where x is the distance of the capillary tip from the electrode, A is the electrode area, and κ is the solution conductivity. The effect of iR_u can be particularly serious for spherical microelectrodes, such as the hanging mercury drop electrode or the dropping mercury electrode (DME). For a spherical electrode of radius r_0,

$$R_u = \frac{1}{4\pi\kappa r_0}\left(\frac{x}{x + r_0}\right) \tag{1.3.8}$$

In this case, most of the resistive drop occurs close to the electrode. For a reference electrode tip placed just one electrode radius away ($x = r_0$), R_u is already half of the value for the tip placed infinitely far away. Any resistances in the working electrode itself (e.g., in thin wires used to make ultramicroelectrodes, in semiconductor electrodes, or in resistive films on the electrode surface) will also appear in R_u.

▶ 1.4 INTRODUCTION TO MASS-TRANSFER-CONTROLLED REACTIONS

C.T. "fast" ⟹ reversible

1.4.1 Modes of Mass Transfer

Let us now be more quantitative about the size and shape of current-potential curves. As shown in equation 1.3.4, if we are to understand i, we must be able to describe the rate of the reaction, v, at the electrode surface. The simplest electrode reactions are those in which the rates of all associated chemical reactions are very rapid compared to those of the mass-transfer processes. Under these conditions, the chemical reactions can usually be treated in a particularly simple way. If, for example, an electrode process involves only fast heterogeneous charge-transfer kinetics and mobile, reversible homogeneous reactions, we will find below that (a) the homogeneous reactions can be regarded as being at equilibrium and (b) the *surface concentrations* of species involved in the faradaic process are related to the electrode potential by an equation of the Nernst form. The net rate of the electrode reaction, v_{rxn}, is then governed totally by the rate at which the electroactive species is brought to the surface by mass transfer, v_{mt}. Hence, from equation 1.3.4,

$$v_{\text{rxn}} = v_{\text{mt}} = i/nFA \tag{1.4.1}$$

$$v = \frac{dN}{dt}\cdot\frac{1}{A}$$

$$N = \frac{Q}{n\mathcal{F}}$$

$$\therefore v = \frac{1}{n\mathcal{F}A}\frac{dQ}{dt} = \frac{i}{n\mathcal{F}A}$$

Such electrode reactions are often called *reversible* or *nernstian*, because the principal species obey thermodynamic relationships at the electrode surface. Since mass transfer plays a big role in electrochemical dynamics, we review here its three modes and begin a consideration of mathematical methods for treating them.

Mass transfer, that is, the movement of material from one location in solution to another, arises either from differences in electrical or chemical potential at the two locations or from movement of a volume element of solution. The modes of mass transfer are:

1. *Migration.* Movement of a charged body under the influence of an electric field (a gradient of electrical potential).
2. *Diffusion.* Movement of a species under the influence of a gradient of chemical potential (i.e., a concentration gradient).
3. *Convection.* Stirring or hydrodynamic transport. Generally fluid flow occurs because of *natural convection* (convection caused by density gradients) and *forced convection*, and may be characterized by stagnant regions, laminar flow, and turbulent flow.

Mass transfer to an electrode is governed by the *Nernst–Planck equation*, written for one-dimensional mass transfer along the x-axis as

Nernst-Planck 1-D

$$\boxed{J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v(x)} \tag{1.4.2}$$

where $J_i(x)$ is the flux of species i (mol s^{-1}cm^{-2}) at distance x from the surface, D_i is the diffusion coefficient (cm^2/s), $\partial C_i(x)/\partial x$ is the concentration gradient at distance x, $\partial \phi(x)/\partial x$ is the potential gradient, z_i and C_i are the charge (dimensionless) and concentration (mol cm^{-3}) of species i, respectively, and $v(x)$ is the velocity (cm/s) with which a volume element in solution moves along the axis. This equation is derived and discussed in more detail in Chapter 4. The three terms on the right-hand side represent the contributions of diffusion, migration, and convection, respectively, to the flux.

While we will be concerned with particular solutions of this equation in later chapters, a rigorous solution is generally not very easy when all three forms of mass transfer are in effect; hence electrochemical systems are frequently designed so that one or more of the contributions to mass transfer are negligible. For example, the migrational component can be reduced to negligible levels by addition of an inert electrolyte (a *supporting electrolyte*) at a concentration much larger than that of the electroactive species (see Section 4.3.2). Convection can be avoided by preventing stirring and vibrations in the electrochemical cell. In this chapter, we present an approximate treatment of steady-state mass transfer, which will provide a useful guide for these processes in later chapters and will give insight into electrochemical reactions without encumbrance by mathematical details.

1.4.2 Semiempirical Treatment of Steady-State Mass Transfer

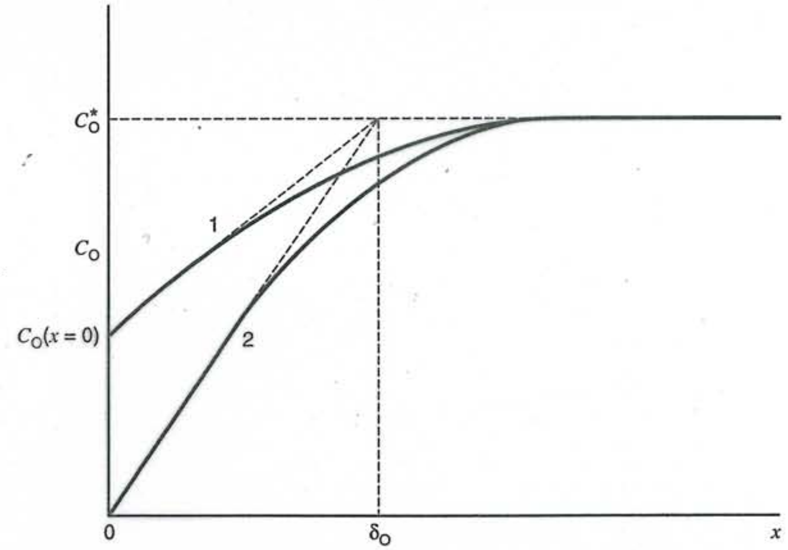
Consider the reduction of a species O at a cathode: $O + ne \rightleftarrows R$. In an actual case, the oxidized form, O, might be $Fe(CN)_6^{3-}$ and R might be $Fe(CN)_6^{4-}$, with only $Fe(CN)_6^{3-}$ initially present at the millimolar level in a solution of 0.1 M K_2SO_4. We envision a three-electrode cell having a platinum cathode, platinum anode, and SCE reference electrode. In addition, we furnish provision for agitation of the solution, such as by a stirrer. A particularly reproducible way to realize these conditions is to make the cathode in the form of a disk embedded in an insulator and to rotate the assembly at a known rate; this is called the *rotating disk electrode* (RDE) and is discussed in Section 9.3.

