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Publication Date
1971-11-01

To be presented at the International
Conference Localized Corrosion,
National Assn. of Corrosion Engineers,
Williamsburg, Va. Dec. 9-10, 1971

LBL-408
Preprint c.2

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AEC Contract No. W-7405-eng-48

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LBL-408

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Mass Transport and Potential Distribution in the Geometries of Localized Corrosion

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November, 1971

Abstract

The principles of current and potential distribution and mass transfer in electrochemical systems are developed with a view toward their application in analyzing and understanding the processes of localized corrosion, such as pitting and corrosion in crevices, under deposits, and in regions near gas-liquid-solid contact.

Introduction

Frequently, the rate of a corrosion process is governed by the transport of a species like oxygen to the corroding surface by diffusion and convection. Other corrosion processes, like pitting, involve mass transfer and fluid flow in the transport of products as well as reactants in such a way that the different parts of a surface are subjected to different environments, and a galvanic cell can be set up.

When the surface is homogeneous and exposed to uniform mass transfer conditions, the process occurs uniformly and is governed by electrode kinetics and thermodynamics as well as mass transfer. No current flows in the solution because the cathodic and anodic reactions are balanced everywhere on the surface. However, current and potential distributions are involved when the anodic and cathodic reactions occur on different surfaces or on different parts of the same surface. Examples are inclusions, cathodic and anodic protection, and most cases of corrosion in local geometries: cracking, pitting, corrosion in crevices, under deposits, and at liquid lines.

In cathodic protection one first needs to calculate the rate of transport of oxygen to the surface. This is a mass-transfer limited process and determines the amount of current which needs to be supplied to each part of the protected surface. Next, the potential and current distributions in the solution need to be evaluated to ensure that the current will actually reach, in appropriate amount, each part of the protected surface. Otherwise, hydrogen will be evolved on some parts of the surface while leaving other parts unprotected.

We want to consider first the fundamentals of transport processes in electrolytic solutions.[1,2] This serves as an introduction to the discussion of current and potential distributions as well as the treatment of mass-transfer limited phenomena. These two subjects are thus limiting cases[2,3,4] of the basic transport processes. For problems of local corrosion, it will usually be necessary to consider simultaneously matters of mass transfer and potential distribution.[2,5]

Transport processes in electrolytic solutions

Mass transfer in an electrolytic solution requires a description of

1. The movement of mobile ionic species.
2. Material balances.
3. Current flow.
4. Electroneutrality.
5. Fluid mechanics.

The flux of a minor component is given by

$$\underbrace{\underline{N}_i}_{\text{flux}} = \underbrace{-z_i u_i F c_i \nabla\Phi}_{\text{migration}} \quad \underbrace{-D_i \nabla c_i}_{\text{diffusion}} \quad + \quad \underbrace{c_i \underline{v}}_{\text{convection}} . \qquad (1)$$

The mass transfer of a given constituent can be associated with three mechanisms, known as migration, diffusion, and convection. The flux is the amount moving past a plane (oriented perpendicular to the direction of the flow) per unit time, measured in moles per square centimeter per second. This movement is due first of all to the motion of the fluid with the bulk velocity $\underline{v}$. However, the movement of the species can deviate from this average velocity by diffusion if there is a concentration gradient ∇c_i or by migration if there is an electric field $-\nabla\Phi$ and if the species is charged (z_i is the number of proton charges carried by an ion). Thus, $z_i F$ is the charge per mole. Multiplication by the electric field $-\nabla\Phi$ gives the force per mole. Multiplication by the mobility u_i gives the migration velocity, and finally multiplication by the concentration c_i gives the contribution of migration to the flux of the species.

This equation thus serves to define two transport properties, the diffusion coefficient D_i and the mobility u_i. The validity of this equation will be considered later.

The current in an electrolytic solution is, of course, due to the motion of charged particles, and we can easily express this quantitatively:

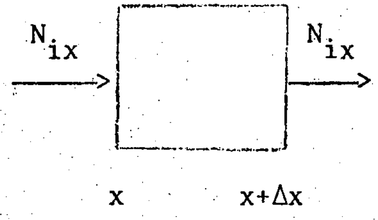
$$\underline{i} = F\sum_i z_i \underline{N}_i \quad . \tag{2}$$

Here $\underline{i}$ is the current density expressed in amperes per square centimeter, and $z_i F$ is again the charge per mole.

Next we need to state a material balance for a minor component:

$$\underset{\text{accumulation}}{\frac{\partial c_i}{\partial t}} = \underset{\text{net input}}{-\nabla\cdot\underline{N}_i} + \underset{\substack{\text{production (in homogeneous}\\ \text{chemical reactions)}}}{R_i} \quad . \tag{3}$$

In engineering parlance, accumulation is equal to input minus output plus production. For a differential volume element, accumulation is simply the time rate of change of concentration. For the net input it is necessary to compute the net amount of material brought in by the different fluxes on the various faces of the volume element.



$$\nabla \cdot \underline{N}_i = \frac{\partial N_{ix}}{\partial x} + \frac{\partial N_{iy}}{\partial y} + \frac{\partial N_{iz}}{\partial z} \quad . \tag{4}$$

The difference in fluxes contributes to accumulation or depletion:

$$\lim_{\Delta x \to 0} \frac{N_{ix}|_x - N_{ix}|_{x+\Delta x}}{\Delta x} = - \frac{\partial N_{ix}}{\partial x} \quad . \tag{5}$$

The Δx in the denominator comes from dividing by the volume of the element. The production per unit volume R_i involves chemical reactions in the bulk of the solution, but not any electrode reactions, which occur at the boundaries of the solution.

Finally, we may say that the solution is electrically neutral.

$$\sum_i z_i c_i = 0 \quad . \tag{6}$$

This is not, however, a fundamental law of nature. Perhaps a more nearly correct realtionship would be Poisson's equation

$$\sum_i z_i c_i = - \frac{\varepsilon}{F} \nabla^2 \Phi \quad , \tag{7}$$

which relates the charge density to the Laplacian of the electric potential. The proportionality constant in this equation is the permittivity or dielectric constant ε divided by Faraday's constant F. The value of this proportionality constant is quite small, so that it is usually permissible to set the charge density equal to zero. This, of course, does not mean that Laplace's equation is satisfied by the potential:

$$\nabla^2\Phi = 0 \quad . \tag{8}$$

(We shall find later under what conditions Laplace's equation is applicable.) Another way of saying the same thing is that F/ε is so large that an appreciable separation of charge would require prohibitively large electric forces. Still another way is that the conductivity is so large that any initial charge density would be neutralized very rapidly or would rapidly flow to the boundaries of the solution.

On the other hand, it is not permissible to neglect the charge density in the electrode double layer since the electric field is indeed very large in this region. In extremely dilute solutions, the charge density may also be appreciable compared to the total ionic concentration. The double layer can legitimately be regarded as part of the interface and not part of the solution. This region is on the order of 10 to 100 angstroms thick.

These four equations (1, 2, 3, and 6) provide a consistent description of transport processes in electrolytic solutions. Note that in order to solve a mass-transfer problem it is necessary to know the convective velocity $\underline{v}$. Thus, it is necessary to work with the equations of fluid mechanics, which I shall not discuss here. It is also necessary to specify carefully the boundary conditions. We shall come to these presently. An understanding of the physical content of the four equations presented above provides a consistent picture of the field and allows one to follow more easily any discussion of the subject and to see what approximations are being made.

We can also obtain physical insight by considering the validity of these equations themselves. The validity of the electroneutrality equation has already been considered. We conclude that it is an accurate approximation. The current equation and the expression of conservation of matter are valid physical laws subject to little dispute. However, the uncertainty is in the rate processes, in the expression of the production rate and the flux. The production rate involves chemical kinetics, for which the rate expressions are not predictable or general. Fortunately, the production rate can be ignored in most electrochemical systems. We have attempted to express the flux by the first equation, but even this breaks down in concentrated solutions for a number of reasons.

As a point of historical perspective, it should be noted that these equations were known in 1890. Usually the convective term did not appear in the flux equation. It was also known that the flux equation was valid only in dilute solutions. At that time its breakdown was attributed to incomplete dissociation of the electrolyte.

The flux equation breaks down, first of all, because we have not specified the fluid velocity. In a concentrated solution it is not just the solvent velocity which contributes to the average velocity. Furthermore, this flux equation incorrectly defines the transport properties; in fact, it defines an incorrect number of transport properties. This equation considers the interaction or friction force of an ion with the solvent and essentially neglects interactions with the other ions. Finally, the correct driving force for diffusion and migration is the gradient of an electrochemical potential, and any decomposition of this into ∇c_i and $c_i \nabla \Phi$ is unnecessary.

We can avoid these difficulties by using the multicomponent diffusion equation

$$c_i \nabla \mu_i = RT \sum_j \frac{c_i c_j}{c_T \mathcal{D}_{ij}} (\underline{v}_j - \underline{v}_i) \quad , \tag{9}$$

where μ_i is the electrochemical potential. Here $c_i \nabla \mu_i$ is the driving force for diffusion and migration, and it is equated to the interaction or friction force between species i and all other species j. This friction force is proportional to the difference of velocities $\underline{v}_j - \underline{v}_i$, and the question of the reference velocity is thereby avoided. For comparison, the first flux equation can be expressed as

$$c_i (\underline{v}_i - \underline{v}) = \underline{N}_i - \underline{v} c_i = -z_i u_i F c_i \nabla \Phi - D_i \nabla c_i \quad . \tag{10}$$

The left side shows an interaction between the species and the fluid; the right side shows the driving forces for diffusion and migration and the corresponding transport properties. The multicomponent diffusion equation is somewhat more general than the first flux equation because it relates the driving force to a linear combination of resistances instead of just to one resistance, that with the solvent.

A similar multicomponent diffusion equation is necessary even for concentrated solutions of nonelectrolytes, so we shouldn't feel too bad about this one.

Figure 1 shows multicomponent diffusion coefficients for the system $KCl-H_2O$ calculated from literature values of the conductivity, diffusion coefficient, and transference number. $\mathscr{D}_{0+}$ and $\mathscr{D}_{0-}$, representing interactions of the ions with the solvent, are relatively independent of concentration. Because of the strong electric interaction between ions, $\mathscr{D}_{+-}$ shows a strong concentration dependence.

The multicomponent diffusion equation is essential to the understanding of basic transport processes, but it is not widely used in the analysis of electrochemical systems for a number of reasons:

1. It complicates the analysis. Even the flux equation for dilute solutions is frequently simplified in applications.
2. All the requisite transport properties are not known over a range of concentrations for any solution of two or more electrolytes.
3. The flux equation for dilute solutions frequently gives an adequate account of the observed behavior of an electrochemical system.

Let us now examine further the meaning and application of the basic transport relations. Let us expand the expression for the current density in the solution in terms of the species fluxes.

$$\underline{i} = -F^2 \nabla\Phi \sum_i z_i^2 u_i c_i - F \sum_i z_i D_i \nabla c_i + F\underline{v} \sum_i z_i c_i \quad . \qquad (11)$$

By virtue of electroneutrality, the last term on the right is zero, which is equivalent to saying that bulk motion of a fluid with no charge density can contribute nothing to the current density. When there are no

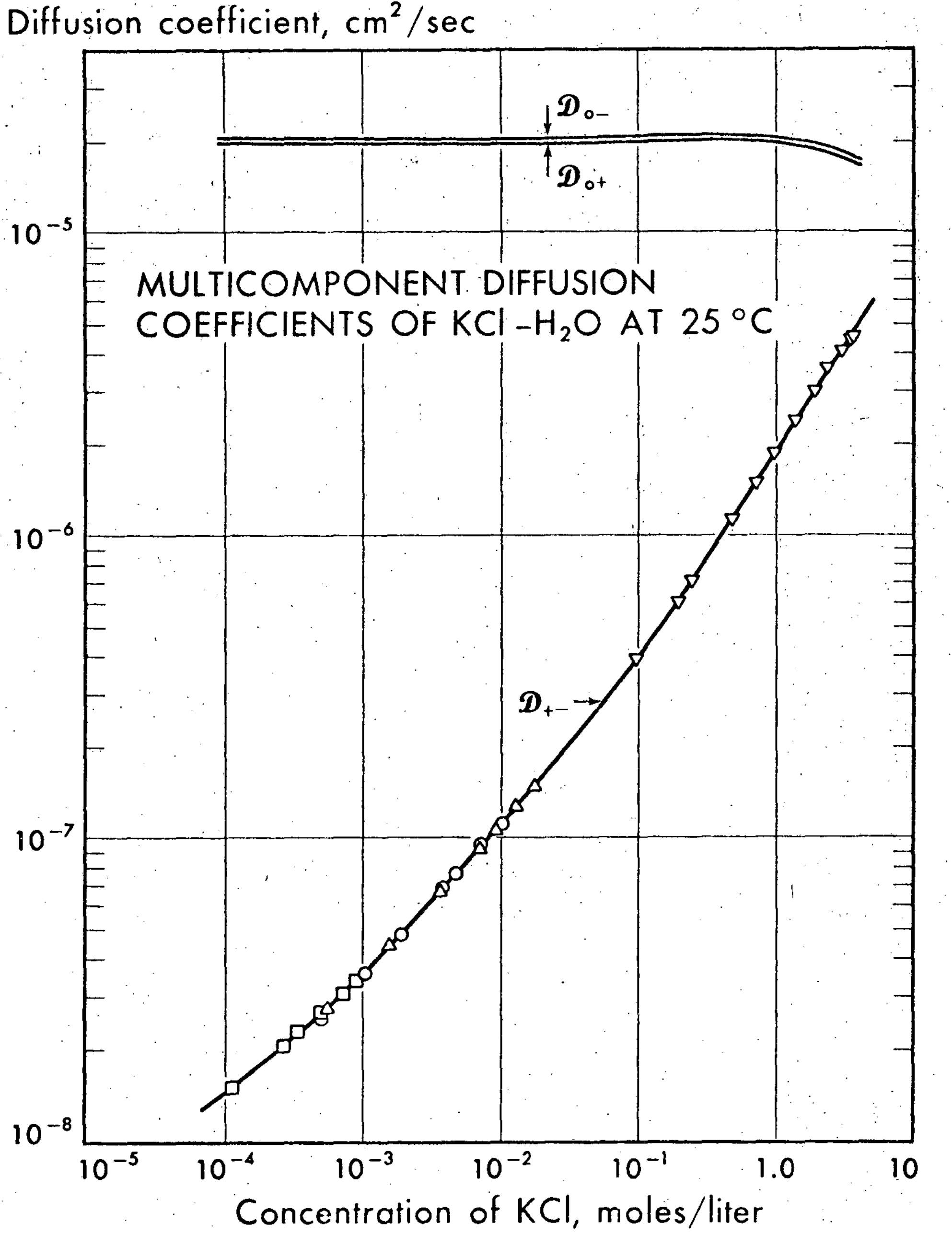


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Figure 1. Multicomponent diffusion coefficients of KCl-H_2O at 25°C.

concentration variations in the solution, this equation reduces to the common concept of electrolytic conductance.

$$\underline{i} = -\kappa\nabla\Phi \quad , \tag{12}$$

where

$$\kappa = F^2\sum_i z_i^2 u_i c_i \tag{13}$$

is the conductivity of the solution. This is an expression of Ohm's law, valid for electrolytes in the absence of concentration gradients.

