e^{(0)} K_e dx', \tag{56}$$

where

$$\delta = -\sum_{i=1}^{n} \sum_{j=1}^{n-1} z_i [d_{ij}^{(0)} - (z_j/z_n)d_{in}^{(0)}]\mu_j/k^{(0)}. \tag{57}$$

X. FORMAL PERTURBATION SOLUTION

Although we shall eventually abandon this approach in favor of an equivalent scheme more convenient for numerical analysis, let us briefly summarize the successive steps by which the electrode current densities are calculated to first order in ϵ. There are three such steps:

(i) The nonlinear potential problem. First, we calculate the harmonic function $\bar{\varphi}^{(0)}$, satisfying nonlinear, mixed-boundary conditions. As is usual in boundary layer theory, we begin with a nonlinear problem, the only nonlinear problem in the sequence. It yields first approximations to the electrode current densities, which may be adequate for many purposes. It also furnishes a boundary condition for the boundary layer concentration variations.

(ii) Concentration variations. The concentration variations $\tilde{c}_i^{(1)}$, or rather $\tilde{c}_i^{(1)}$ and $\Delta\varphi_e$, which are the only quantities involved in $\bar{j}_e^{(1)}$, are calculated from eqs. (55) and (56), giving them in terms of a single integral of the product of electrode current density and given kernels.

(iii) The linear potential problem. With $\tilde{c}_i^{(1)}$, $\Delta\varphi_e$ known, the harmonic function $\bar{\varphi}^{(1)}$, satisfying linear, mixed-boundary conditions in $\bar{\varphi}^{(1)}$, $\tilde{c}_i^{(1)}$, $\Delta\varphi_e$ is calculated and, from it, a second approximation to the electrode current densities, good to order ϵ.

XI. SOLUTION BY BOUNDARY INTEGRALS

Instead of following the above rather cumbersome procedure, we can adopt the approach suggested by J. L. Blue,[2] forming a nonlinear, coupled set of integral equations whose solution, e.g., by successive approximation, yields the electrode current densities directly to order ϵ. From this point of view, the formal perturbation scheme simply validates this method. For example, perturbation tells us that the integral solution of the boundary layer equation is good to order ϵ and no more.

We begin with Green's third identity for a plane region:

$$2\pi\varphi(P) = \int_{\Gamma_a} [j_a(Q)/k]G(P, Q)ds(Q) - \int_{\Gamma_c} [j_c(Q)/k]$$
$$\cdot G(P, Q)ds(Q) - \int_{\Gamma} \varphi(Q)\frac{\partial G}{\partial n}(P, Q)d(Q),$$

where G has the fundamental singularity at $P = Q$, Γ_a is the anode, Γ_c the cathode, and Γ the whole boundary, and we now denote $\bar{\varphi}^{(0)} + \epsilon\bar{\varphi}^{(1)}$ by φ and the bulk conductivity $k^{(0)}$ by k. For each set of values of j_a, j_c, φ, and points P on the boundary, the solution of this integral equation gives φ. Similarly, from the integrals

$$c_1 = c_1^{(0)} + \epsilon\mu_1 \int_0^x j_e K_e dx',$$

$$\Delta\varphi_e = +\epsilon\delta \int_0^x j_e K_e dx',$$

with $e = a, c$, we can calculate c_1 and $\Delta\varphi_e$ from the given values of j_a and j_c. With φ, c_1, and $\Delta\varphi_e$ now known on the electrodes, we can calculate new values of j_a and j_c from the relations

$$j_e = j_e^*(c_1)^{\gamma_e}[\exp(\alpha_e|\varphi + \Delta\varphi_e - \varphi_e|) - \exp(-\beta_e|\varphi + \Delta\varphi_e - \varphi_e|)],$$

for $e = a, c$, the anode potential $\varphi_a > 0$, and the cathode potential $\varphi_c = 0$ (for a grounded cathode). Using these new values of electrode

current densities, compared with the old values, a successive approximation scheme can be developed which converges rapidly.

Note that this scheme is formally identical with that for the dilute, binary electrolyte. Furthermore, within the framework of this calculation, the concentrated, n-component electrolyte can be characterized completely by giving its bulk conductivity k and the constants μ_1 and δ. The values of the individual diffusivities d_{ij} and mobilities u_i, from which μ_1 and δ can be calculated, are of no importance. Only k, μ_1, and δ enter the final set of equations.