Once electrolysis of species O begins, its concentration at the electrode surface, $C_O(x = 0)$ becomes smaller than the value, C_O^*, in the *bulk solution* (far from the electrode). We assume here that stirring is ineffective at the electrode surface, so the solution velocity term need not be considered at $x = 0$. This simplified treatment is based on the idea that a stagnant layer of thickness δ_O exists at the electrode surface (*Nernst diffusion layer*), with stirring maintaining the concentration of O at C_O^* beyond $x = \delta_O$ (Figure 1.4.1). Since we also assume that there is an excess of supporting electrolyte, migration is not important, and the rate of mass transfer is proportional to the concentration gradient at the electrode surface, as given by the first (diffusive) term in equation 1.4.2:

$$v_{mt} \propto (dC_O/dx)_{x=0} = D_O(dC_O/dx)_{x=0} \tag{1.4.3}$$

If one further assumes a linear concentration gradient within the diffusion layer, then, from equation 1.4.3

$$v_{mt} = D_O[C_O^* - C_O(x = 0)]/\delta_O \tag{1.4.4}$$



E_1

E_2

E_2 more cathodic than E_1

Figure 1.4.1 Concentration profiles (solid lines) and diffusion layer approximation (dashed lines). $x = 0$ corresponds to the electrode surface and δ_O is the diffusion layer thickness. Concentration profiles are shown at two different electrode potentials: (*1*) where $C_O(x = 0)$ is about $C_O^*/2$, (*2*) where $C_O(x = 0) \approx 0$ and $i = i_l$.

fast c.t. $\Rightarrow$ set E $\therefore$ set $C_O(0,t)$

Since δ_O is often unknown, it is convenient to combine it with the diffusion coefficient to produce a single constant, $m_O = D_O/\delta_O$, and to write equation 1.4.4 as

$$v_{\mathrm{mt}} = m_O[C_O^* - C_O(x = 0)] \tag{1.4.5}$$

The proportionality constant, m_O, called the *mass-transfer coefficient*, has units of cm/s (which are those of a rate constant of a first-order heterogeneous reaction; see Chapter 3). These units follow from those of v and C_O, but can also be thought of as volume flow/s per unit area ($\mathrm{cm}^3\ \mathrm{s}^{-1}\ \mathrm{cm}^{-2}$).[11] Thus, from equations 1.4.1 and 1.4.5 and taking a reduction current as positive [i.e., i is positive when $C_O^* > C_O(x = 0)$], we obtain

O supply

$$\boxed{\frac{i}{nFA} = m_O[C_O^* - C_O(x = 0)]} \tag{1.4.6}$$

Under the conditions of a net cathodic reaction, R is produced at the electrode surface, so that $C_R(x = 0) > C_R^*$ (where C_R^* is the bulk concentration of R). Therefore,

R removal

$$\boxed{\frac{i}{nFA} = m_R[C_R(x = 0) - C_R^*]} \tag{1.4.7}$$

---

[11] While m_O is treated here as a phenomenological parameter, in more exact treatments the value of m_O can sometimes be specified in terms of measurable quantities. For example, for the rotating disk electrode, $m_O = 0.62D_O^{2/3}\omega^{1/2}\nu^{-1/6}$, where ω is the angular velocity of the disk (i.e., $2\pi f$, with f as the frequency in revolutions per second) and ν is the kinematic viscosity (i.e., viscosity/density, with units of cm^2/s) (see Section 9.3.2). Steady-state currents can also be obtained with a very small electrode (such as a Pt disk with a radius, r_0, in the μm range), called an ultramicroelectrode (UME, Section 5.3). At a disk UME, $m_O = 4D_O/\pi r_0$.

or for the particular case when $C_R^* = 0$ (no R in the bulk solution),

$$\boxed{\frac{i}{nFA} = m_R C_R(x = 0)} \tag{1.4.8}$$

The values of $C_O(x = 0)$ and $C_R(x = 0)$ are functions of electrode potential, E. The largest rate of mass transfer of O occurs when $C_O(x = 0) = 0$ (or more precisely, when $C_O(x = 0) << C_O^*$, so that $C_O^* - C_O(x = 0) \approx C_O^*$). The value of the current under these conditions is called the *limiting current*, i_l, where

max $\nabla C = C_O^* - 0$

$$\boxed{i_l = nFAm_O C_O^*} \tag{1.4.9}$$

When the limiting current flows, the electrode process is occurring at the maximum rate possible for a given set of mass-transfer conditions, because O is being reduced as fast as it can be brought to the electrode surface. Equations 1.4.6 and 1.4.9 can be used to obtain expressions for $C_O(x = 0)$:

Conversion of $C_O(0,t)/C_O^*$

$$\boxed{\frac{C_O(x = 0)}{C_O^*} = 1 - \frac{i}{i_l}} \tag{1.4.10}$$

$$C_O(x = 0) = \frac{i_l - i}{nFAm_O} \tag{1.4.11}$$

Thus, the concentration of species O at the electrode surface is linearly related to the current and varies from C_O^*, when $i = 0$, to a negligible value, when $i = i_l$.

If the kinetics of electron transfer are rapid, the concentrations of O and R at the electrode surface can be assumed to be at equilibrium with the electrode potential, as governed by the Nernst equation for the half-reaction[12]

$$E = E^{0'} + \frac{RT}{nF}\ln\frac{C_O(x = 0)}{C_R(x = 0)} \tag{1.4.12}$$

Such a process is called a *nernstian reaction*. We can derive the steady-state *i-E* curves for nernstian reactions under several different conditions.