We may say that the current carried by species j is

$$t_j\underline{i} = -F^2 z_j^2 u_j c_j \nabla\Phi = \frac{z_j^2 u_j c_j}{\sum_i z_i^2 u_i c_i}\,\underline{i} \quad , \tag{14}$$

where

$$t_j = \frac{z_j^2 u_j c_j}{\sum_i z_i^2 u_i c_i} \tag{15}$$

is the fraction of the current carried by species j and is also known as the transference number.

The conductivity and the transference number are additional transport properties, defined in terms of the ionic mobilities introduced earlier. These transport properties have relevance in solutions of varying composition, but Ohm's law is valid and the transference number has the physical meaning of the fraction of the current carried by an ionic species only in the absence of concentration gradients.

It is a physical law of nature that electric charge is conserved, and this fact is already built into the basic transport relations. Multiplication of the material balance equation by z_iF and addition over species yields

$$\nabla \cdot \underline{i} = 0 \quad . \tag{16}$$

Since the charge density is zero, it cannot change with time, and it is appropriate that the divergence of the charge flux or current density should be zero. Insertion of Ohm's law

$$\underline{i} = -\kappa \nabla \Phi \tag{17}$$

yields Laplace's equation for the potential

$$\nabla^2 \Phi = 0 \tag{18}$$

if the conductivity is independent of position. Thus, Laplace's equation holds in a region of uniform composition. This justification of Laplace's equation is considerably different from the statement that electroneutrality implies Laplace's equation for the potential. The development of Laplace's equation provides the basis for the determination of the distributions of current and potential in some corroding systems, which will be considered later in more detail.

For the reaction of uncharged and minor ionic species from a solution containing excess supporting electrolyte, it should be permissible to neglect the contribution of ionic migration to the flux of the reacting ions, giving

$$\underline{N}_i = -D_i \nabla c_i + \underline{v} c_i \quad . \tag{19}$$

Substitution into the material balance gives the equation of convective diffusion (in the absence of homogeneous reactions).

$$\frac{\partial c_i}{\partial t} + \underline{v}\cdot\nabla c_i = D_i\nabla^2 c_i \quad . \tag{20}$$

A similar equation applies to convective heat transfer and convective mass transfer in non-electrolytic solutions. Since these fields have been studied in detail, it is possible to apply many results to electrochemical systems which obey this equation. This will occupy our attention in the next part of this paper.

It should be pointed out that mass transfer in a solution of a single electrolyte also obeys the equation of convective diffusion. For the two ions we have

$$\frac{\partial c}{\partial t} + \underline{v}\cdot\nabla c = z_+u_+F\nabla\cdot(c\nabla\Phi) + D_+\nabla^2 c \quad , \tag{21}$$

$$\frac{\partial c}{\partial t} + \underline{v}\cdot\nabla c = z_-u_-F\nabla\cdot(c\nabla\Phi) + D_-\nabla^2 c \quad , \tag{22}$$

where $c = c_+/\nu_+ = c_-/\nu_-$ and ν_+ and ν_- are the numbers of moles of cations and anions per mole of electrolyte. Elimination of $\nabla\cdot(c\nabla\Phi)$ between these two equations yields

$$\frac{\partial c}{\partial t} + \underline{v}\cdot\nabla c = D\nabla^2 c \quad . \tag{23}$$

This is the equation of convective diffusion, with however the diffusion coefficient of the salt

$$D = \frac{z_+u_+D_- - z_-u_-D_+}{z_+u_+ - z_-u_-} \tag{24}$$

appearing rather than an ionic diffusion coefficient. We mention this to bring out the fact that the measurement of the diffusion coefficient of a salt does not yield directly the diffusion coefficient of either ion.

We mentioned earlier that a single driving force, the gradient of the electrochemical potential of a species, is appropriate for diffusion and migration. We are thus led to expect that the ionic mobility and diffusion coefficient are related. The Nernst-Einstein equation provides this relationship

$$D_i = RT\,u_i \quad . \tag{25}$$

We now wish to consider the magnitudes of the transport properties which have been introduced. Table 1 gives an indication of ionic diffusion coefficients and mobilities. Ionic mobilities are usually not found directly in the literature; instead one finds ionic equivalent conductances. These are related to ionic mobilities by

$$\lambda_i = |z_i|F^2u_i \quad . \tag{26}$$

The diffusion coefficients were then calculated with the Nernst-Einstein relation

$$D_i = \frac{RT\lambda_i}{|z_i|F^2} \quad . \tag{27}$$

Table 1. Values of equivalent conductances and diffusion coefficients of selected ions at infinite dilution at 25°C.

ion	z_i	λ_i° $mho\text{-}cm^2/equiv$	$D_i x10^5$ cm^2/sec	ion	z_i	λ_i°	$D_i x10^5$
H^+	1	349.8	9.312	OH^-	-1	197.6	5.260
Li^+	1	38.69	1.030	Cl^-	-1	76.34	2.032
Na^+	1	50.11	1.334	Br^-	-1	78.3	2.084
K^+	1	73.52	1.957	I^-	-1	76.8	2.044
NH_4^+	1	73.4	1.954	NO_3^-	-1	71.44	1.902
Ag^+	1	61.92	1.648	HCO_3^-	-1	41.5	1.105
Tl^+	1	74.7	1.989	HCO_2^-	-1	54.6	1.454
Mg^{++}	2	53.06	0.7063	$CH_3CO_2^-$	-1	40.9	1.089
Ca^{++}	2	59.50	0.7920	$SO_4^=$	-2	80	1.065
Sr^{++}	2	59.46	0.7914	$Fe(CN)_6^{3-}$	-3	101	0.896
Ba^{++}	2	63.64	0.8471	$Fe(CN)_6^{4-}$	-4	111	0.739
Cu^{++}	2	54	0.72	IO_4^-	-1	54.38	1.448
Zn^{++}	2	53	0.71	ClO_4^-	-1	67.32	1.792
La^{+++}	3	69.5	0.617	BrO_3^-	-1	55.78	1.485
$C_o(NH_3)_6^{+++}$	3	102.3	0.908	HSO_4^-	-1	50	1.33

We see that most ionic diffusion coefficients are about 1 or 2 x 10^{-5} cm^2/sec. Exceptions are hydrogen ions and hydroxyl ions for which D_i values are 9.3 and 5.3x10^{-5} cm^2/sec.

The equivalent conductance of a single electrolyte is the sum of the values for the two ions

$$\Lambda = \lambda_+ + \lambda_- \quad . \tag{28}$$

The value of Λ will thus be about 100 mho-cm^2/equiv except for acids and bases. The conductivity will be given by multiplying Λ by the equivalent concentration, but this should be in equivalents per cubic centimeter to have consistent units. Thus, the conductivity of sea water will be about 0.05 ohm^{-1}-cm^{-1}. The transference number of an ion in a binary solution will be

$$t_+ = 1 - t_- = \frac{\lambda_+}{\lambda_+ + \lambda_-} \tag{29}$$

and will be close to 0.5 except for acids and bases where t_+ may be 0.8 or 0.2. For solutions with an excess of inert electrolyte, the transference number of a minor ionic species will be proportional to its concentration and inversely proportional to the concentration of the supporting electrolyte and hence will be small.

A rough guide to the temperature dependence is provided by the relationship

$$D_i \mu / T = \text{constant}, \tag{30}$$

where μ is the viscosity of the solution. Thus, ionic diffusion coefficients and conductivities can vary by 2 to 3 percent per degree C. This is a fairly strong temperature dependence.

Mass transport controlled phenomena

In an electrochemical system, many processes occur simultaneously, and the treatment of such problems involves consideration of the ohmic potential drop, concentration changes near electrodes, and the kinetics of the heterogeneous electrode reaction. Application of these principles has followed two main courses.

There are systems where the ohmic potential drop can be neglected. The current distribution is then determined by the same principles which apply to heat transfer and non-electrolytic mass transfer. This usually involves systems operated at the limiting current with an excess of supporting electrolyte. Let us call these "convective-transport problems."

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

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

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

In porous electrodes, convection may not be present, but it is usually necessary to consider the ohmic potential drop, concentration variations, and electrode kinetics. Most treatments, adopt a macroscopic model which does not take account of the detailed, random geometry of the porous structure. Results of potential theory are then not applicable since Laplace's equation does not hold.

In some cases it may be possible to take into account the concentration dependence of the transport properties.

Let us now turn our attention to convective-transport problems. As we have said before, for the reaction of minor ionic species in a solution containing excess supporting electrolyte, it should be permissible to neglect the contribution of ionic migration to the flux of the reacting ions, giving

$$\underline{N}_i = -D_i \nabla c_i + \underline{v} c_i \quad . \tag{31}$$

Substitution into the material balance gives the equation of convective diffusion:

$$\frac{\partial c_i}{\partial t} + \underline{v} \cdot \nabla c_i = D_i \nabla^2 c_i \quad . \tag{32}$$

A similar equation applies to convective heat transfer and convective mass transfer in nonelectrolytic solutions. Since these fields have been studied in detail, it is possible to apply many results to electrochemical systems which obey this equation.

Essential to the understanding of convective-transport problems is the concept of the diffusion layer. Frequently, due to the small value of the diffusion coefficient, the concentrations differ significantly from their bulk values only in a thin region near the surface of an electrode (see figure 2). In this region the velocity is small, and diffusion is important to the transport process. The thinness of this region permits a simplification in the analysis, but it is erroneous to treat the diffusion layer as a stagnant region. Figure 3 shows the concentration profile in the diffusion layer, with the electrode surface at the left. Far from the surface, convective transport dominates, while at the surface itself there is only diffusion.

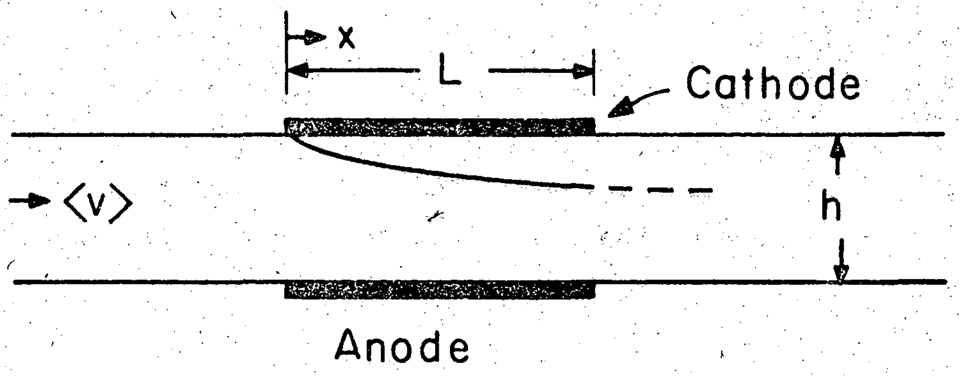

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Figure 2. Plane electrodes in the walls of a flow channel.

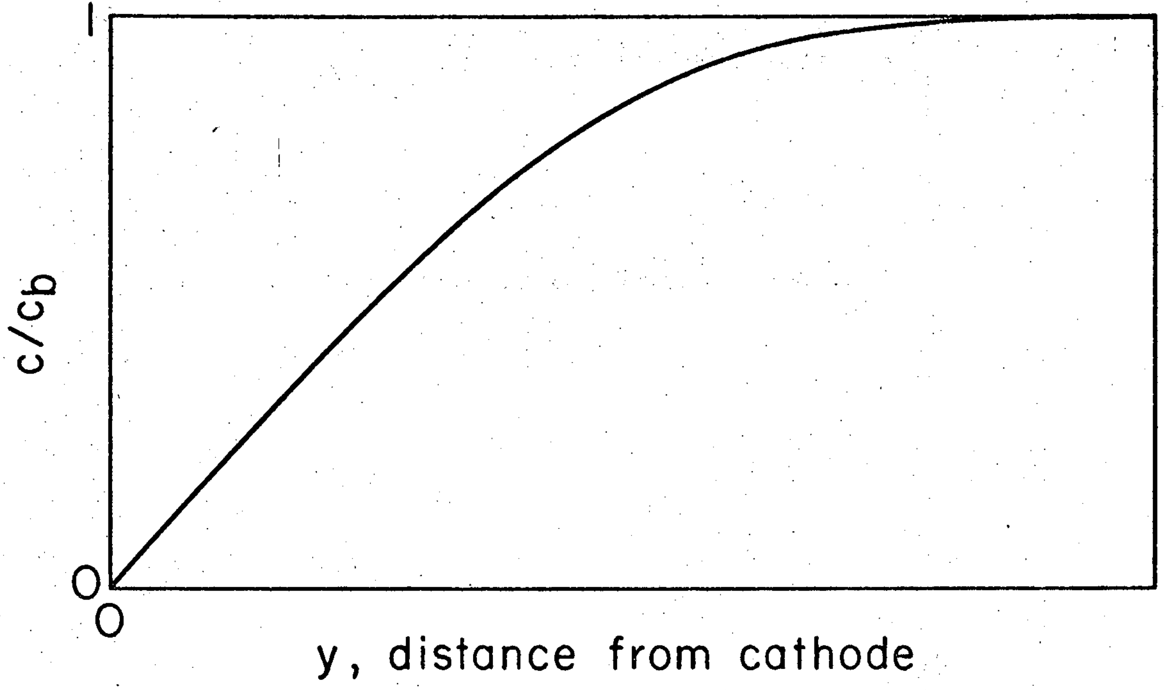

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Figure 3. Concentration profile in the diffusion layer.