APPENDIX A

Integral Solution of the Boundary Layer Equation

Let $c(x, y)$ satisfy the boundary layer equation

$$c_{yy} = \psi_y c_x - \psi_x c_y \tag{58}$$

in $x > 0$, $y > 0$, with $\psi = y^2 f(x)$ and

$$c(0, y) = c(x, \infty) = 0. \tag{59}$$

For use in the method of boundary integrals, we wish to express the boundary values of c in terms of an integral over the boundary values of c_y, i.e., we seek the kernel function K in the relation

$$c(x, 0) = \int_0^x c_y(x', 0) K(x, x') dx'. \tag{60}$$

Following Levich[3] and Lighthill,[4] we make the change of variable

$$\xi = \int_0^x [f(z)]^{\frac{1}{3}} dz, \qquad \eta = (\psi)^{\frac{1}{3}} = y[f(x)]^{\frac{1}{3}},$$

the form of η being motivated by the observation that the right-hand side of eq. (58) vanishes when c is a function of ψ alone. We find that $v(\xi, \eta) = c(x, y)$ satisfies the equation

$$v_{\eta\eta} = 2\eta v_\xi, \tag{61}$$

if $\xi > 0$, $\eta > 0$, and

$$v(0, \eta) = v(\xi, \infty) = 0. \tag{62}$$

Denote the boundary values of v_η by g, so that

$$v_\eta(\xi, 0) = g(\xi).$$

Then the Laplace transform $\bar{v}$, given by

$$\bar{v}(\eta, s) = \int_0^\infty e^{-s\xi} v(\xi, \eta) d\xi,$$

satisfies the ordinary differential equation

$$\bar{v}'' - 2s\eta\bar{v} = 0,$$

in $0 < \eta < \infty$, and the boundary conditions

$$\bar{v}'(0, s) = \bar{g}(s), \qquad \bar{v}(\infty, s) = 0,$$

where $\bar{g}$ is the transform of g. Now suppose $u(\xi, \eta)$ is *any* solution of eq. (61), satisfying eq. (62). Then we have the identity between transforms

$$\bar{v}(\eta, s) = \bar{g}(s)\bar{u}(\eta, s)/\bar{u}'(0, s),$$

giving

$$\bar{v}(0, s) = \bar{v}'(0, s)[\bar{u}(0, s)/\bar{u}'(0, s)]. \tag{63}$$

A convenient choice for u is the similar solution of eqs. (61) and (62), satisfying the condition

$$u(\xi, 0) = 1,$$

so that $\bar{u}(0, s) = 1/s$. In this case, u is a function of $\zeta = \eta/\xi^{\frac{1}{3}}$ alone, given by

$$u = \left[\int_\zeta^\infty \exp(-2z^3/9)\,dz \right] \Big/ \left(\frac{1}{6}\right)^{\frac{1}{3}} \Gamma\left(\frac{1}{3}\right),$$

so that

$$u_\eta(\xi, 0) = -\xi^{-\frac{1}{3}}/\left(\tfrac{1}{6}\right)^{\frac{1}{3}}\Gamma\left(\tfrac{1}{3}\right)$$

and, with $\Gamma(k)/s^k$ the transform of ξ^{1-k},

$$\bar{u}'(0, s) = -\Gamma\left(\tfrac{2}{3}\right)/\left(\tfrac{1}{6}\right)^{\frac{1}{3}}\Gamma\left(\tfrac{1}{3}\right)s^{\frac{2}{3}}.$$

Thus,

$$\bar{u}(0, s)/\bar{u}'(0, s) = -\left(\tfrac{1}{6}\right)^{\frac{1}{3}}\Gamma\left(\tfrac{1}{3}\right)/\Gamma\left(\tfrac{2}{3}\right)s^{\frac{1}{3}}.$$

Inversion of eq. (63), using the convolution theorem, then yields

$$v(\xi, 0) = \int_0^\xi v_\eta(\xi', 0)\kappa(\xi - \xi')\,d\xi',$$

where κ, the inverse of $\bar{u}(0, s)/\bar{u}'(0, s)$, is given by

$$\kappa(\xi) = -\left(\tfrac{1}{6}\right)^{\frac{1}{3}}\xi^{-\frac{1}{3}}/\Gamma\left(\tfrac{2}{3}\right).$$

Using the relations

$$v(\xi', 0)\,d\xi' = c_y(x', 0)\,dx',$$

$$\xi - \xi' = \int_{x'}^x [f(z)]^{\frac{1}{2}}\,dz,$$

we finally obtain eq. (60), with

$$K(x, x') = -\left(\frac{1}{6}\right)^{\frac{1}{3}} \left(\int_{x'}^x [f(z)]^{\frac{1}{2}}\,dz\right)^{-\frac{1}{3}} \Big/ \Gamma\left(\frac{2}{3}\right). \tag{64}$$