(a) R Initially Absent

When $C_R^* = 0$, $C_R(x = 0)$ can be obtained from (1.4.8):

i-E characteristics

$$C_R(x = 0) = i/nFAm_R \tag{1.4.13}$$

"reversible"

Then, combining equations 1.4.11 to 1.4.13, we obtain

$$\boxed{E = E^{0'} - \frac{RT}{nF}\ln\frac{m_O}{m_R} + \frac{RT}{nF}\ln\left(\frac{i_l - i}{i}\right)} \tag{1.4.14}$$

fast c.t.

m.t. controlled

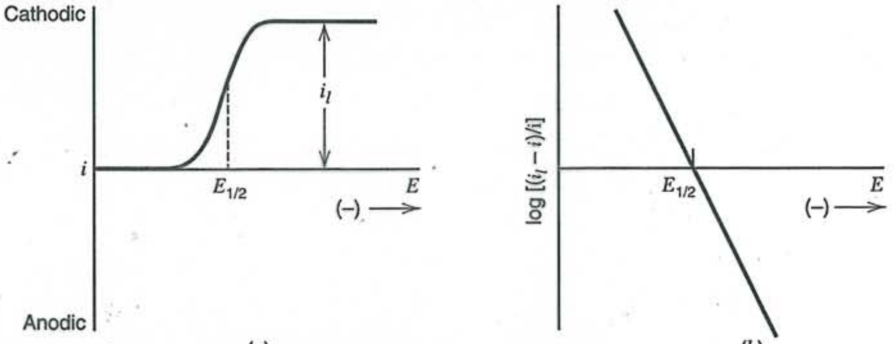
An *i-E* plot is shown in Figure 1.4.2*a*. Note that when $i = i_l/2$,

$$\boxed{E = E_{1/2} = E^{0'} - \frac{RT}{nF}\ln\frac{m_O}{m_R}} \tag{1.4.15}$$

"half-wave potential"

---

[12] Equation 1.4.12 is written in terms of $E^{0'}$, called the *formal potential*, rather than the standard potential E^0. The formal potential is an adjusted form of the standard potential, manifesting activity coefficients and some chemical effects of the medium. In Section 2.1.6, it will be introduced in more detail. For the present it is not necessary to distinguish between $E^{0'}$ and E^0.



(*a*) (*b*)

Figure 1.4.2 (*a*) Current-potential curve for a nernstian reaction involving two soluble species with only oxidant present initially. (*b*) $\log[(i_l - i)/i]$ *vs*. E for this system.

where $E_{1/2}$ is independent of the substrate concentration and is therefore characteristic of the O/R system. Thus,

$$\boxed{E = E_{1/2} + \frac{RT}{nF} \ln\left(\frac{i_l - i}{i}\right)} \tag{1.4.16}$$

test of reversibility

When a system conforms to this equation, a plot of E *vs*. $\log[(i_l - i)/i]$ is a straight line with a slope of $2.3RT/nF$ (or $59.1/n$ mV at 25°C). Alternatively (Figure 1.4.2*b*), $\log[(i_l - i)/i]$ *vs*. E is linear with a slope of $nF/2.3RT$ (or $n/59.1$ mV^{-1} at 25°C) and has an E-intercept of $E_{1/2}$. When m_O and m_R have similar values, $E_{1/2} \approx E^{0'}$.

(b) Both O and R Initially Present

When both members of the redox couple exist in the bulk, we must distinguish between a *cathodic* limiting current, $i_{l,c}$, when $C_O(x = 0) \approx 0$, and an *anodic* limiting current, $i_{l,a}$, when $C_R(x = 0) \approx 0$. We still have $C_O(x = 0)$ given by (1.4.11), but with i_l now specified as $i_{l,c}$. The limiting anodic current naturally reflects the maximum rate at which R can be brought to the electrode surface for conversion to O. It is obtained from (1.4.7):

$$i_{l,a} = -nFAm_RC_R^* \tag{1.4.17}$$

(The negative sign arises because of our convention that cathodic currents are taken as positive and anodic ones as negative.) Thus $C_R(x = 0)$ is given by

$$C_R(x = 0) = \frac{i - i_{l,a}}{nFAm_R} \tag{1.4.18}$$

$$\boxed{\frac{C_R(x = 0)}{C_R^*} = 1 - \frac{i}{i_{l,a}}} \tag{1.4.19}$$

The i-E curve is then

$$\boxed{E = E^{0'} - \frac{RT}{nF} \ln \frac{m_O}{m_R} + \frac{RT}{nF} \ln\left(\frac{i_{l,c} - i}{i - i_{l,a}}\right)} \tag{1.4.20}$$

A plot of this equation is shown in Figure 1.4.3. When $i = 0$, $E = E_{eq}$ and the system is at equilibrium. Surface concentrations are then equal to the bulk values. When current flows,

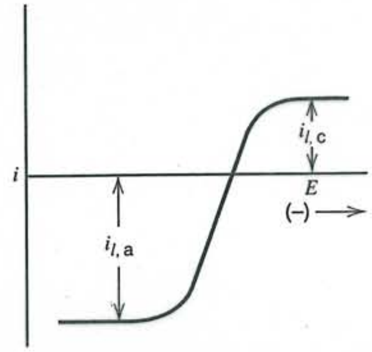


Figure 1.4.3 Current-potential curve for a nernstian system involving two soluble species with both forms initially present.

the potential deviates from E_{eq}, and the extent of this deviation is the concentration overpotential. (An equilibrium potential cannot be defined when $C_{\mathrm{R}}^* = 0$, of course.)

(c) R Insoluble

Suppose species R is a metal and can be considered to be at essentially unit activity as the electrode reaction takes place on bulk R.[13] When $a_{\mathrm{R}} = 1$, the Nernst equation is

$$E = E^{0'} + \frac{RT}{nF} \ln C_{\mathrm{O}}(x = 0) \tag{1.4.21}$$

or, using the value of $C_{\mathrm{O}}(x = 0)$ from equation 1.4.11,

$$\boxed{E = \underbrace{E^{0'} + \frac{RT}{nF} \ln C_{\mathrm{O}}^*}_{E \text{ at } i=0} + \underbrace{\frac{RT}{nF} \ln\left(\frac{i_l - i}{i_l}\right)}_{\eta_{conc}}} \tag{1.4.22}$$