To illustrate the current distribution obtained in this type of problem, consider two plane electrodes (figure 2) of length L and separated by a distance h and which form parts of the walls of a flow channel with otherwise insulating walls. For laminar flow from left to right, with an average velocity $\langle v \rangle$, the limiting current density is highest, even infinite, at the left edge of the electrode where fresh solution is brought in contact with the electrode. The diffusion layer is sketched in exaggerated form on figure 2 and starts with a zero thickness, becoming thicker farther downstream.

By the limiting current we mean the highest possible rate of mass transfer to the surface. This corresponds to a zero concentration of the reactant along the entire length of the electrode. The limiting current manifests itself in the current-potential curve for the electrode. This is sketched in figure 4. An increasing potential difference between the electrodes in a cell results in an increasing current. However, as the concentration of the reactant approaches zero at the electrode surface, a further increase in potential can no longer produce an increase in current. Eventually, the electrode potential becomes so great that a different process, say the evolution of hydrogen, begins to occur. This is also sketched on figure 4.

For the system shown in figure 2, the limiting current density decreases with increasing x since the solution in the diffusion layer has already been depleted by the electrode reaction further upstream. The limiting current density distribution is illustrated in figure 5 and is given by

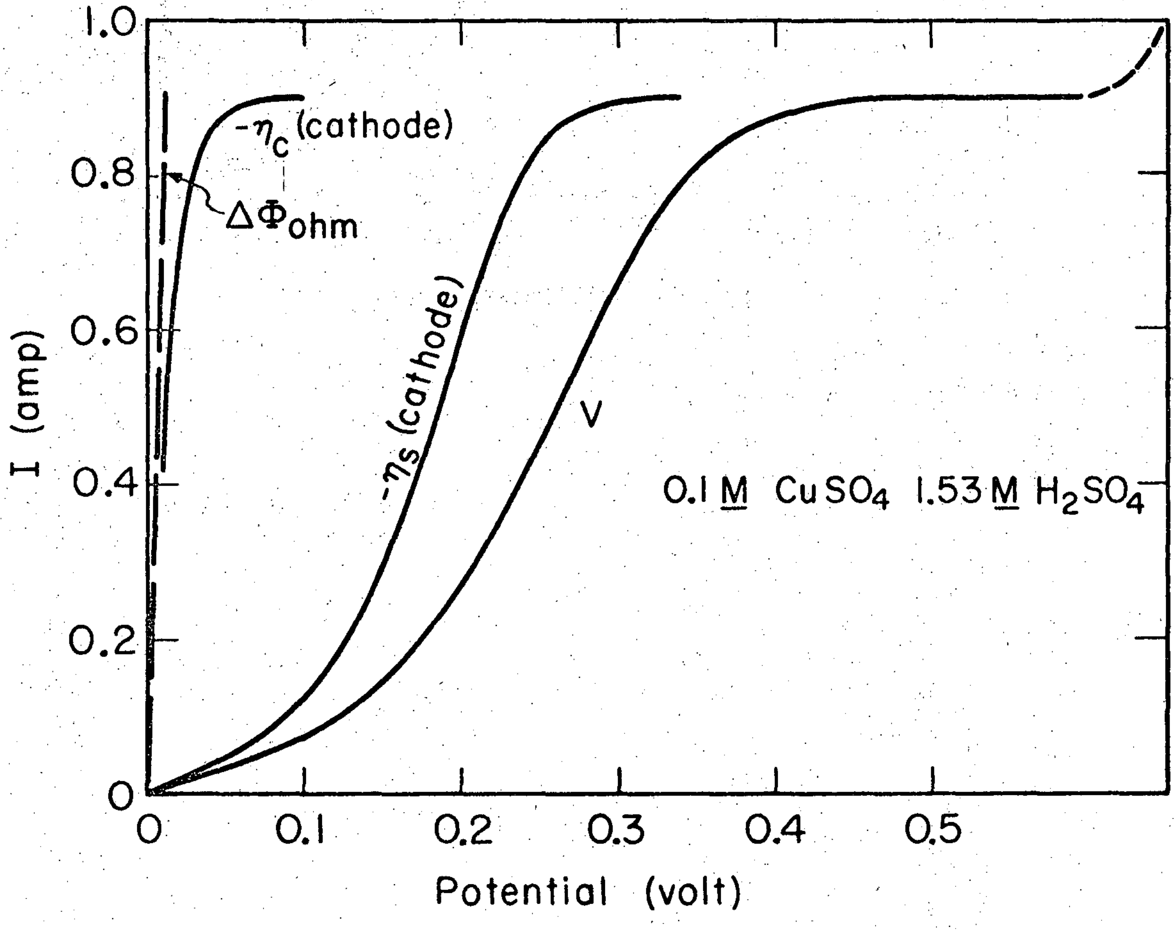

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Figure 4. Current-potential curve for an electrochemical cell.

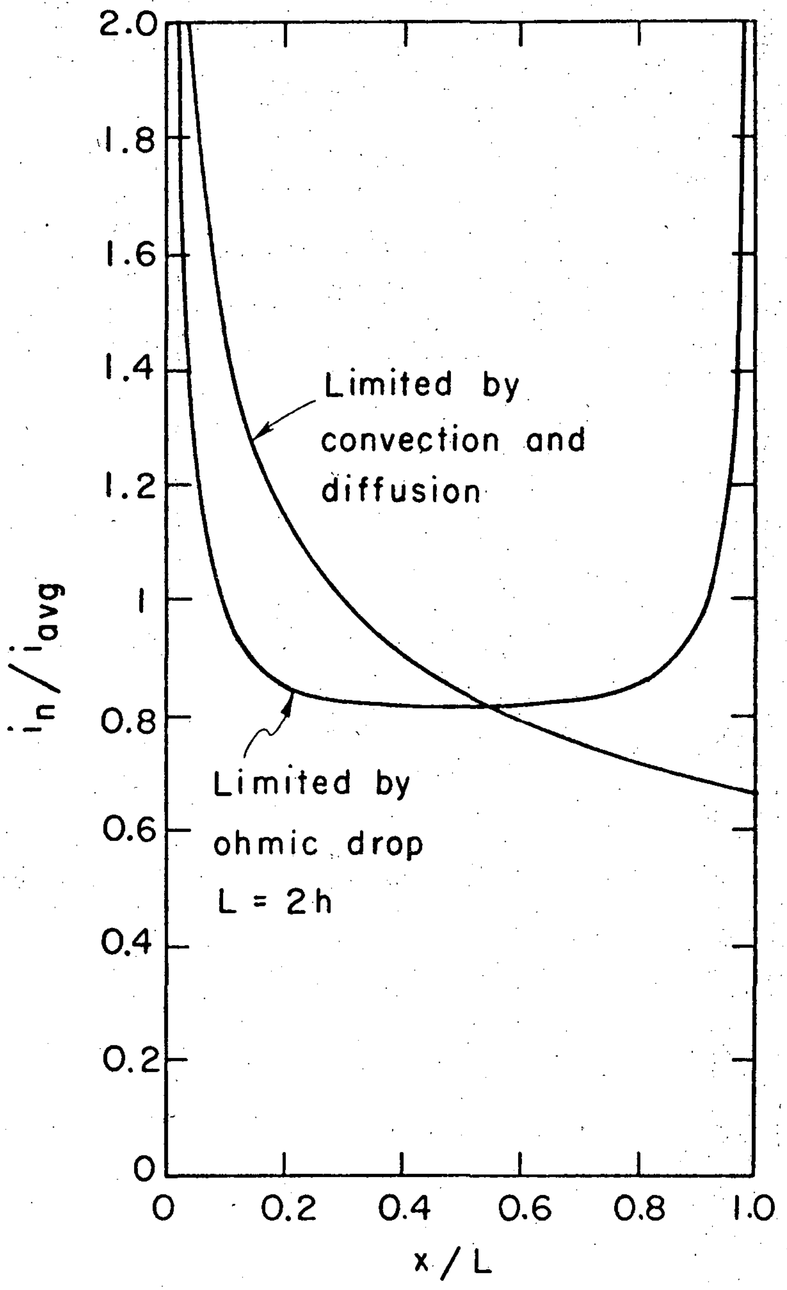

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Figure 5. Current distribution on planar electrodes.

$$i_n = 0.9783 \, \frac{nFD_i c_{i\infty}}{s_i} \left(\frac{\langle v \rangle}{hD_i x}\right)^{1/3} \quad , \tag{33}$$

where $c_{i\infty}$ is the bulk concentration of the limiting reactant, D_i its diffusion coefficient, and n and s_i are the number of electrons transferred and the stoichiometric coefficient of the reactant in the electrode reaction

$$\sum_i s_i M_i^{z_i} \rightarrow ne^- \quad . \tag{34}$$

This distribution, limited by convection and diffusion, on the cathode is independent of the placement and size of the anode as long as the velocity profile is not disturbed. Later it will be instructive to compare this current distribution with that which would be obtained when the ohmic potential drop in the solution is controlling, as developed in the next section.

In the diffusion layer, at steady state, the equation of convective diffusion reduces to the following boundary layer form

$$v_x \frac{\partial c_i}{\partial x} + v_y \frac{\partial c_i}{\partial y} = D_i \frac{\partial^2 c_i}{\partial y^2} \tag{35}$$

or

$$\frac{\partial c_i v_x}{\partial x} + \frac{\partial c_i v_y}{\partial y} = D_i \frac{\partial^2 c_i}{\partial y^2} \quad , \tag{36}$$

where y is the distance perpendicular to the electrode and x is the distance along the electrode measured from its leading edge. I mention this mainly to discuss the mechanism of turbulent mass transport. Turbulent flow is characterized by rapid and random fluctuations of the velocity, pressure, and concentrations. Usually one is interested only in average values of these quantities. However, the average of a nonlinear quantity like $c_i v_y$, which enters into the above equation, cannot be expressed simply in terms of the average concentration and velocity component. Let

$$c_i = \overline{c}_i + c_i' \text{ and } v_y = \overline{v}_y + v_y' \quad , \tag{37}$$

where $\overline{c}_i$ and $\overline{v}_y$ are the average values and c_i' and v_y' are fluctuating parts whose averages are zero. Hence

$$\begin{aligned} \overline{c_i v_y} &= \overline{(\overline{c}_i + c_i')(\overline{v}_y + v_y')} \\ &= \overline{\overline{c}_i \overline{v}_y} + \overline{\overline{c}_i v_y'} + \overline{c_i' \overline{v}_y} + \overline{c_i' v_y'} \\ &= \overline{c}_i \overline{v}_y + \overline{c}_i \overline{v_y'} + \overline{c_i'} \overline{v}_y + \overline{c_i' v_y'} \\ &= \overline{c}_i \overline{v}_y + \overline{c_i' v_y'} \quad . \end{aligned} \tag{38}$$

The term $\overline{c_i' v_y'}$ is not zero and represents the turbulent contribution to the flux of species i. This turbulent flux is, in a sense, similar to the ordinary diffusion flux $-D_i \partial c_i / \partial y$. Both arise from fluctuations about average values, either on a molecular level or on the level of the turbulent fluctuations. Consequently, the turbulent transport term $\overline{c_i' v_y'}$ is frequently written in terms of an "eddy diffusivity" $D^{(t)}$:

$$\overline{c_i' v_y'} = -D^{(t)} \frac{\partial \overline{c}_i}{\partial y} \quad . \tag{39}$$

However, the eddy diffusivity is not a molecular parameter like the diffusion coefficient, and its value depends on the local level of turbulence. In particular, it depends on the distance from a solid wall and goes to zero at the wall itself since the level of turbulence is damped near a wall. This means that at the wall itself the flux is still given by

$$N_{iy} = -D_i \frac{\partial \bar{c}_i}{\partial y} \text{ at } y = 0 \quad , \tag{40}$$

but the turbulence in the diffusion layer can lead to a considerably enhanced overall rate of mass transfer. The turbulence makes the diffusion layer thinner.

After averaging, the boundary layer form of the equation of convective diffusion becomes

$$\bar{v}_x \frac{\partial \bar{c}_i}{\partial x} + \bar{v}_y \frac{\partial \bar{c}_i}{\partial y} = \frac{\partial}{\partial y} (D_i + D^{(t)}) \frac{\partial \bar{c}_i}{\partial y} \quad . \tag{41}$$

One cannot go far in the study of convective-transport problems without realizing the value of dimensionless correlations based on dimensional analysis. They allow the behavior of similar systems to be expressed in the most economical manner. The object of our study here is the limiting current density. This is expressed in dimensionless form in terms of the Nusselt number

$$Nu(x) = -\frac{N_i d_e}{c_\infty D_i} = \frac{s_i d_e i}{nFD_i c_\infty} \quad , \tag{42}$$

where c_∞ is the bulk concentration of the limiting reactant and d_e is a characteristic length of the system. For the present case of a flow channel with parallel walls, d_e is taken to be equal to 2h.