K is of convolution type, i.e., a function of $x - x'$ alone, only when f is constant, e.g., for Poiseuille flow near the wall of a channel or tube. For the laminar boundary layer flow on a semi-infinite flat plate,

$$f \sim x^{-\frac{1}{2}},$$

so that

$$K \sim (x^{\frac{3}{4}} - x'^{\frac{3}{4}})^{-\frac{2}{3}}.$$

A slight modification of the above yields the integral relation

$$c(r, 0) = \int_0^r c_z(r', 0) L(r, r') r' dr', \tag{65}$$

for the axially symmetric problem, where

$$c_{zz} = r^{-1}(\psi_z c_r - \psi_r c_z),$$

in $r > 0$, $z > 0$, with $\psi = z^2 f(r)$ and

$$c(0, z) = c(r, \infty) = 0,$$

where the kernel function

$$L(r, r') = -\left(\frac{1}{6}\right)^{\frac{1}{3}} \left(\int_{r'}^r [f(s)]^{\frac{1}{2}} ds\right)^{-\frac{1}{3}} \bigg/ \Gamma\left(\frac{2}{3}\right). \tag{66}$$

We merely replace the previously defined ξ by

$$\xi = \int_0^r [f(s)]^{\frac{1}{2}} s ds.$$

Equations (65) and (66) apply, for example, to the rotating disk electrode and to "jet plating," where a jet of electrolyte is directed against an electrode.

APPENDIX B

Second-Order Potential Matching

To obtain a boundary condition for the first-order outer potential $\bar{\varphi}^{(1)}$, we must match

$$\bar{\varphi} = \bar{\varphi}^{(0)} + \epsilon \bar{\varphi}^{(1)} + \epsilon^2 \bar{\varphi}^{(2)}$$

with

$$\tilde{\varphi} = \tilde{\varphi}^{(0)} + \epsilon \tilde{\varphi}^{(1)} + \epsilon^2 \tilde{\varphi}^{(2)},$$

where

$$\tilde{\varphi}^{(0)} = \bar{\varphi}^{(0)}(x, 0), \tag{67}$$

$$\tilde{\varphi}^{(1)} = \bar{\varphi}^{(1)}(x, 0) + \tilde{y} j_c^{(0)}/k^{(0)} - \sum\sum z_i d_{ij}^{(0)} \tilde{c}_j^{(1)}/k^{(0)}. \tag{68}$$

The second-order inner potential $\tilde{\varphi}^{(2)}$ satisfies the equation

$$\left[k^{(0)} \tilde{\varphi}_{\tilde{y}}^{(2)} + \tilde{k}^{(1)} \tilde{\varphi}_{\tilde{y}}^{(1)} + \sum_{i=1}^n \sum_{j=1}^n z_i (d_{ij}^{(0)} \tilde{c}_{j\tilde{y}}^{(2)} + \tilde{d}_{ij}^{(1)} \tilde{c}_{j\tilde{y}}^{(1)}) \right]_{\tilde{y}} = -k^{(0)} \tilde{\varphi}_{xx}^{(0)}, \tag{69}$$

and the boundary condition at $\bar{y} = 0$

$$k^{(0)}\bar{\varphi}_{\bar{y}}^{(2)} + \bar{k}^{(1)}\bar{\varphi}_{\bar{y}}^{(1)} + \sum_{i=1}^{n}\sum_{j=1}^{n}z_i(d_{ij}^{(0)}\tilde{c}_{j\bar{y}}^{(2)} + d_{ij}^{(1)}\tilde{c}_{j\bar{y}}^{(1)}) = \bar{j}_c^{(1)}, \qquad (70)$$

where k, d_{ij}, j_c have been expanded in the forms

$$k = k^{(0)} + \epsilon\bar{k}^{(1)} + \cdots,$$
$$d_{ij} = d_{ij}^{(0)} + \epsilon\tilde{d}_{ij}^{(1)} + \cdots,$$
$$j_c = j_c^{(0)} + \epsilon\bar{j}_c^{(1)} + \cdots.$$

Note that $\bar{k}^{(1)}$, $\tilde{d}_{ij}^{(1)}$, $\bar{j}_c^{(1)}$ are linear functions of the $\tilde{c}_i^{(1)}$'s; for example,

$$k = k^{(0)} + \epsilon\sum_{p=1}^{n}(\partial k^{(0)}/\partial c_p)\tilde{c}_p^{(1)}.$$