When $i = 0$, $E = E_{\mathrm{eq}} = E^{0'} + (RT/nF) \ln C_{\mathrm{O}}^*$ (Figure 1.4.4). If we define the *concentration overpotential*, η_{conc} (or the *mass-transfer overpotential*, η_{mt}), as

$$\eta_{\mathrm{conc}} = E - E_{\mathrm{eq}} \tag{1.4.23}$$

then

$$\eta_{\mathrm{conc}} = \frac{RT}{nF} \ln\left(\frac{i_l - i}{i_l}\right) \tag{1.4.24}$$

When $i = i_l$, $\eta_{\mathrm{conc}} \to \infty$. Since η is a measure of polarization, this condition is sometimes called *complete concentration polarization.*

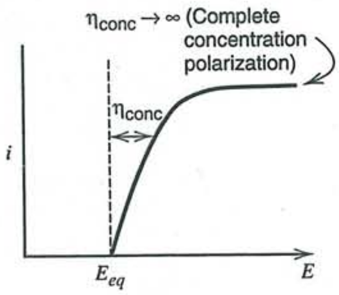


Figure 1.4.4 Current-potential curve for a nernstian system where the reduced form is insoluble.

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[13] This will not be the case for R plated onto an inert substrate in amounts less than a monolayer (e.g., the substrate electrode being Pt and R being Cu). Under those conditions, a_{R} may be considerably less than unity (see Section 11.2.1).

Equation 1.4.24 can be written in exponential form:

$$1 - \frac{i}{i_l} = \exp\left(\frac{nF\eta_{\text{conc}}}{RT}\right) \tag{1.4.25}$$

The exponential can be expanded as a power series, and the higher-order terms can be dropped if the argument is kept small; that is,

$$e^x = 1 + x + \frac{x^2}{2} + \cdots \simeq 1 + x \text{ (when } x \text{ is small)} \tag{1.4.26}$$

Thus, under conditions of small deviations of potential from E_{eq}, the i-η_{conc} characteristic is linear:

$$\eta_{\text{conc}} = \frac{-RTi}{nFi_l} \tag{1.4.27}$$

Since $-\eta/i$ has dimensions of resistance (ohms), we can define a "small signal" mass-transfer resistance, R_{mt}, as

$$\boxed{R_{\text{mt}} = \frac{RT}{nF|i_l|}} \tag{1.4.28}$$

Here we see that the mass-transfer-limited electrode reaction resembles an actual resistance element only at small overpotentials.

1.4.3 Semiempirical Treatment of the Transient Response

The treatment in Section 1.4.2 can also be employed in an approximate way to time-dependent (transient) phenomena, for example, the buildup of the diffusion layer, either in a stirred solution (before steady state is attained) or in an unstirred solution where the diffusion layer continues to grow with time. Equation 1.4.4 still applies, but in this case we consider the diffusion layer thickness to be a time-dependent quantity, so that

$$i/nFA = v_{\text{mt}} = D_{\text{O}}[C_{\text{O}}^* - C_{\text{O}}(x = 0)]/\delta_{\text{O}}(t) \tag{1.4.29}$$

Consider what happens when a potential step of magnitude E is applied to an electrode immersed in a solution containing a species O. If the reaction is nernstian, the concentrations of O and R at $x = 0$ instantaneously adjust to the values governed by the Nernst equation, (1.4.12). The thickness of the approximately linear diffusion layer, $\delta_{\text{O}}(t)$, grows with time (Figure 1.4.5). At any time, the volume of the diffusion layer is

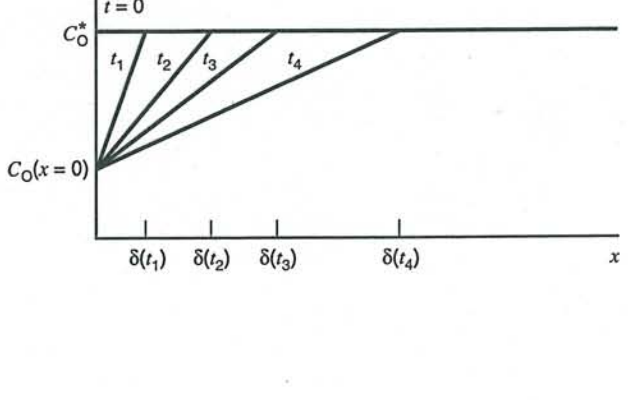


Figure 1.4.5 Growth of the diffusion-layer thickness with time.

CHAPTER

4

MASS TRANSFER BY MIGRATION AND DIFFUSION

electrochemical potential

$\bar{\mu}_i = \mu_i + z_i F \phi$

4.1 DERIVATION OF A GENERAL MASS TRANSFER EQUATION

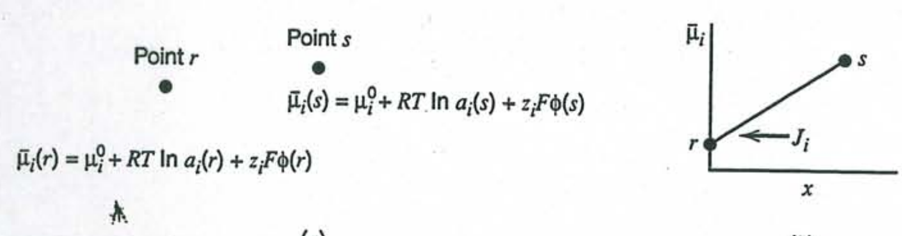
In this section, we discuss the general partial differential equations governing mass transfer; these will be used frequently in subsequent chapters for the derivation of equations appropriate to different electrochemical techniques. As discussed in Section 1.4, mass transfer in solution occurs by diffusion, migration, and convection. Diffusion and migration result from a gradient in electrochemical potential, $\overline{\mu}$. Convection results from an imbalance of forces on the solution.

Consider an infinitesimal element of solution (Figure 4.1.1) connecting two points in the solution, r and s, where, for a certain species j, $\overline{\mu_j}(r) \neq \overline{\mu_j}(s)$. This difference of $\overline{\mu_j}$ over a distance (a gradient of electrochemical potential) can arise because there is a difference of concentration (or activity) of species j (a concentration gradient), or because there is a difference of ϕ (an electric field or potential gradient). In general, a flux of species j will occur to alleviate any difference of $\overline{\mu_j}$. The flux, $\mathbf{J}_j$ (mol s^{-1}cm^{-2}), is proportional to the gradient of $\overline{\mu_j}$:

$$\mathbf{J}_j \propto \mathbf{grad}\,\overline{\mu_j} \qquad \text{or} \qquad \mathbf{J}_j \propto \nabla\,\overline{\mu_j} \tag{4.1.1}$$

where **grad** or ∇ is a vector operator. For linear (one-dimensional) mass transfer, $\nabla = \mathbf{i}(\partial/\partial x)$, where $\mathbf{i}$ is the unit vector along the axis and x is distance. For mass transfer in a three-dimensional Cartesian space,

$$\nabla = \mathbf{i}\frac{\partial}{\partial x} + \mathbf{j}\frac{\partial}{\partial y} + \mathbf{k}\frac{\partial}{\partial z} \tag{4.1.2}$$



(a) (b)

Figure 4.1.1 A gradient of electrochemical potential.