Clearly, the Nusselt number or dimensionless limiting current should depend on the degree of stirring or convection, also expressed in dimensionless form. For this purpose we use the Reynolds number

$$Re = \langle v \rangle d_e/\nu \quad , \qquad (43)$$

where ν is the kinematic viscosity of the fluid. The value of the Reynolds number determines the nature of the flow. For the channel, laminar flow is possible for Reynolds numbers less than 2000 or 3000. At higher Reynolds numbers, turbulent flow prevails.

The Nusselt number can also depend on the physical properties of the fluid, again expressed in dimensionless ratios. Relevant here is the Schmidt number

$$Sc = \nu/D_i \quad , \qquad (44)$$

the ratio of the kinematic viscosity to the diffusion coefficient. The value of the Schmidt number determines the thickness of the diffusion layer relative to the nature of the hydrodynamic flow. For aqueous electrolytic solutions, the Schmidt number will generally be 1000 or higher. High Schmidt numbers favor thin diffusion layers, and still further simplifications are possible in the boundary layer form of the equation of convective diffusion. However, we shall not go into these ramifications here.

For turbulent flow in the channel, the limiting current density will become relatively uniform a short distance from the edge of the electrode, and the Nusselt number can be expressed as

$$Nu = 0.023\, Re^{0.8}\, Sc^{1/3} \quad , \tag{45}$$

and is independent of the distance from the leading edge. However, within 0.5 to 2 times d_e from the leading edge, the mass-transfer process is not yet fully developed, and the Nusselt number should be expressed for short electrodes as

$$Nu_{avg} = 0.276\, Re^{0.58}\, Sc^{1/3}\, (d_e/L)^{1/3} \quad . \tag{46}$$

An advantage of the dimensionless correlations can be seen at this point. Dimensionless correlations for heat and nonelectrolytic mass transfer are expressed in the same form (with the Prandtl number replacing the Schmidt number for heat transfer) and can be applied directly in electrochemical systems. The above equation for fully developed mass transfer was developed by Chilton and Colburn in 1934 from the analysis of heat-transfer data.

The rotating disk electrode is of considerable interest in fundamental studies of electrochemistry since its hydrodynamic characteristics in laminar flow are well known and the limiting current density is uniform on the surface of the disk. One usually has a disk electrode embedded in a large insulating plane. Rotation of the disk causes a swirling of the fluid. Fluid is thrown out along the radius and an axial flow toward the disk convects fresh reactant to the electrode. (See figure 6.) The limiting current density in laminar flow is given by

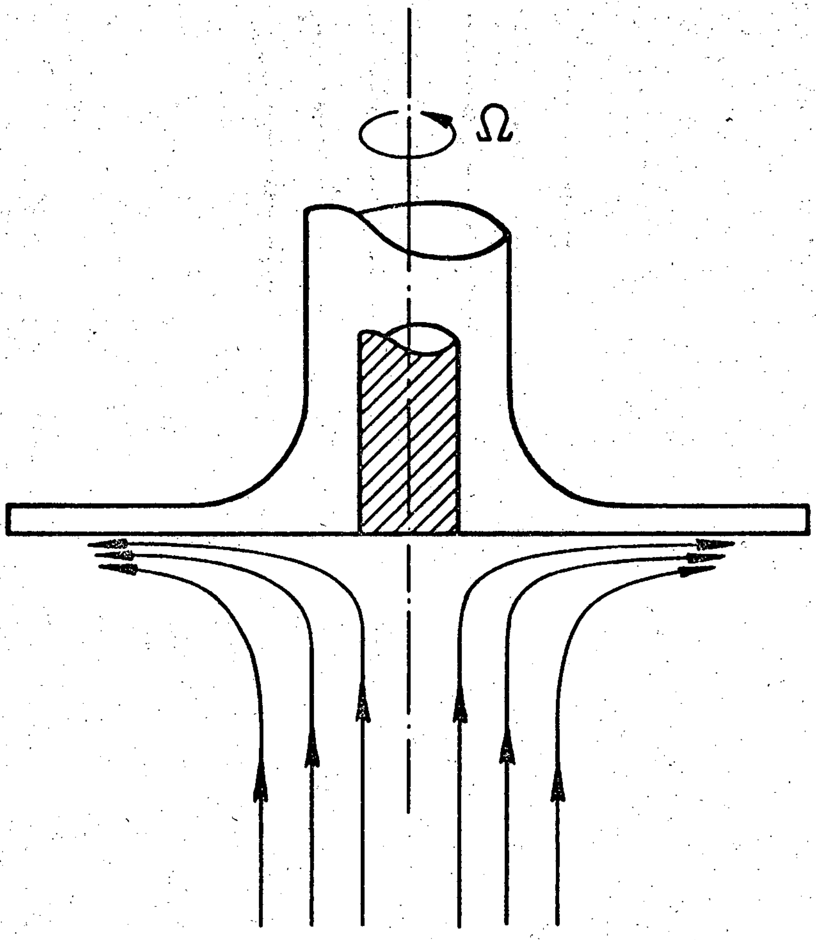

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Figure 6. Rotating disk electrode.

$$i_n = 0.62048 \frac{nFc_\infty}{s_i} \sqrt{\Omega\nu} \left(\frac{D_i}{\nu}\right)^{2/3} . \qquad (47)$$

The flow becomes turbulent for a Reynolds number $Re = r^2\Omega/\nu$ on the order of 10^5. However, the flow in the center of the disk remains laminar. The limiting current density is higher in the turbulent region than in the laminar region. Hence a large disk which includes a turbulent region will have a nonuniform limiting current density. Ellison and Cornet[6] provide us with the correlation

$$Nu_{avg} = 0.0117\ Re^{0.896}\ Sc^{0.249} \qquad (48)$$

for the rotating disk in turbulent flow.

In many electrochemical processes no external means of stirring the solution is provided; the convection which exists results from buoyancy effects and the density differences which are produced in the diffusion layer as a consequence of the electrode reaction itself. The stirring which results can be comparable to that in moderate forced convection.

For free convection in laminar flow to a vertical electrode of length L, the limiting current density is

$$i_{avg} = 0.66 \frac{nFD_i c_\infty}{s_i} \left[\frac{g(\rho_\infty - \rho_o)}{\rho_\infty D_i \nu L}\right]^{1/4} , \qquad (49)$$

where g is the gravitational acceleration and $\rho_\infty - \rho_o$ is the density difference between the bulk solution and the electrode surface. We should also like to express this as a dimensionless correlation. To characterize the stirring we no longer use the Reynolds number; instead we use a dimensionless density difference, since this is the driving force for fluid motion in a free convection system. This is expressed as the Grashof number:

$$\mathrm{Gr} = \frac{g(\rho_\infty - \rho_o)L^3}{\rho_\infty \nu^2} \quad . \tag{50}$$

In dimensionless form, the above expression becomes

$$\mathrm{Nu}_{avg} = \frac{s_i L i_{avg}}{nFD_i c_\infty} = 0.66(\mathrm{ScGr})^{1/4} \quad . \tag{51}$$

Here the electrode length enters as the characteristic length in the formation of the Nusselt number.

For turbulent natural convection at a vertical plate,

$$\mathrm{Nu}_{avg} = 0.31 \ (\mathrm{ScGr})^{0.28} \quad . \tag{52}$$

This is applicable in the range $4 \times 10^{13} < \mathrm{ScGr} < 10^{15}$, while the laminar flow equation was obtained for

$$10^4 < \mathrm{ScGr} < 10^{12} \quad . \tag{53}$$

Thus we see that turbulent flow in natural convection results from high values of the Grashof number, just as high values of the Reynolds number favor turbulent flow in forced convection.

For a horizontal, bounded plate with a stabilizing density gradient there is no chance for convection to result. With an adverse density gradient, turbulent flow is more likely than laminar flow, and the limiting current density can be expressed as

$$i_n = 0.19 \frac{nFD_i c_\infty}{s_i} \left[\frac{g(\rho_\infty - \rho_o)}{\rho_\infty \nu D_i}\right]^{1/3} \tag{54}$$

for electrodes with a minimum dimension greater than 2 cm.

Now let us consider the limiting current for transport of oxygen to a steel piling in the sea. Take a diameter of 30 cm, or about 1 ft, a velocity of 50 cm/sec or about 1 knot, and a kinematic viscosity of 10^{-2} cm^2/sec. Then

$$Re = 50x30/10^{-2} = 1.5x10^5. \tag{55}$$

From correlations for heat and mass transfer past a cylinder[7] we find

$$Nu/Re\ Sc^{1/3} \approx 0.003 \text{ at } Re = 1.5x10^5 \quad . \tag{56}$$

Take the diffusion coefficient of oxygen in sea water to be about $2x10^{-5}$ cm^2/sec, so that Sc = 500. Then

$$\begin{aligned} Nu &= 0.003x1.5x10^5x10/2^{1/3} = 3560 \\ &= d_e s_i i_L / nFD_i c_{i\infty} \quad . \end{aligned} \tag{57}$$

For $n = 4$ and $c_{i\infty} = 2.33\text{x}10^{-7}$ mole/cm^3, the average limiting current density is

$$i_L = 3560\text{x}4\text{x}10^5\text{x}2\text{x}10^{-5}\text{x}2.33\text{x}10^{-7}/30 = 0.219 \text{ mA/cm}^2 \quad . \tag{58}$$

The total limiting current for a 20 foot piling is thus about

$$I = 0.219\text{x}10^{-3}\text{x}\pi\text{x}30\text{x}20\text{x}30 = 12.4 \text{ A}. \tag{59}$$

This is the total current which would be needed for cathodic protection. One might also wish to consider the distribution of this current. Around the circumference it would be expected to look like that sketched in figure 7, the distance from the circle to the curve representing the magnitude of the local limiting current density as a function of the angular position. If cathodic protection were not supplied, one might expect the piling to corrode at the rate corresponding to equation 59, with the anodic current supplied by the reaction

$$Fe \rightarrow Fe^{++} + 2e^- \quad .$$

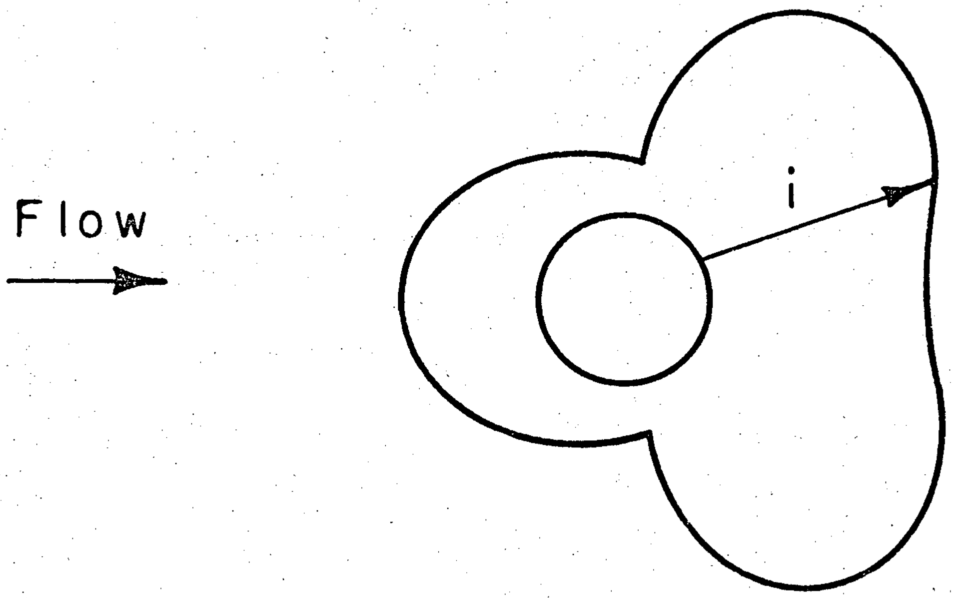

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Figure 7. Limiting current distribution around a cylinder at high Reynolds number.

Distribution of current and potential

In the preceding section, we considered the distribution of reaction rates in systems where migration effects could be ignored. Now let us turn our attention to the other limiting case where concentration variations in the solution can be ignored. In this case the current density is given by Ohm's law

$$\underline{i} = -\kappa\nabla\Phi \quad , \tag{60}$$

and the potential distribution satisfies Laplace's equation

$$\nabla^2\Phi = 0 \quad . \tag{61}$$

On insulating surfaces, the boundary condition is that the normal component of the current density is zero,

$$i_y = 0 \quad , \tag{62}$$

which implies that

$$\partial\Phi/\partial y = 0 \text{ at } y = 0 \quad . \tag{63}$$

On electrodes, it is necessary to define the surface overpotential, η_s:

$$\eta_s = V - U^\circ - \Phi_o \text{ at } y = 0 \quad , \tag{64}$$

where V is the electrode potential, Φ_o is the potential in the solution adjacent to the electrode measured with a reference electrode, and U° is the equilibrium potential of the electrode for the reaction being considered, measured relative to the reference electrode.

In corroding systems we want to consider the possibility of several reactions occurring simultaneously. Then, the normal component of the current density is the sum of the currents for the several reactions:

$$i_y = -\kappa \partial \Phi / \partial y = f_1(\eta_{s1}) + f_2(\eta_{s2}) + \cdots \text{ at } y = 0 \quad , \tag{65}$$

where the f's describe the kinetics of the various reactions, relating the current to the surface overpotential. Laplace's equation for the potential must thus be solved in conjunction with these boundary conditions which relate the normal component of the potential gradient to the potentials of the electrodes and the potential in the solution adjacent to the electrodes. The potentials of the electrodes are constant, but the potential in the solution adjacent to an electrode need not be constant since it depends on the local current density.