Two integrations give

$$\bar{\varphi}^{(2)} = \hat{\varphi}^{(2)} + \bar{y}\,\bar{j}_c^{(1)}/k^{(0)} - \bar{y}^2\bar{\varphi}_{xx}^{(0)}/2 - \sum_{i=1}^{n}\sum_{j=1}^{n}z_id_{ij}^{(0)}\tilde{c}_j^{(2)}$$

$$+ \int_0^{\bar{y}}\left[\sum_{i=1}^{n}\sum_{j=1}^{n}z_i(\bar{k}^{(1)}d_{ij}^{(0)}/k^{(0)} - \tilde{d}_{ij}^{(1)})\tilde{c}_{j\bar{y}}^{(1)} - \bar{k}^{(1)}\bar{j}_c^{(0)}/k^{(0)}\right]d\bar{y}'/k^{(0)},$$

where $\hat{\varphi}^{(2)}$ is an arbitrary function of x and eq. (68) has been used to eliminate $\bar{\varphi}^{(1)}$. We wish to calculate $\bar{\varphi}^{(2)}$ in the limit $\bar{y} = \epsilon^{\alpha-1}y^*$, with $0 < \alpha < 1$, y^* fixed, $\epsilon \to 0$. The first three terms all contribute to the limit, while the fourth term vanishes, since $\tilde{c}^{(2)} \to 0$, as $\bar{y} \to \infty$. Finally, we must evaluate the limit of the integral. Consider the last term first. Since $j_c^{(0)}$ is a function of x only and

$$\bar{k}^{(1)} = \sum_{p=1}^{n}(\partial k^{(0)}/\partial c_p)\tilde{c}_p^{(1)},$$

we have n integrals like

$$\int_0^{\bar{y}}\tilde{c}_p^{(1)}(x, \bar{y}')d\bar{y}'.$$

Changing variable gives

$$\int_0^{\epsilon^{\alpha-1}y^*}\tilde{c}_p^{(1)}(x, \bar{y})d\bar{y} = \epsilon^{\alpha-1}\int_0^{y^*}\tilde{c}_p^{(1)}(x, \epsilon^{\alpha-1}z)dz \to \epsilon^{\alpha-1}I(\epsilon),$$

where $I(\epsilon) \to 0$, as $\epsilon \to 0$. Similar limits are obtained for the other integrals with integrands of the form $\tilde{c}_p^{(1)}\tilde{c}_{j\bar{y}}^{(1)}$. Thus,

$$\bar{\varphi} \sim \bar{\varphi}^{(0)}(x, 0) + \epsilon[\bar{\varphi}^{(1)}(x, 0) + \epsilon^{\alpha-1}y^*j_c^{(0)}/k^{(0)}] + \epsilon^2[\hat{\varphi}^{(2)}(x)$$
$$+ \epsilon^{\alpha-1}y^*\bar{j}_c^{(1)}/k^{(0)} - (\epsilon^{\alpha-1}y^*)^2\bar{\varphi}_{xx}^{(0)}(x, 0)/2],$$

since $\bar{\varphi}_{xx}^{(0)} = \bar{\varphi}_{xx}^{(0)}(x, 0)$, to be matched with

$$\bar{\varphi} \sim \bar{\varphi}^{(0)}(x,\,0) + \epsilon^{\alpha} y^* \bar{\varphi}_y^{(0)}(x,\,0) + (\epsilon^{\alpha} y^*)^2 \bar{\varphi}_{yy}^{(0)}(x,\,0)/2$$
$$+ \epsilon[\,\bar{\varphi}^{(1)}(x,\,0) + \epsilon^{\alpha} y^* \bar{\varphi}_y^{(1)}(x,\,0)\,] + \epsilon^2 \bar{\varphi}^{(2)}(x,\,0).$$

Since $\bar{\varphi}^{(0)}$ is harmonic, $\bar{\varphi}_{xx}^{(0)}(x,\,0) = -\bar{\varphi}_{yy}^{(0)}(x,\,0)$, and matching term by term gives the previous boundary condition on $\bar{\varphi}^{(0)}$

$$\bar{\varphi}_y^{(0)}(x,\,0) = j_c^{(0)}/k^{(0)},$$

the boundary condition on $\bar{\varphi}^{(1)}$

$$\bar{\varphi}_y^{(1)}(x,\,0) = \tilde{j}_c^{(1)}/k^{(0)},$$

and the "penetration" condition

$$\hat{\phi}^{(2)}(x) = \bar{\varphi}^{(2)}(x,\,0).$$

APPENDIX C

The Electrochemical Potential

In Section IV, we expressed the fluxes in terms of the gradients in the form

$$\mathbf{N}_i = C_i \mathbf{V} - \sum_{j=1}^{n} D_{ij} \nabla C_j - F z_i C_i U_i \nabla \Phi, \tag{71}$$