The constant of proportionality in (4.1.1) turns out to be $-C_jD_j/RT$; thus,

$$\mathbf{J}_j = -\left(\frac{C_jD_j}{RT}\right)\nabla\overline{\mu}_j \tag{4.1.3}$$

For linear mass transfer, this is

$$J_j(x) = -\left(\frac{C_jD_j}{RT}\right)\frac{\partial\overline{\mu}_j}{\partial x} \tag{4.1.4}$$

The minus sign arises in these equations because the direction of the flux opposes the direction of increasing $\overline{\mu}_j$.

If, in addition to this $\overline{\mu}$ gradient, the solution is moving, so that an element of solution [with a concentration $C_j(s)$] shifts from s with a velocity $\mathbf{v}$, then an additional term is added to the flux equation:

$$\mathbf{J}_j = -\left(\frac{C_jD_j}{RT}\right)\nabla\overline{\mu}_j + C_j\mathbf{v} \tag{4.1.5}$$

For linear mass transfer,

valid at high dilution + in ideal sol$^{\text{ns}}$

$$J_j(x) = -\left(\frac{C_jD_j}{RT}\right)\left(\frac{\partial\overline{\mu}_j}{\partial x}\right) + C_jv(x) \tag{4.1.6}$$

Taking $a_j \approx C_j$, we obtain the *Nernst–Planck equations*, which can be written as

$$J_j(x) = -\left(\frac{C_jD_j}{RT}\right)\left[\frac{\partial}{\partial x}(RT\ln C_j) + \frac{\partial}{\partial x}(z_jF\phi)\right] + C_jv(x) \tag{4.1.7}$$

$$\boxed{J_j(x) = -D_j\frac{\partial C_j(x)}{\partial x} - \frac{z_jF}{RT}D_jC_j\frac{\partial\phi(x)}{\partial x} + C_jv(x)} \tag{4.1.8}$$

or in general,

Nernst–Planck

$$\boxed{\mathbf{J}_j = -D_j\nabla C_j - \frac{z_jF}{RT}D_jC_j\nabla\phi + C_j\mathbf{v}} \tag{4.1.9}$$

⇒ linear eq$^{\text{n}}$ ⇒ sol$^{\text{n}}$'s additive

In this chapter, we are concerned with systems in which convection is absent. Convective mass transfer will be treated in Chapter 9. Under quiescent conditions, that is, in an unstirred or stagnant solution with no density gradients, the solution velocity, $\mathbf{v}$, is zero, and the general flux equation for species j, (4.1.9), becomes

$$\mathbf{J}_j = -D_j\nabla C_j - \frac{z_jF}{RT}D_jC_j\nabla\phi \tag{4.1.10}$$

For linear mass transfer, this is

1-D problem

$$J_j(x) = -D_j\left(\frac{\partial C_j(x)}{\partial x}\right) - \frac{z_jF}{RT}D_jC_j\left(\frac{\partial\phi(x)}{\partial x}\right) \tag{4.1.11}$$

where the terms on the right-hand side represent the contributions of diffusion and migration, respectively, to the total mass transfer.

If species j is charged, then the flux, J_j, is equivalent to a current density. Let us consider a linear system with a cross-sectional area, A, normal to the axis of mass flow. Then, J_j (mol s^{-1} cm^{-2}) is equal to $-i_j/z_jFA$ [C/s per (C mol^{-1} cm^2)], where i_j is the current component at any value of x arising from a flow of species j. Equation 4.1.11 can then be written as

$$-J_j = \frac{i_j}{z_jFA} = \frac{i_{d,j}}{z_jFA} + \frac{i_{m,j}}{z_jFA} \quad \text{|| additivity} \tag{4.1.12}$$

with

$$\frac{i_{d,j}}{z_jFA} = D_j\frac{\partial C_j}{\partial x} \leftarrow \text{different} \tag{4.1.13}$$

$$\frac{i_{m,j}}{z_jFA} = \frac{z_jFD_j}{RT}C_j\frac{\partial \phi}{\partial x} \leftarrow \text{driving forces} \tag{4.1.14}$$

where $i_{d,j}$ and $i_{m,j}$ are *diffusion* and *migration currents* of species j, respectively.

At any location in solution during electrolysis, the total current, i, is made up of contributions from all species; that is,

$$i = \sum_j i_j \tag{4.1.15}$$

or

$$i = \frac{F^2A}{RT}\cdot\frac{\partial \phi}{\partial x}\sum_j z_j^2D_jC_j + FA\sum_j z_jD_j\frac{\partial C_j}{\partial x} \tag{4.1.16}$$

where the current for each species at that location is made up of a migrational component (first term) and a diffusional component (second term).

We will now discuss migration and diffusion in electrochemical systems in more detail. The concepts and equations derived below date back to at least the work of Planck (1). Further details concerning the general problem of mass transfer in electrochemical systems can be found in a number of reviews (2–6).