For a large class of electrode reactions, the current density depends exponentially on the surface overpotential in the following form:

$$f = i_o \left[\exp\left(\frac{\alpha_a F}{RT} \eta_s \right) - \exp\left(- \frac{\alpha_c F}{RT} \eta_s \right) \right] \quad , \tag{66}$$

where i_o is the exchange current density and depends on the concentrations of species adjacent to the electrode. Both α_a and α_c are kinetic parameters called "transfer coefficients."

However, many reactions important in corroding systems exhibit a passivation phenomenon. For large anodic overpotentials, an oxide film is formed, and the dissolution process is suppressed. This behavior is depicted in figure 8. In the passive region the current density can be very small.

We might also mention the current-potential behavior of an electrode which exhibits a limiting current. This is sketched in figure 9. (Compare figure 4.) For large cathodic overpotentials, the rate of the oxygen reaction is determined by the rate of mass transfer of oxygen to the electrode by diffusion and convection, as discussed in the preceding section. Strictly speaking, a limiting-current reaction should not be discussed here since concentration variations in the solution cannot be ignored. However, it is useful for indicating the nature of corrosion processes. The current-potential curve for a passivating reaction is also indicated on figure 9. When the corrosion process is such that the local currents balance, the current density for the anodic process must be equal and opposite to that for the cathodic process, and the corrosion potential is determined accordingly, as shown on figure 9. In this case, if the rate of stirring can be increased so that the limiting current for the oxygen reaction is greater than the maximum current density for the anodic process, then the potential must shift nearly to the oxygen potential, and the anodic process is passivated.

A corroding system in which the current densities are in local balance is not of interest here since no current flows in the solution, and the rate of corrosion is determined by the principles of mass transfer, discussed in the preceding section. The current and potential distributions are of interest when the anodic and cathodic reactions occur on different surfaces, as in cathodic and anodic protection, or on

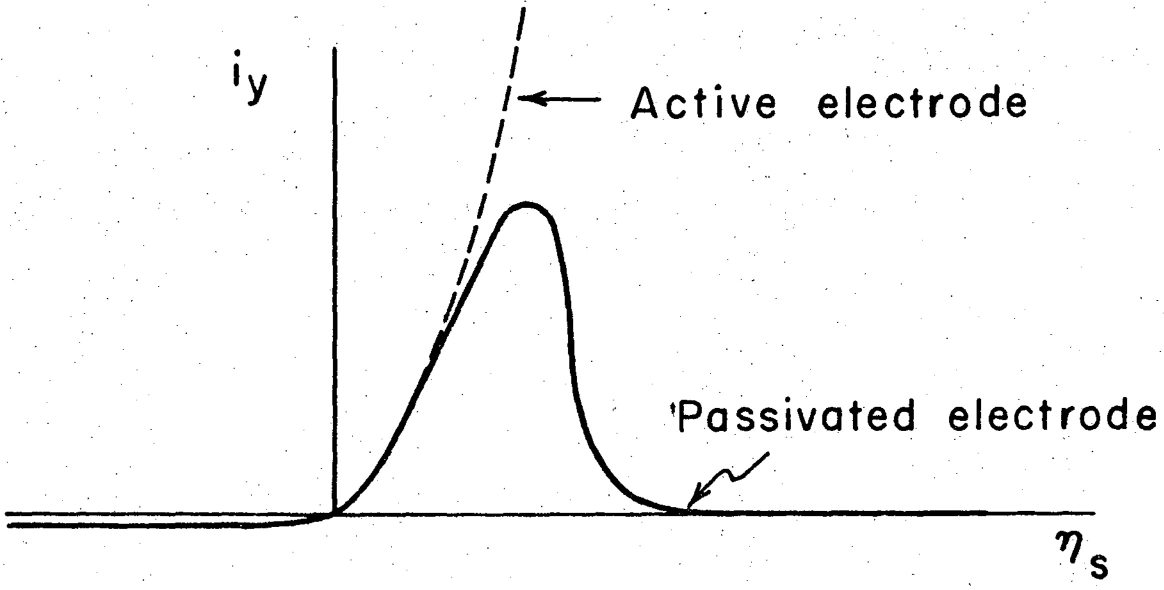

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Figure 8. Current-potential behavior of a passivating electrode, in contrast to a non-passivating electrode.

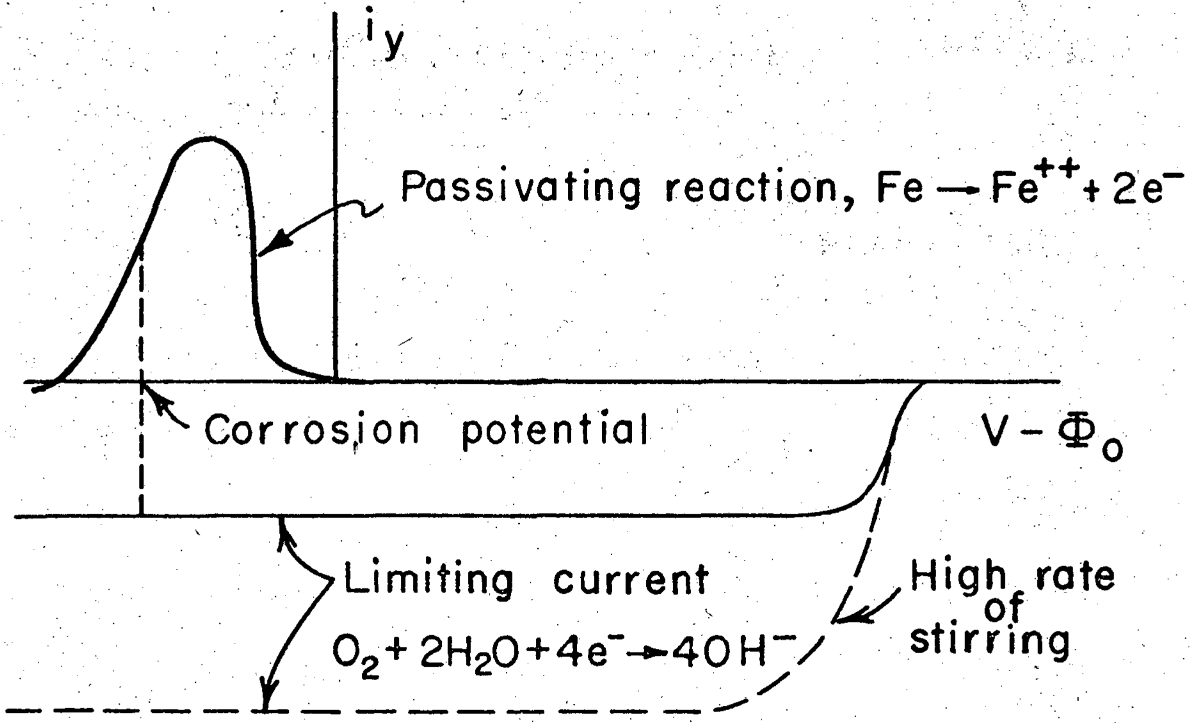

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Figure 9. Reaction exhibiting a limiting current.

different parts of the same surface, as in the case of inclusions and pitting and on a surface formed of dissimilar metals.

Let us consider the principles of current and potential distribution in more detail. Take first the simple case of a rod in the center of a tube. Then the radial component of the current density is

$$i_r = -\kappa \partial\Phi/\partial r \quad , \tag{67}$$

and the total current is

$$I = 2\pi r H i = -2\pi r \kappa H \partial\Phi/\partial r \quad . \tag{68}$$

Since I is a constant, independent of r, this equation can be integrated to yield the potential distribution

$$\Phi - \Phi(r=r_o) = \frac{I}{2\pi\kappa H} \ln \frac{r_o}{r} \quad . \tag{69}$$

Hence, the ohmic potential drop is

$$\Delta\Phi_{ohm} = \frac{I}{2\pi\kappa H} \ln \frac{r_o}{r_i} \quad , \tag{70}$$

and the ohmic resistance is

$$R = \frac{\Delta\Phi_{ohm}}{I} = \frac{1}{2\pi\kappa H} \ln \frac{r_o}{r_i} \quad . \tag{71}$$

These formulas would be useful to estimate the potential difference required to protect cathodically the inside of a pipe by means of a counter electrode consisting of a rod in the center of the pipe. To the ohmic drop one would need to add the magnitudes of the surface overpotentials at the anode and the cathode and the difference in equilibrium potentials for the two electrode reactions.

Next let us use an approximate analysis to indicate how well we could cathodically protect the inside of the pipe by means of a counter electrode at one end of the pipe. The current flowing in a section of the pipe is (see figure 10)

$$\int_0^x i_w 2\pi r_o dx = i_x \pi r_o^2 = -\pi r_o^2 \kappa \frac{\partial \Phi}{\partial x} \quad . \qquad (72)$$

Here i_w is the current density required for protection and is taken to be constant. Integration gives

$$i_w \frac{2\pi r_o x}{\pi r_o^2 \kappa} = -\frac{\partial \Phi}{\partial x} \quad . \qquad (73)$$

A second integration gives the difference in Φ over a distance L from the electrode.

$$\Delta\Phi = \int_0^L \frac{\partial \Phi}{\partial x} dx = \frac{i_w 2}{r_o \kappa} \frac{L^2}{2} = \frac{i_w L^2}{r_o \kappa} \quad . \qquad (74)$$

Now, we want to avoid hydrogen evolution at the end of the pipe near the counter electrode, and yet we want to ensure that the other end of the pipe is still protected. This fixes the maximum value of $\Delta\Phi$ which can be tolerated. Hence, the maximum length of pipe which we can protect in this manner is

$$L = \sqrt{r_o \kappa \Delta\Phi / i_w} \quad . \qquad (75)$$

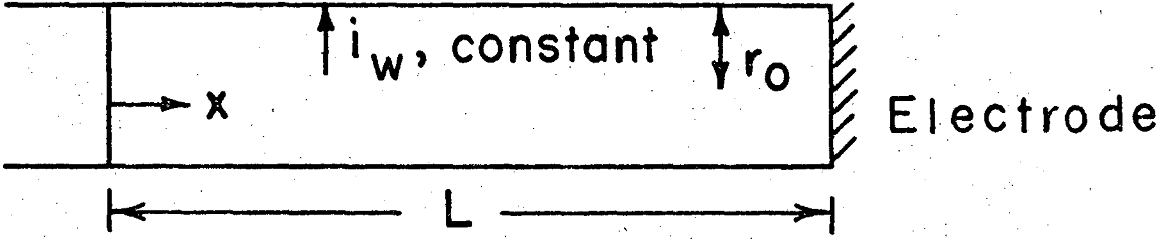

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Figure 10. Cathodic protection of a pipe by means of an electrode placed at the end.

The so-called primary current and potential distributions apply when there is one reaction and the surface overpotential can be neglected altogether. The solution adjacent to an electrode is then taken to be an equipotential surface. Laplace's equation is not trivial to solve, even for relatively simple geometries. We may note that the potential-distribution problem is similar to the problem of the steady temperature distribution in solids, with the potential playing the rôle of the temperature, the current density that of the heat flux, and the electrical conductivity that of the thermal conductivity. Consequently, many solutions can be carried over directly from that field of applied physics. Electrostatics and the irrotational flow of inviscid fluids also provide a wealth of solutions to Laplace's equation.

Consider two electrodes in the walls of a flow channel. This is sketched in figure 11. Here current lines are represented by solid curves and equipotential surfaces by dashed curves. If the drawing were accurate, these two sets of curves would be perpendicular to each other everywhere in the solution. The equipotential lines are close together near the edge of the electrode, and at this point the primary current density is infinite.

The primary current distribution on the electrode was shown in figure 5 for L = 2h and is given by the equation (x being measured here from the center of the electrode)

$$\frac{i_n}{i_{avg}} = \frac{\varepsilon \cosh \varepsilon / K(\tanh^2 \varepsilon)}{\sqrt{\sinh^2 \varepsilon - \sinh^2 (2x\varepsilon/L)}} , \qquad (76)$$

where $\varepsilon = \pi L/2h$ and K(m) is the complete elliptic integral of the first kind. From the complexity of this expression for the current density,

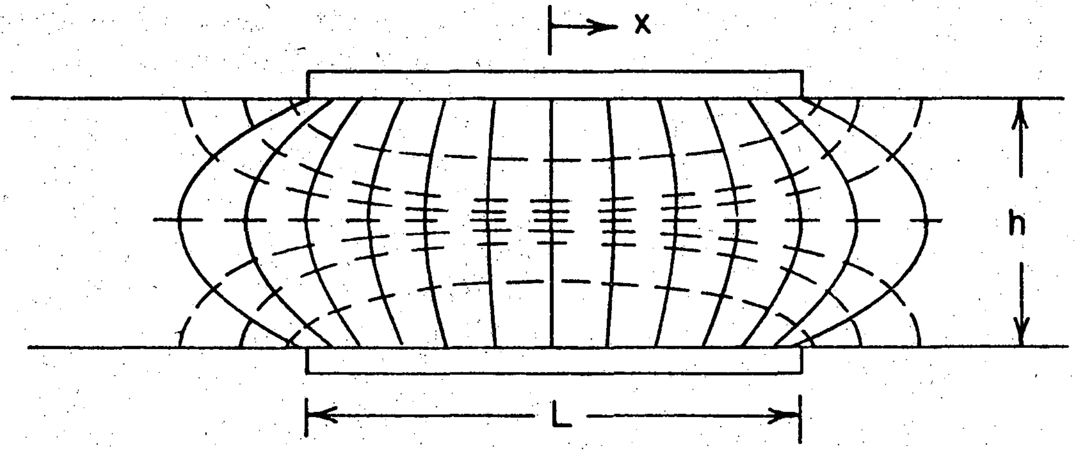

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Figure 11. Two plane electrodes opposite each other in the walls of an insulating flow channel.

one can perhaps appreciate the difficulty involved in obtaining the potential distribution. For contrast, the mass-transfer limiting current distribution for laminar flow, discussed in the preceding section, is also shown on figure 5.