in effect *defining* the diffusivities D_{ij} and mobilities U_i, functions of the concentrations, by this relation. In electrochemistry, it is more usual to give the gradients of the electrochemical potentials, i.e., well-defined thermodynamic functions, in terms of the fluxes. Thus, Newman[1] gives the relations (for $n + 1$ species in our notation)

$$c_i \nabla \mu_i = \sum_{j=0}^{n} K_{ij}(\mathbf{V}_j - \mathbf{V}_i), \tag{72}$$

for $i = 0, 1, \cdots, n$, where the μ_i's are the electrochemical potentials, the K_{ij}'s are the interaction coefficients, functions of the concentrations, and $\mathbf{V}_i$'s are subject to certain constraints. Thus,

$$\sum_{i=0}^{n} C_i \nabla \mu_i = 0$$

and

$$\sum_{i=0}^{n} \rho_i \mathbf{V}_i = \rho \mathbf{V},$$

where $\mathbf{V}$ is the fluid velocity, $\rho_i = M_i C_i$ is the partial density for molecular weight M_i, and

$$\rho = \sum_{i=0}^{n} \rho_i.$$

These restrictions imply that

$$\sum_{i=0}^{n} (K_{ij} - K_{ji}) = 0,$$

for $j = 0, 1, \cdots, n$. In particular, Newman assumes the Stefan-Maxwell relations $K_{ij} = K_{ji}$, i.e., pairwise interaction between species. With these restrictions, eq. (72) has a unique solution for $\mathbf{V}_i = \mathbf{V}$. Thus we find, following Newman, that

$$\mathbf{V}_i - \mathbf{V}_0 = -\sum_{p=1}^{n} L_{ip} C_p \nabla \mu_p,$$

for $i = 1, \cdots, n$, where $-[L_{ij}]$ is the inverse of $[M_{ij}]$, with

$$M_{ij} = \begin{cases} -\sum_{k=1 \neq i}^{n} K_{ik}, & \text{for} \quad i = j, \\ K_{ij}, & \text{for} \quad i \neq j. \end{cases}$$

(Note that we may assume that $K_{ij} = 0$, for $i = j$.) Once $\mathbf{V}_i - \mathbf{V}_0$ is calculated, $\mathbf{V}_i - V$ may be determined from the identities

$$\mathbf{V}_0 - \mathbf{V} = -\sum_{k=1}^{n} (\rho_k/\rho)(\mathbf{V}_k - \mathbf{V}_0),$$

$$\mathbf{V}_i - \mathbf{V} = \mathbf{V}_i - \mathbf{V}_0 + \mathbf{V}_0 - \mathbf{V}.$$

With

$$\nabla \mu_p = \sum_{j=0}^{n} (\partial \mu_p/\partial C_j) \nabla C_j + (\partial \mu_p/\partial \Phi) \nabla \Phi,$$

we finally find

$$D_{0j} = -\sum_{k=1}^{n} \sum_{p=1}^{n} (\rho_k/\rho) L_{kp} C_0 C_p (\partial \mu_p/\partial C_j),$$

$$F z_0 U_0 = -\sum_{k=1}^{n} \sum_{p=1}^{n} (\rho_k/\rho) L_{kp} C_p (\partial \mu_p/\partial \Phi),$$

$$D_{ij} = \sum_{p=1}^{n} \left[L_{ip} - \sum_{k=1}^{n} (\rho_k/\rho) L_{kp} \right] C_i C_p (\partial \mu_p/\partial C_j),$$

$$F z_i U_i = \sum_{p=1}^{n} \left[L_{ip} - \sum_{k=1}^{n} (\rho_k/\rho) L_{kp} \right] C_p (\partial \mu_p/\partial \Phi).$$

REFERENCES

1. J. S. Newman, *Electrochemical Systems*, 1st ed., New York: Prentice-Hall, 1973.
2. J. L. Blue, unpublished work.
3. V. G. Levich, *Physicochemical Hydrodynamics*, 1st ed., Prentice-Hall, 1962.
4. M. J. Lighthill, "Contributions to the Theory of Heat Transfer Through a Laminar Boundary Layer," Proc. Roy. Soc., *A202* (1950), pp. 359–377.