▶ 4.2 MIGRATION

In the bulk solution (away from the electrode), concentration gradients are generally small, and the total current is carried mainly by migration. All charged species contribute. For species j in the bulk region of a linear mass-transfer system having a cross-sectional area A, $i_j = i_{m,j}$ or

$$i_j = \frac{z_j^2F^2AD_jC_j}{RT}\cdot\frac{\partial \phi}{\partial x} \tag{4.2.1}$$

The mobility of species j, defined in Section 2.3.3, is linked to the diffusion coefficient by the *Einstein–Smoluchowski equation*:

$u_j \equiv$ mobility
$\Rightarrow$ velocity of ion j in a unit field

$$\boxed{u_j = \frac{|z_j|FD_j}{RT}} \tag{4.2.2}$$

hence i_j can be reexpressed as

$u_j = \frac{v}{E} = \frac{cm/s}{V/cm} = cm^2V^{-1}s^{-1}$

$$i_j = |z_j|FAu_jC_j\frac{\partial \phi}{\partial x} \tag{4.2.3}$$

For a linear electric field,

$$\frac{\partial \phi}{\partial x} = \frac{\Delta E}{l} \tag{4.2.4}$$

where $\Delta E/l$ is the gradient (V/cm) arising from the change in potential ΔE over distance l. Thus,

$$i_j = \frac{|z_j| FAu_jC_j \, \Delta E}{l} \tag{4.2.5}$$

and the total current in bulk solution is given by

$$i = \sum_j i_j = \frac{FA\,\Delta E}{l} \sum_j |z_j| u_j C_j \tag{4.2.6}$$

which is (4.1.16) expressed in particular for this situation. The conductance of the solution, L (Ω^{-1}), which is the reciprocal of the resistance, R (Ω), is given by Ohm's law,

5

$$L = \frac{1}{R} = \frac{i}{\Delta E} = \frac{FA}{l} \sum_j |z_j| u_j C_j = \frac{A}{l}\kappa \tag{4.2.7}$$

where κ, the *conductivity* (Ω^{-1} cm^{-1}; Section 2.3.3) is given by

$$\boxed{\kappa = F \sum_j |z_j| u_j C_j} \tag{4.2.8}$$

Equally, one can write an equation for the solution resistance in terms of ρ, the *resistivity* (Ω-cm), where $\rho = 1/\kappa$:

$$R = \frac{\rho l}{A} \tag{4.2.9}$$

The fraction of the total current that a given ion j carries is t_j, the *transference number* of j, given by

$$\boxed{t_j = \frac{i_j}{i} = \frac{|z_j| u_j C_j}{\sum_k |z_k| u_k C_k} = \frac{|z_j| C_j \lambda_j}{\sum_k |z_k| C_k \lambda_k}} \tag{4.2.10}$$

See also equations 2.3.11 and 2.3.18.

▶ 4.3 MIXED MIGRATION AND DIFFUSION NEAR AN ACTIVE ELECTRODE

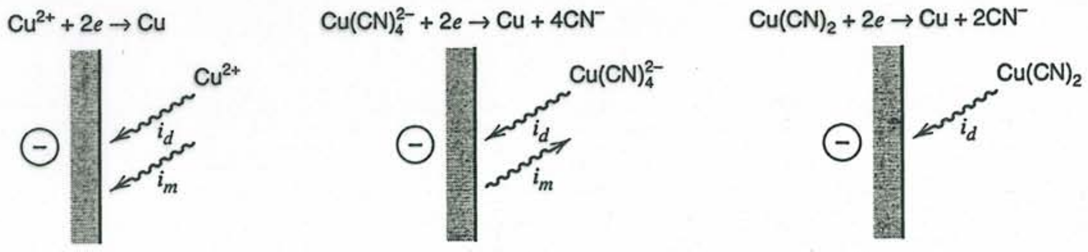
The relative contributions of diffusion and migration to the flux of a species (and of the flux of that species to the total current) differ at a given time for different locations in solution. Near the electrode, an electroactive substance is, in general, transported by both processes. The flux of an electroactive substance at the electrode surface controls the rate of reaction and, therefore, the faradaic current flowing in the external circuit (see Section 1.3.2). That current can be separated into diffusion and migration currents reflecting the diffusive and migrational components to the flux of the electroactive species at the surface:

$$\boxed{i = i_d + i_m} \tag{4.3.1}$$

look ↓

Note that i_m and i_d may be in the same or opposite directions, depending on the direction of the electric field and the charge on the electroactive species. Examples of three reductions—of a positively charged, a negatively charged, and an uncharged substance—are shown in Figure 4.3.1. The migrational component is always in the same direction as i_d for cationic species reacting at cathodes and for anionic species reacting at anodes. It opposes i_d when anions are reduced at cathodes and when cations are oxidized at anodes.

3 cases ✓



(*a*) $i = i_d + |i_m|$ (*b*) $i = i_d - |i_m|$ (*c*) $i = i_d$

Figure 4.3.1 Examples of reduction processes with different contributions of the migration current: (*a*) positively charged reactant, (*b*) negatively charged reactant, (*c*) uncharged reactant.

For many electrochemical systems, the mathematical treatments are simplified if the migrational component to the flux of the electroactive substance is made negligible. We discuss in this section the conditions under which that approximation holds. The topic is discussed in greater depth in references 7–10.

4.3.1 Balance Sheets for Mass Transfer During Electrolysis

Although migration carries the current in the bulk solution during electrolysis, diffusional transport also occurs in the vicinity of the electrodes, because concentration gradients of the electroactive species arise there. Indeed, under some circumstances, the flux of electroactive species to the electrode is due almost completely to diffusion. To illustrate these effects, let us apply the "balance sheet" approach (11) to transport in several examples.

Example 4.1
Consider the electrolysis of a solution of hydrochloric acid at platinum electrodes (Figure 4.3.2*a*). Since the equivalent ionic conductance of H^+, λ_+, and of Cl^-, λ_-, relate as $\lambda_+ \approx 4\lambda_-$, then from (4.2.10), $t_+ = 0.8$ and $t_- = 0.2$. Assume that a total current equivalent to $10e$ per unit time is passed through the cell, producing five H_2 molecules