The primary current distribution shown in figure 5 is independent of the flow rate since convection is great enough to eliminate concentration variations, and hence the distribution is symmetric. The current density is infinite at the ends of the electrodes since the current can flow through the solution beyond the ends of the electrodes. This is a general characteristic of primary current distributions. The current density where an electrode meets an insulator is either infinite or zero unless they form a right angle (see figure 12). When the electrode and the insulator lie in the same plane, the primary current density is inversely proportional to the square root of the distance from the edge for positions sufficiently close to the edge. This behavior is exhibited by the above equation for the current density.

The primary current distribution is determined by geometric factors alone. Thus, only the geometric ratios of the cell enter into the parameter ε, but the conductivity of the solution does not enter. The resistance for the cell in figure 11 is

$$R = \frac{1}{\kappa W} \frac{K(1/\cosh^2\varepsilon)}{K(\tanh^2\varepsilon)} \quad , \qquad (77)$$

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

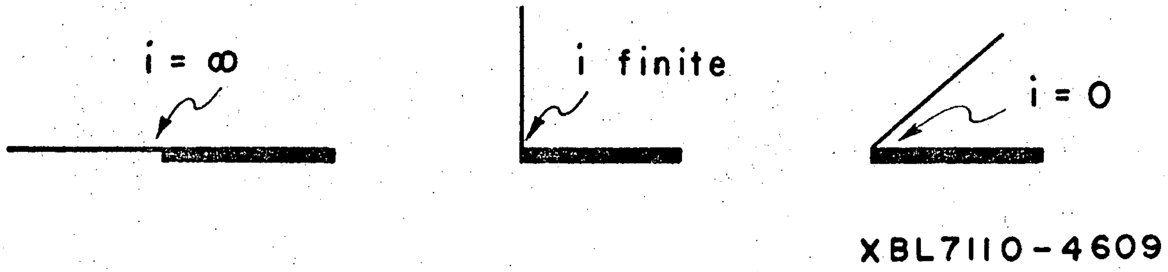

Figure 12. Behavior of the primary current distribution near the edge of an electrode.

For a disk electrode of radius r_o embedded in an infinite insulating plane and with the counter electrode far away (see figure 6), the primary current distribution is given by

$$\frac{i_n}{i_{avg}} = \frac{0.5}{\sqrt{1-(r/r_o)^2}} \quad , \tag{78}$$

and the equipotential and current lines in the solution are shown in figure 13. Again, the equipotential lines are close together near the edge of the electrode, and at this point the current density is infinite, being proportional to the reciprocal of the square root of the distance from the edge near this point. Only geometric factors enter into the current distribution, and the resistance to a hemispherical counter electrode at infinity is

$$R = 1/4\kappa r_o \quad . \tag{79}$$

When slow electrode kinetics are taken into account, the electrolytic solution near the electrode is no longer an equipotential surface, and the result of the calculations is the so-called "secondary current distribution." The general effect of electrode polarization is to make the secondary current distribution more nearly uniform than the primary current distribution, and an infinite current density at the edge of electrodes is eliminated. This can be regarded as the result of imposing an additional resistance at the electrode interface.

In practice, the electrode kinetic equation 66 is frequently replaced by a linear or a logarithmic (Tafel) relation between the surface

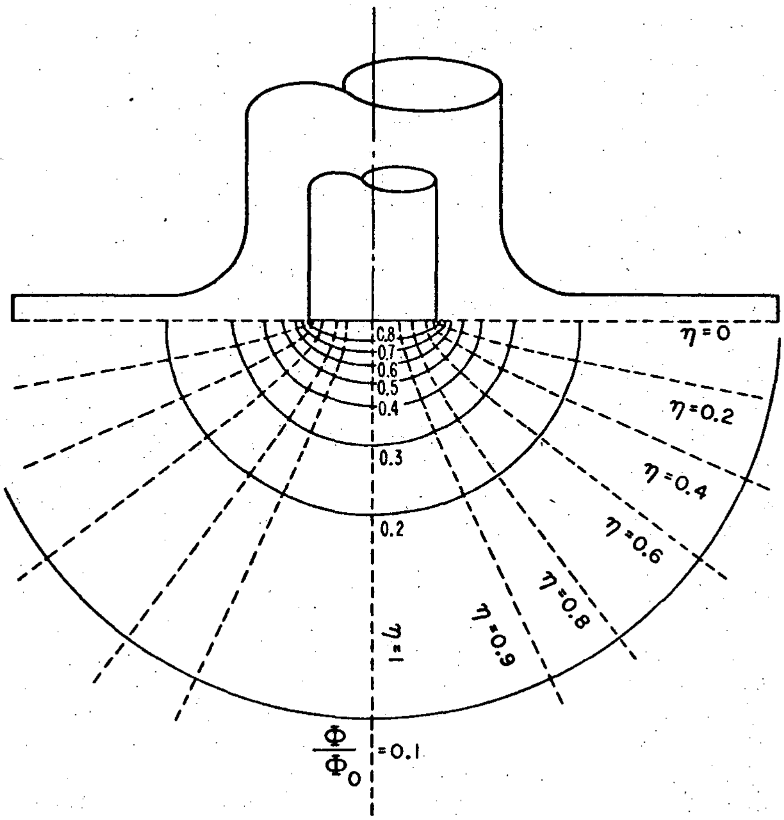

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Figure 13. Potential distribution near an equipotential disk in an insulating plane.

overpotential and the potential derivative at the electrode. In any case, additional parameters besides geometric ratios are required to specify the current distribution. The advantage of the linear and logarithmic approximations is that they add only one new parameter. Thus, fairly realistic cases can be treated without excessive complication.

For sufficiently small surface overpotentials, the kinetic relation for active electrodes can be linearized to read

$$i_n = \left.\frac{di_n}{d\eta_s}\right|_{\eta_s=0} \eta_s = (\alpha_a+\alpha_c)\frac{i_oF}{RT}\eta_s = -\kappa\frac{\partial\Phi}{\partial y} \text{ at } y = 0 \quad . \qquad (80)$$

This provides a linear boundary condition for Laplace's equation. Furthermore, if the range of current densities at the electrode is sufficiently narrow, as one wants to achieve in electroplating, it is, of course, justified to linearize the polarization equation about some other, nonzero value of the surface overpotential. For a disk electrode, the additional parameter for linear polarization is

$$(\alpha_a+\alpha_c)J = (\alpha_a+\alpha_c)\frac{i_oFr_o}{RT\kappa} \quad . \qquad (81)$$

The secondary current distribution for linear polarization on a disk electrode is shown in figure 14. For large values of J, one obtains the primary current distribution. Then the ohmic resistance dominates over the kinetic resistance at the interface. For any finite value of J, the distribution is more nearly uniform and is finite at the edge of disk. For J → 0, the distribution is uniform, but the average current must be

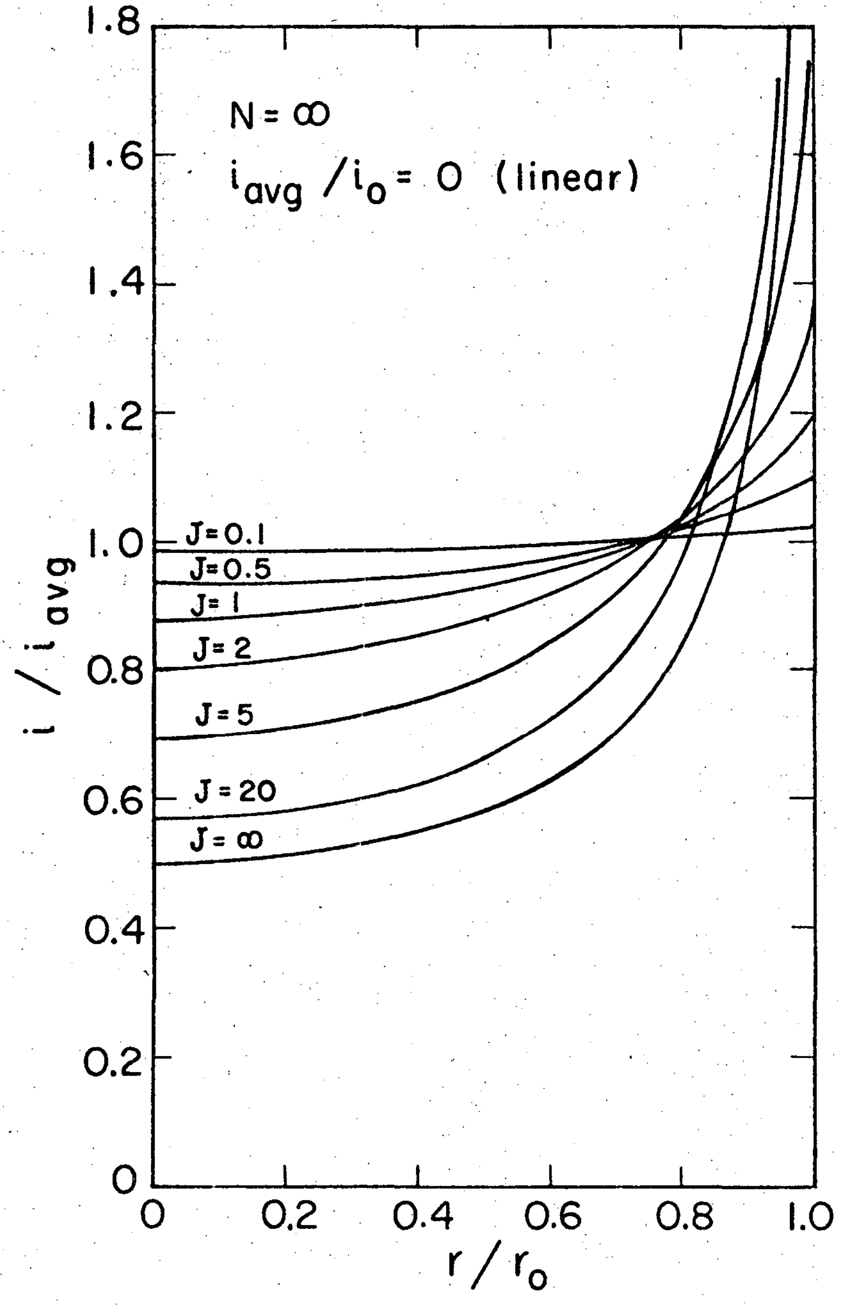

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Figure 14. Secondary current distribution for linear polarization.

small in order for the linear law still to apply. Otherwise, the current distribution is still independent of the magnitude of the current.

The Tafel polarization law, where one of the exponential terms in the kinetic equation 66 for an active electrode is negligible, is also popular in the literature. For a cathodic reaction we have

$$\eta_s = -\frac{RT}{\alpha_c F}\left[\ln(-i_n) - \ln i_o\right] \quad . \qquad (82)$$

This is popular because, while being a fairly realistic polarization law, Tafel's equation introduces a minimum of additional parameters into the problem, as stated before. In addition to depending on the same geometric ratios as the primary current distribution, the current distribution i_n/i_{avg} now depends on the parameter

$$\delta = |i_{avg}|\alpha_c F r_o/RT\kappa \quad , \qquad (83)$$

where the characteristic length r_o is appropriate for the disk electrode. The current distribution now depends on the magnitude of the current, but it is independent of the value of the exchange current density i_o, insofar as Tafel polarization is applicable only for current densities appreciably above the exchange current density.

The secondary current distribution for Tafel polarization on a disk electrode is shown in figure 15. This is similar to the secondary current distribution with linear polarization, but the parameter δ now plays the rôle of the parameter J. In particular, the primary current distribution is still approached as δ becomes large. The parameter for polarization always is proportional to a characteristic length and

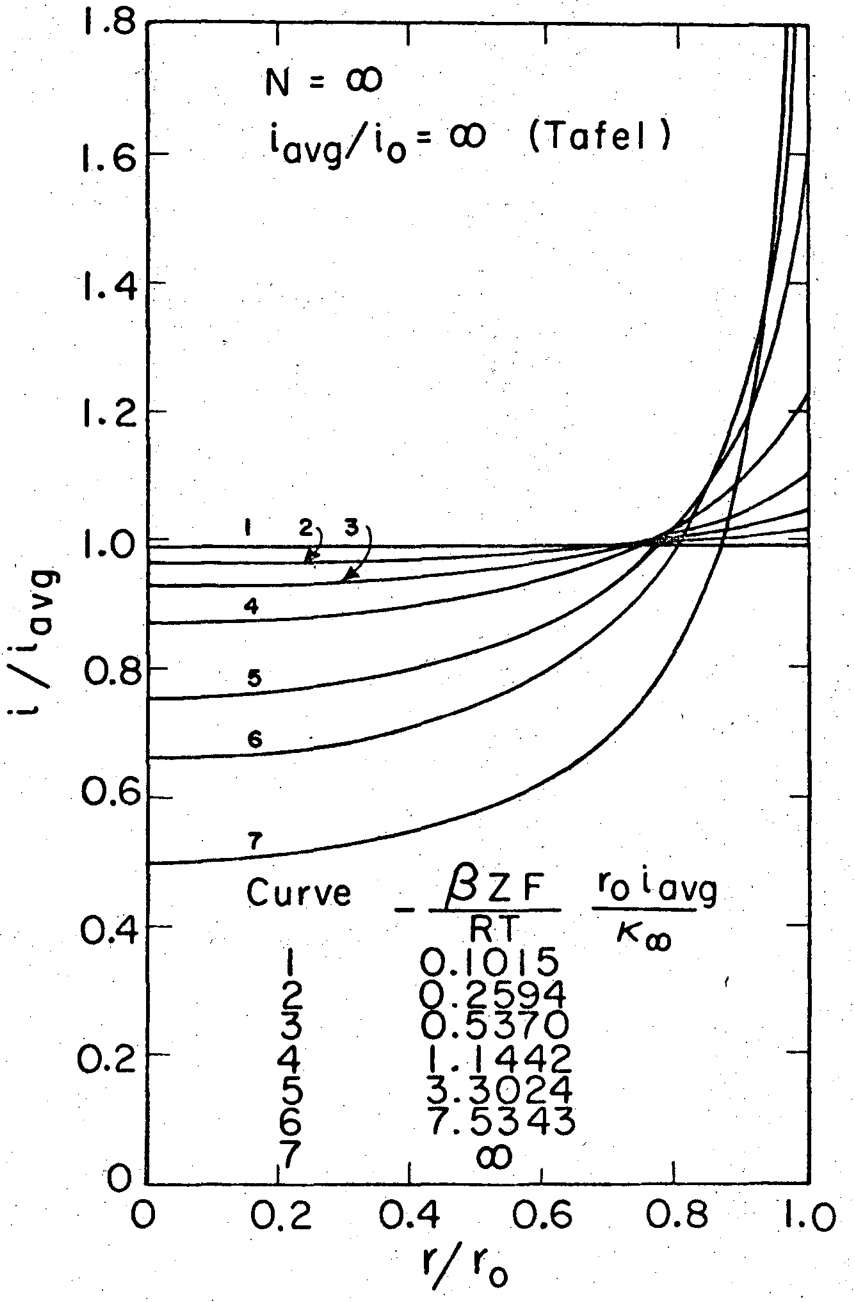

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Figure 15. Secondary current distribution for Tafel polarization.

inversely proportional to the conductivity κ and involves the nature of the polarization. Therefore, we may state as a general rule of thumb that for large systems the primary current distribution will be approached, independent of the nature of the polarization law.