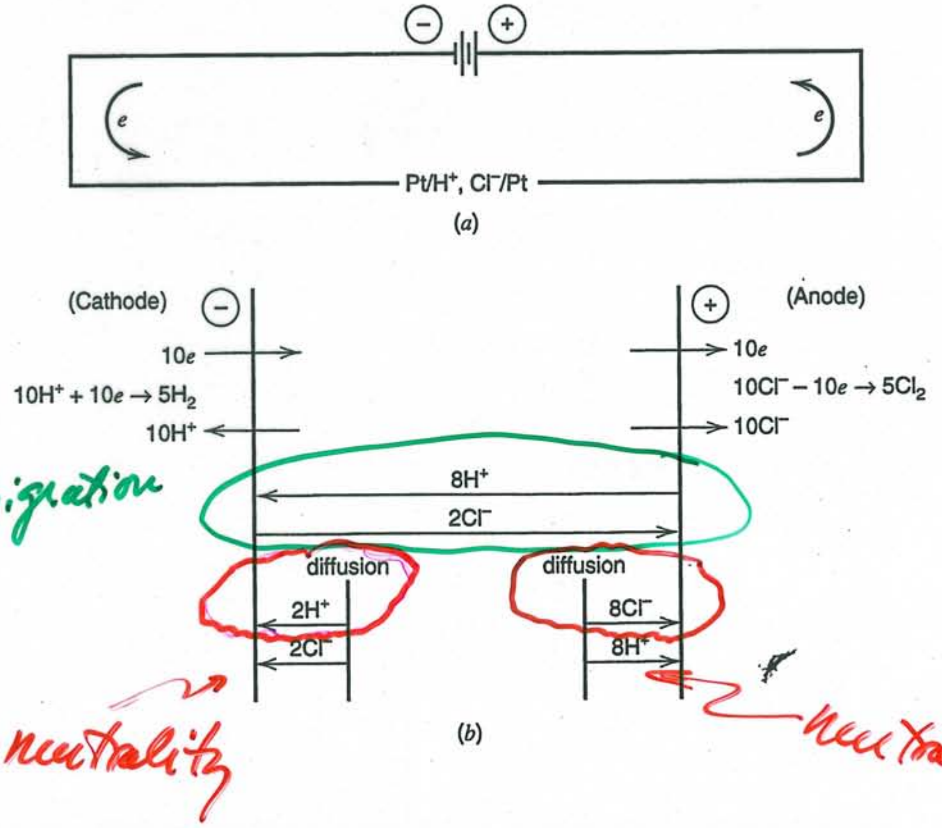


Figure 4.3.2 Balance sheet for electrolysis of hydrochloric acid solution. (*a*) Cell schematic. (*b*) Various contributions to the current when $10e$ are passed in the external circuit per unit time.

at the cathode and five Cl_2 molecules at the anode. (Actually, some O_2 could also be formed at the anode; for simplicity we neglect this reaction.) The total current is carried in the bulk solution by the movement of $8H^+$ toward the cathode and $2Cl^-$ toward the anode (Figure 4.3.2*b*). To maintain a steady current, 10 H^+ must be supplied to the cathode per unit time, so an additional $2H^+$ must diffuse to the electrode, bringing along $2Cl^-$ to maintain electroneutrality. Similarly at the anode, to supply 10 Cl^- per unit time, $8Cl^-$ must arrive by diffusion, along with $8H^+$. Thus, the different currents (in arbitrary *e* -units per unit time) are: for H^+, $i_d = 2$, $i_m = 8$; for Cl^-, $i_d = 8$, $i_m = 2$. The total current, *i*, is 10. Equation 4.3.1 holds, with migration in this case being in the same direction as diffusion.

use t_i

For mixtures of charged species, the fraction of current carried by the *j*th species is t_j; and the amount of the total current, *i*, carried by the *j*th species is $t_j i$. The number of moles of the *j*th species migrating per second is $t_j i/z_j F$. If this species is undergoing electrolysis, the number of moles electrolyzed per second is $|t_j i|/nF$, while the number of moles arriving at the electrode per second by migration is $\pm\, i_m/nF$, where the positive sign applies to reduction of *j*, and the negative sign pertains to oxidation. Thus,

$$\pm \frac{i_m}{nF} = \frac{t_j i}{z_j F} \tag{4.3.2}$$

or

$$i_m = \pm \frac{n}{z_j} t_j i \tag{4.3.3}$$

From equation 4.3.1,

$$\boxed{i_d = i - i_m} \tag{4.3.4}$$

electrolysis current

$$i_d = i\left(1 \mp \frac{n t_j}{z_j}\right) \tag{4.3.5}$$

where the minus sign is used for cathodic currents and the positive sign for anodic currents. Note that both *i* and z_j are signed.

In this simplified treatment, we assume that the transference numbers are essentially the same in the bulk solution and in the diffusion layer near an electrode. This will be true when the concentrations of ions in the solution are high, so that only small fractional changes in local concentration are caused by the electrolytic generation or removal of ions. This condition is met in most experiments. If the electrolysis significantly perturbs the ionic concentrations in the diffusion layer compared to those in the bulk solution, the t_j values clearly will differ, as shown by equation 4.2.10 (12).