Applications to cathodic protection

As we have said before, one is interested in solving Laplace's equation in corroding systems only if the cathodic and anodic reactions take place on different surfaces or on different parts of the same surface. First one calculates the limiting current for the corrosion agent; this gives the magnitude of the current source needed. Next one calculates the potential distribution for a possible placement of counter electrodes. It is not enough for the counter electrode to generate the requisite total current. An improper placement of the counter electrodes will result in hydrogen evolution on one part of the protected surface. This represents an unproductive comsumption of current and will leave other parts of the surface unprotected. The counter electrode on the left in figure 16 will be able to protect a greater length of the pipe line, without evolving hydrogen on the adjacent part of the pipe line. Of course, the cell potential will be higher, as well as the magnitude of the useful current.

Consider the current distribution on two parallel cylinders, sketched in figure 17. For the primary distribution, the equipotential lines will be circles, and the current lines will intersect them at right angles. Clearly, the farther apart the cylinders, the more nearly uniform the current distribution will be, see figure 18. Hence, we can expect the cathodic protection to be more uniform.

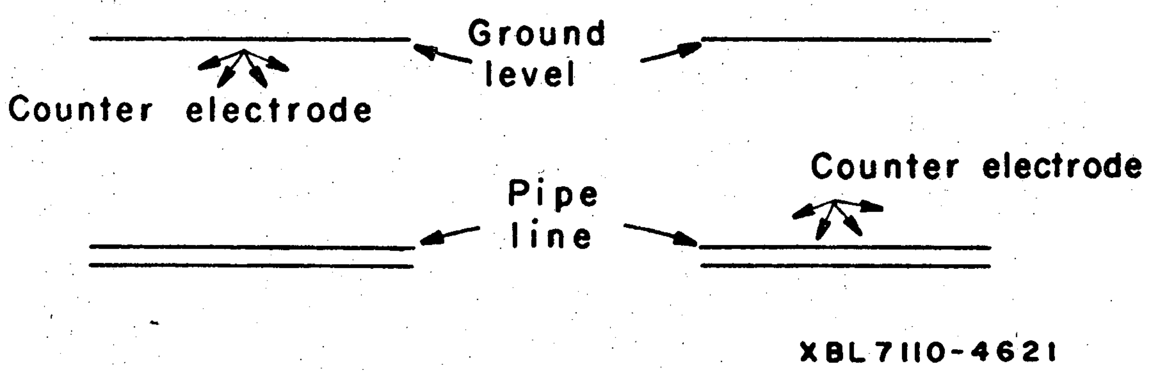

Figure 16. Placement of counter electrodes in cathodic protection.

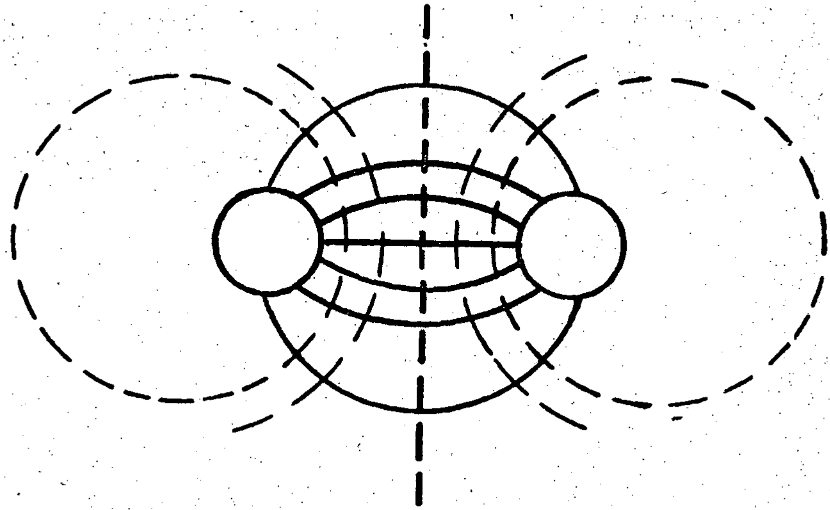

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Figure 17. Parallel cylinders.

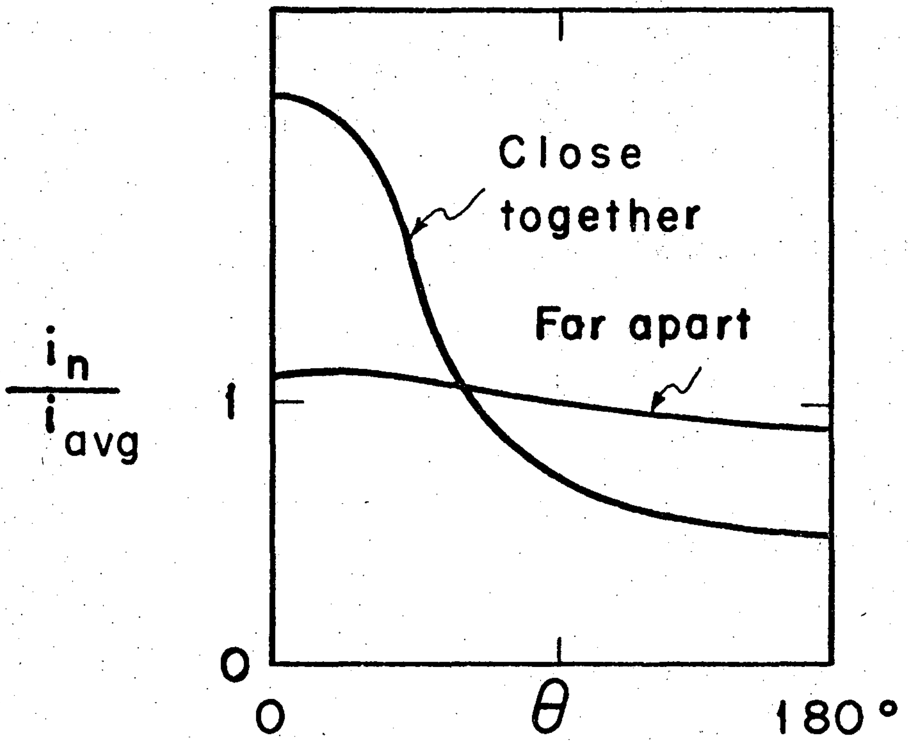

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Figure 18. Sketch of the primary current distribution on parallel cylinders.

But does the nonuniformity of the primary current distribution really give any indication of whether cathodic protection will reach all parts of a body? Clearly it cannot give the complete picture since the primary distribution is purely geometric and does not depend upon the size of the system. The desired current distribution for cathodic protection is determined by a limiting current distribution, not by a primary current distribution. What one wants to know from the potential calculations is whether the potential variation in the solution adjacent to the protected surface is greater than an allowed maximum, so that all parts are protected without hydrogen evolution. This cannot be obtained from a calculation which begins by assuming that Φ is uniform near the surface. To repeat, the size of the system is important in cathodic protection but not in the primary current distribution. (Incidently, it may not be obvious that a large surface cannot be protected even if one is willing to waste current in hydrogen evolution.)

We might ask how large a disk electrode can be protected cathodically by a counter electrode at infinity. We assume that the disk is rotated, the flow is laminar, and the limiting current for the oxygen reaction is uniform, as discussed in the section on mass transport controlled phenomena. Figure 19 shows the potential distribution Φ_o adjacent to the surface of the disk. This is made dimensionless with the total current I, the disk radius r_o, and the solution conductivity κ_∞. This curve can be regarded as a plot of $-\Phi_o$, since I is negative for a cathode. Imagine that the top of the graph, at the ordinate value of 1.8, represents the electrode potential V made dimensionless in the same way as Φ_o. The electrode potential is uniform with radial position

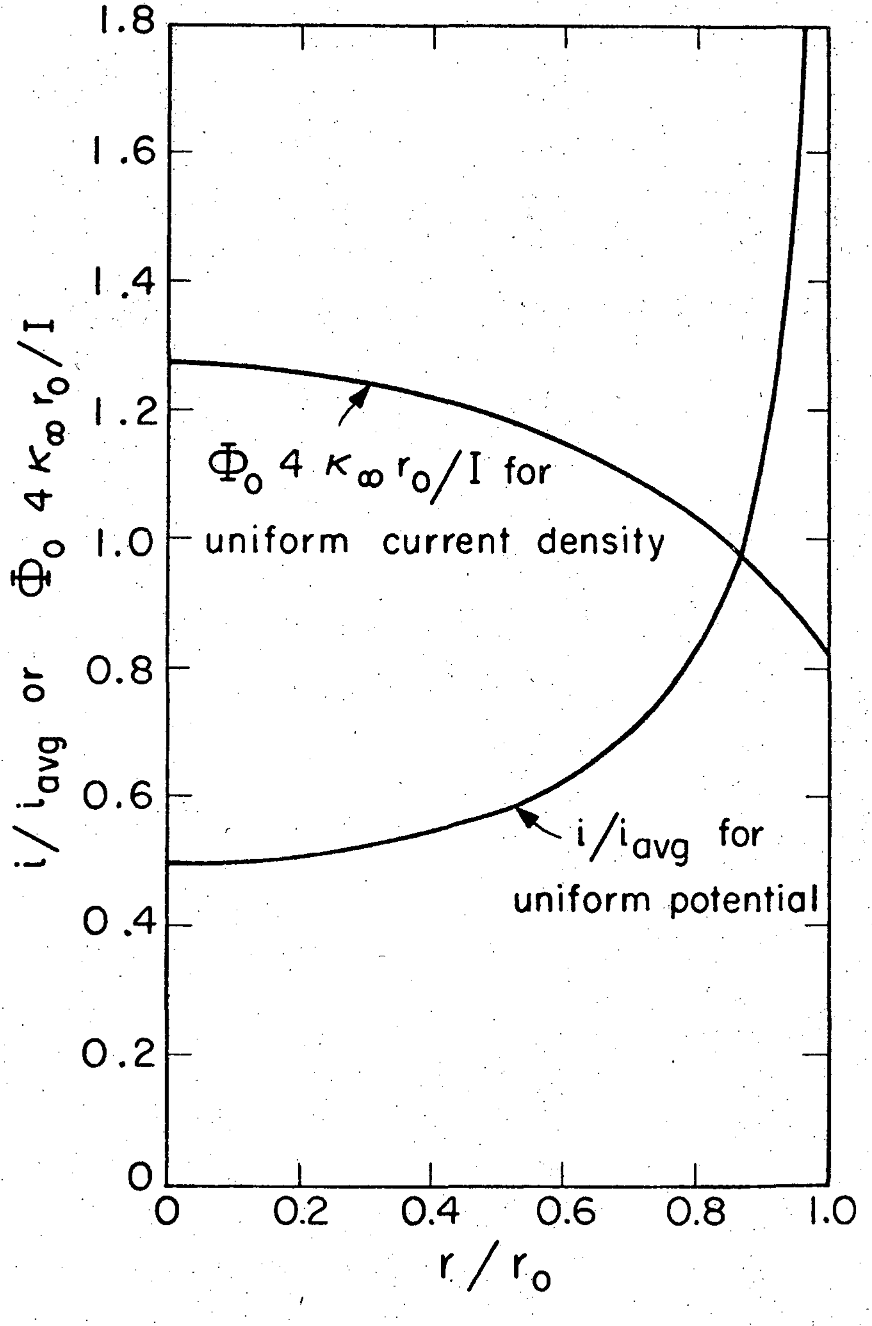

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Figure 19. Primary current distribution and potential distribution for a uniform current density.

r since the disk material has a high conductivity.

The difference between V and Φ_o is the potential available for carrying out electrode reactions, and we see that this difference varies over the surface of the disk. At the center, this difference must be sufficiently cathodic to ensure that oxygen reduction occurs at the limiting current or, more precisely, so that the disk material does not corrode, say -0.1 V (versus the normal hydrogen electrode). Near the edge of the disk, we should like to avoid having this difference be so cathodic that hydrogen is evolved, say -1.0 V. The allowable variation $\Delta\Phi_o$ in Φ_o is thus 0.9 V. From figure 19, we see that the maintenance of a uniform current density i (that required for cathodic protection for oxygen transport in laminar flow) produces a potential variation

$$\Delta\Phi_o = 0.363\, r_o i/\kappa \quad . \tag{84}$$

For a limiting current density of 0.7 mA/cm^2 and a conductivity of 0.05 (ohm-cm)$^{-1}$, the largest disk which can be cathodically protected is r_o = 177 cm.

This result can be contrasted with that represented by equation 75. Characteristic lengths enter into these formulas in different ways. Equations 75 and 84 can also be used to estimate the size of objects which can be protected anodically (that is, by application of an anodic potential such that a passivated state is maintained).

Corrosion in local geometries

Localized corrosion is a complicated situation, and all the factors discussed above can operate simultaneously:

1. The anodic and cathodic reactions occur on different parts of the same surface; consequently, potential-distribution problems and the ohmic potential drop are of interest. The conductivity of the solution determines how far away the cathodic reaction site can be located from the anode.
2. Nonuniform mass-transfer conditions are responsible, in many cases, for establishing the galvanic cell which allows the cathodic and anodic reactions to occur in different places. Otherwise these reactions would be balanced locally, as sketched in figure 9.
3. The electrochemical response of the interface is crucial in corrosion processes. Localized corrosion frequently involves a passivating surface (see figure 8), which adds to the variety of phenomena which can occur. In cracking, fresh surfaces have a different character from old surfaces.
4. Not only do nonuniform concentrations set up the thermodynamic driving force for the galvanic cell, but they also affect the kinetic or catalytic response of the surface. The chloride ion concentration and the pH have particularly strong effects.

An idealized representation of a localized corrosion process is a disk inclusion embedded in a metal surface. Levich and Frumkin[8] treated the potential distribution for a uniform current density on the disk, which may be taken to be the anode, and a uniform potential in the solution adjacent to the remainder of the surface, which acts as the cathode (see figure 20). The potential in the solution adjacent to the

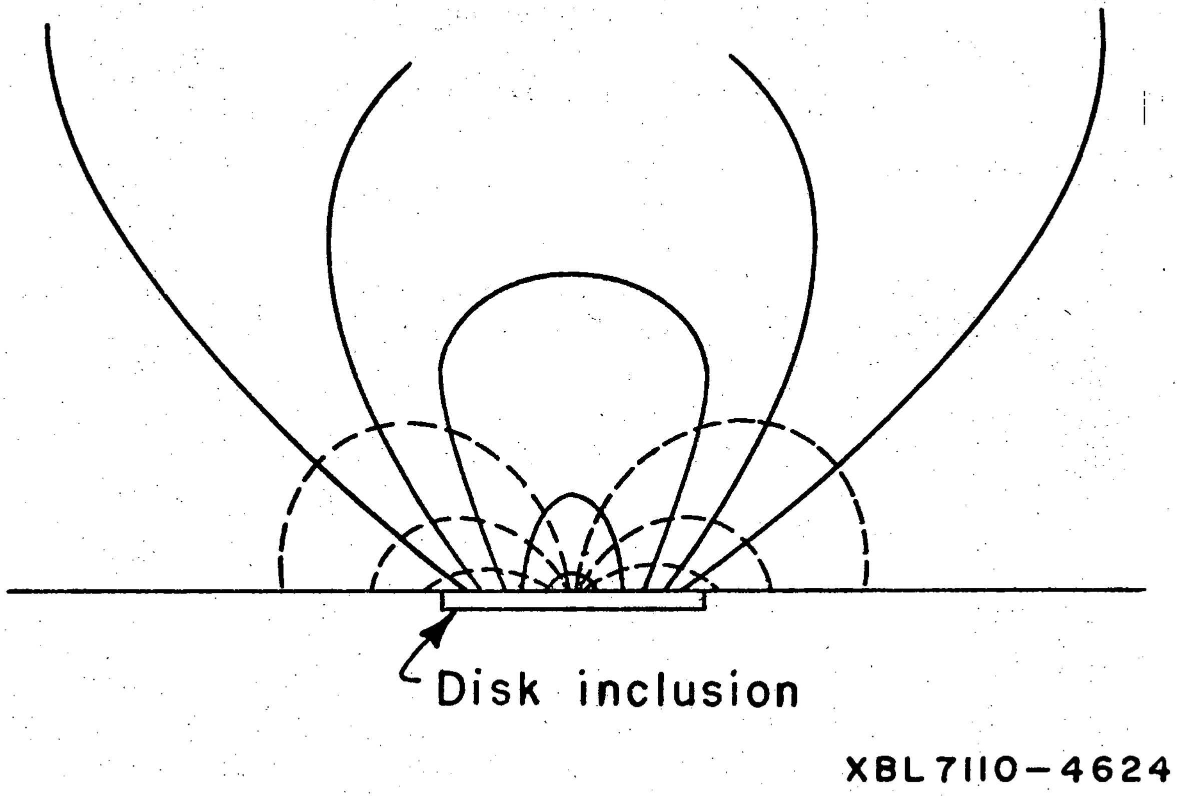

Figure 20. Potential distribution and current lines for a disk inclusion, with a uniform current density, and an equipotential plane. Solid lines are equipotential surfaces and dashed lines show the direction of the current density.

disk is expressed as

$$\Phi_o = \frac{2}{\pi}\frac{ir_o}{\kappa}\sqrt{1 - \left(\frac{r}{r_o}\right)^2} \quad . \tag{85}$$

This situation is similar to that represented by the uniform-current-density curve in figure 19. For the inclusion, however, the counter electrode is the plane surrounding the disk. At this counter electrode, the potential in the solution was assigned the value $\Phi = 0$ in obtaining equation 85. Thus, concentration variations and electrode overpotentials have been neglected at this electrode.

In their original work, Levich and Frumkin intended that the inclusion should be the cathode, on which hydrogen evolves, while the remainder of the plane is the dissolving anode. We have reversed these rôles in order to introduce pitting, where the center of the pit is the anode and the surrounding surface is the cathode. Thus, the current in the solution is flowing from the pit to the surrounding plane, in a manner similar to that depicted in figure 20 for the inclusion, and the potential Φ_o adjacent to the surface must behave as shown in figure 21. Φ_o is more positive near the center of the pit.

From figure 21, we see that the electrode potential is more cathodic at the anode and more anodic at the cathode. This condition can persist only if there is a reaction exhibiting passivation, so that the anodic current decreases with increasing anodic overpotential, or there are concentration variations which establish a galvanic cell. On discharge, the anode of a battery is negative relative to the cathode. The corroding pit is thus similar to a shorted battery.

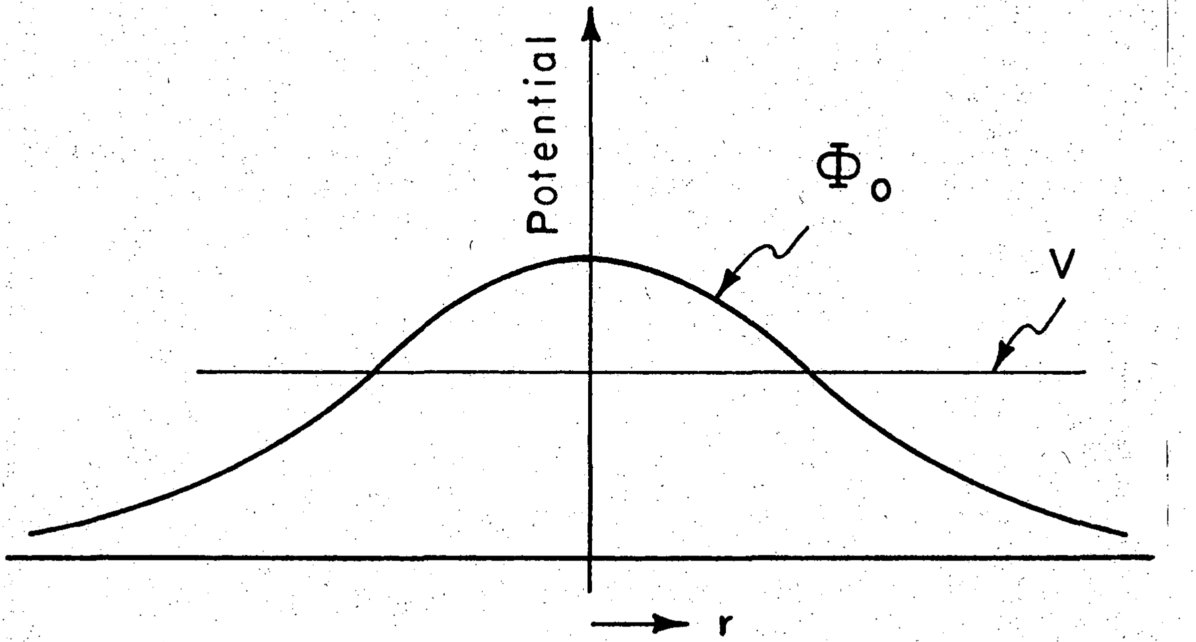

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Figure 21. Electrode potential V and adjacent-solution potential Φ_0 for pit corrosion. Note that the electrode potential is more cathodic at the anode and more anodic at the cathode.

The plane surrounding the pit is more accessible to the cathodic reactant, oxygen or hydrogen ions:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{86}$$

or

$$2H^+ + 2e^- \rightarrow H_2 \quad . \tag{87}$$

The anodic reaction

$$Fe \rightarrow Fe^{++} + 2e^- \tag{88}$$

tends to promote the reaction

$$Fe^{++} + 2OH^- \rightarrow Fe(OH)_2 \tag{89}$$

in the vicinity of the anode. These factors tend to make the solution more acidic near the anode. The only mitigating circumstance is that H^+ ions migrate toward the cathode and OH^- ions toward the anode; however, the transference numbers of these ions are low in sea water and would not in any case reverse the effect. The effect of these variations in pH is to promote anodic passivation on the cathode and discourage it on the anode.

Furthermore, chloride ions migrate toward the anode and away from the cathode. This is important since chloride ions are noted for their effect in preventing passivation.

In several situations of localized corrosion; crevice corrosion, pitting, and water-line corrosion; one can see how different conditions of mass transfer give rise to a galvanic cell, how the corrosion process itself maintains and enhances the conditions for corrosion, and how active-passive electrode kinetics play an important rôle. Pitting corrosion can occur in a stagnant fluid, under apparently uniform conditions, by building on natural fluctuations to establish differential concentrations. The mechanism for maintaining corrosion, once it has been started, has been described above. The development of pitting corrosion is discouraged in a well-agitated fluid.

LaQue[9] has called our attention to the fact that rotating iron disks corrode in sea water in a dramatically different fashion from copper disks. The copper disks corrode near the edge; the iron disks near the center. This is presumably due to the nonuniform mass-transfer conditions arising from the presence of turbulent flow near the edge of the disk and laminar flow near the center.

These disks would appear to be the ideal situation for the theoretical study of localized corrosion. The hydrodynamic flow is reasonably well known near a rotating disk, even for turbulent flow. This is a prerequisite for the calculation of concentration distributions. The disk is also a geometry which permits the computation of potential distributions. These studies would then reveal how active-passive electrode kinetics interact with concentration variations and the ohmic potential drop to produce a situation typical of localized corrosion.

Acknowledgment

This work was supported by the United States Atomic Energy Commission.

Nomenclature

c	molar concentration of a single electrolyte, mole/cm^3
c_i	concentration of species i, mole/cm^3
c_T	total solution concentration, mole/cm^3
d_e	equivalent diameter of annulus or channel, cm
D	measured diffusion coefficient of electrolyte, cm^2/sec
D_i	diffusion coefficient of species i, cm^2/sec
$D^{(t)}$	eddy diffusivity, cm^2/sec
$\mathcal{D}_{ij}$	diffusion coefficient for interaction of species i and j, cm^2/sec
F	Faraday's constant, 96,487 C/equiv
g	gravitational acceleration, cm/sec^2
Gr	Grashof number
h	distance between walls of flow channel, cm
i	current density, A/cm^2
i_o	exchange current density, A/cm^2
I	total current, A
J	dimensionless exchange current density
L	length of electrode, cm
M_i	symbol for the chemical formula of species i
n	number of electrons transferred in electrode reaction
N_i	flux of species i, mole/cm^2-sec
Nu	Nusselt number

r	radial position coördinate, cm
r_o	radius of disk electrode or pipe, cm
R	universal gas constant, 8.3143 J/mole deg
R	resistance, ohm
R_i	homogeneous rate of production of species i, mole/cm^3-sec
Re	Reynolds number
s_i	stoichiometric coefficient of species i in electrode reaction
Sc	Schmidt number
t	time, sec
t_i	transference number of species i
T	absolute temperature, deg K
u_i	mobility of species i, cm^2-mole/J-sec
U°	equilibrium electrode potential for a given reaction, V
v	fluid velocity, cm/sec
$\langle v \rangle$	average velocity, cm/sec
$\underline{v}_i$	velocity of species i, cm/sec
V	potential of an electrode, V
x	distance measured along an electrode surface, cm
y	normal distance from the surface, cm
z_i	charge number of species i
α_a, α_c	transfer coefficients
δ	dimensionless average current density
ε	permittivity, farad/cm
ε	$\pi L/2h$
η	rotational elliptic coördinate
η_s	surface overpotential, V

κ	conductivity, mho/cm
λ_i	ionic equivalent conductance, mho-cm^2/equiv
Λ	equivalent conductance of single electrolyte, mho-cm^2/equiv
μ	viscosity, g/cm-sec
μ_i	electrochemical potential, J/mole
ν	kinematic viscosity, cm^2/sec
ν_+,ν_-	number of moles of cations and anions per mole of electrolyte
ρ	density, g/cm^3
Φ	electric potential, V
Φ_o	potential adjacent to electrode, outside diffusion layer, V
Ω	rotational speed, radian/sec
o	at the electrode
∞	far from the electrode

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