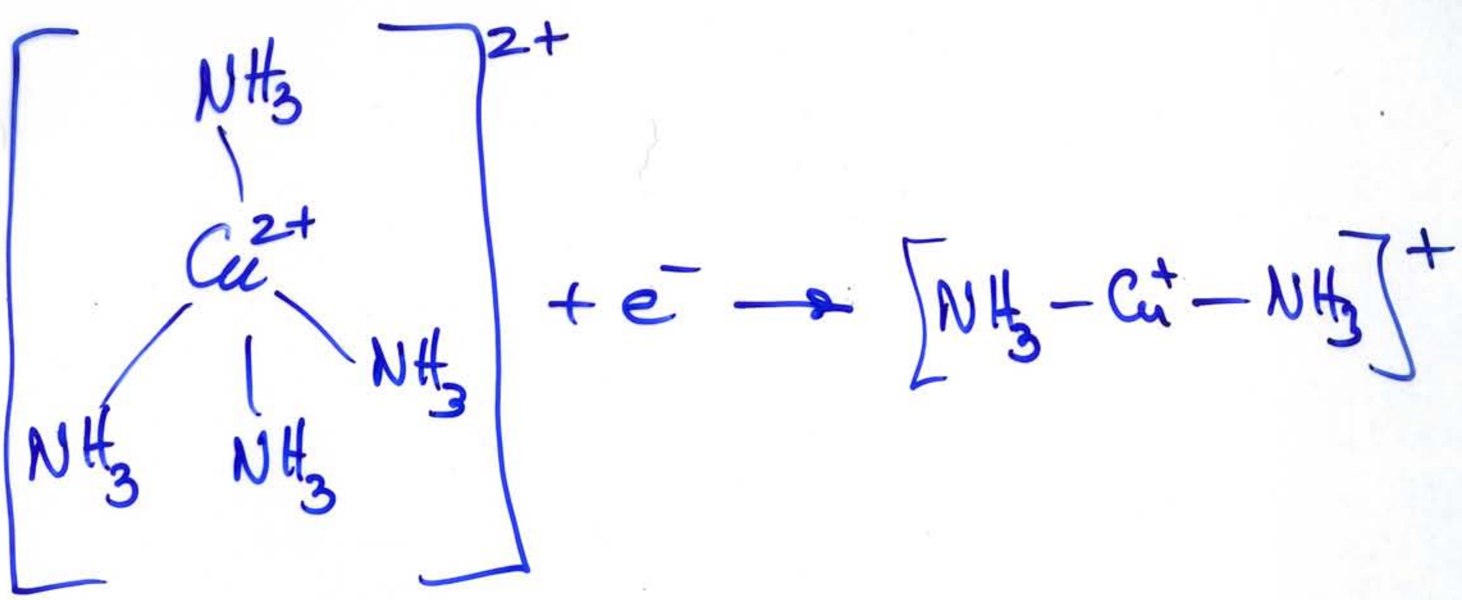
Example 4.2

Consider the electrolysis of a solution of 10^{-3} *M* $Cu(NH_3)_4^{2+}$, 10^{-3} *M* $Cu(NH_3)_2^+$, and 3×10^{-3} *M* Cl^- in 0.1 *M* NH_3 at two Hg electrodes (Figure 4.3.3*a*). Assuming the limiting equivalent conductances of all ions are equal, that is,

$Cu(TA)^{2+} + e \rightarrow Cu(DA)^{+}$

$$\lambda_{Cu(II)} = \lambda_{Cu(I)} = \lambda_{Cl^-} = \lambda \tag{4.3.6}$$

we obtain the following transference numbers from (4.2.10): $t_{Cu(II)} = 1/3$, $t_{Cu(I)} = 1/6$ and $t_{Cl^-} = 1/2$. With an arbitrary current of 6*e* per unit time being passed, the migration current in bulk solution is carried by movement of one Cu(II) and one Cu(I) toward the cathode, and three Cl^- toward the anode. The total balance sheet for this system is shown in Figure 4.3.3*b*. At the cathode, one-sixth of the current for the electrolysis of Cu(II) is provided by migration and five-sixths by diffusion. The NH_3, being uncharged, does not con-



$Cu(TA)Cl_2$ $10^{-3}M$

$\downarrow$

$Cu(TA)^{2+} + 2Cl^-$

10^{-3} 2×10^{-3}

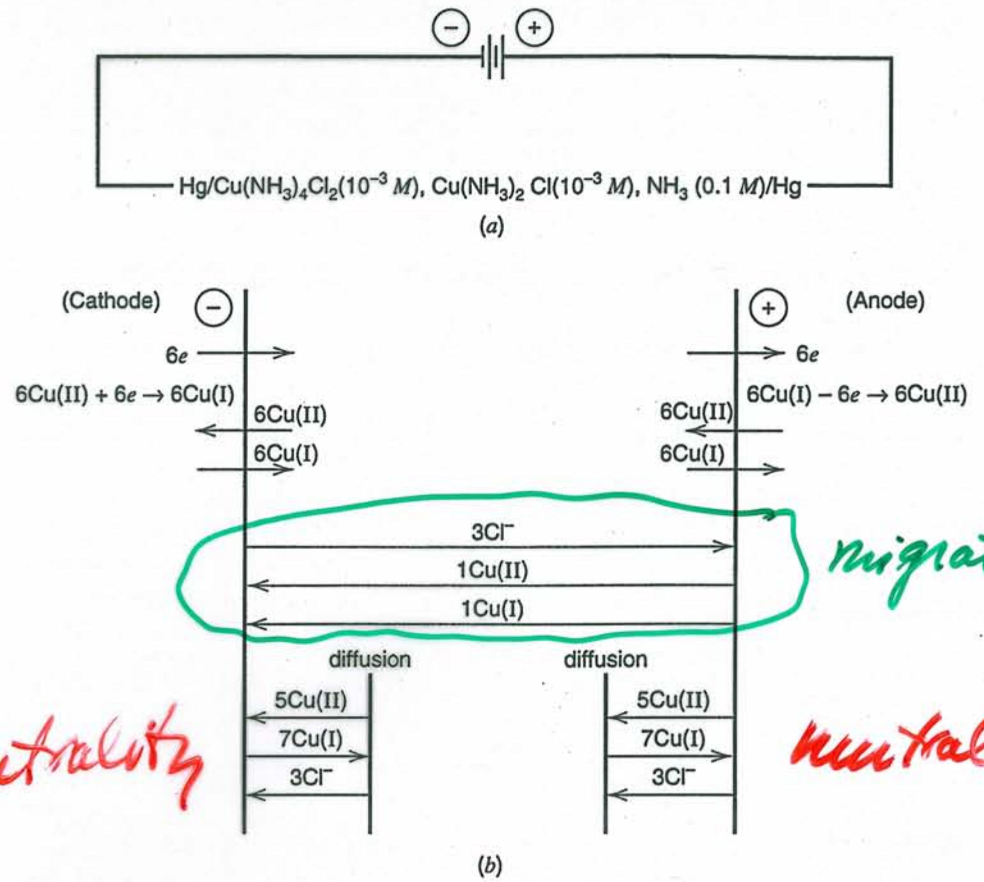
$Cu(DA)Cl$ 10^{-3}

$\downarrow$

$Cu(DA)^+ + Cl^-$

10^{-3} 10^{-3}

$$C_{Cl^-} = 3\times10^{-3}$$



migration

neutrality

neutrality

Figure 4.3.3 Balance sheet for electrolysis of the Cu(II), Cu(I), NH_3 system. (*a*) Cell schematic. (*b*) Various contributions to the current when 6*e* are passed in the external circuit per unit time; $i = 6$, $n = 1$. For Cu(II) at the cathode, $|i_m| = (1/2)(1/3)(6) = 1$ (equation 4.3.3), $i_d = 6 - 1 = 5$ (equation 4.3.4). For Cu(I) at the anode, $|i_m| = (1/1)(1/6)(6) = 1$, $i_d = 6 + 1 = 7$.

tribute to the carrying of the current, but serves only to stabilize the copper species in the +1 and +2 states. The resistance of this cell would be relatively large, since the total concentration of ions in the solution is small.

100 X Conc. of Solutes

4.3.2 Effect of Adding Excess Electrolyte

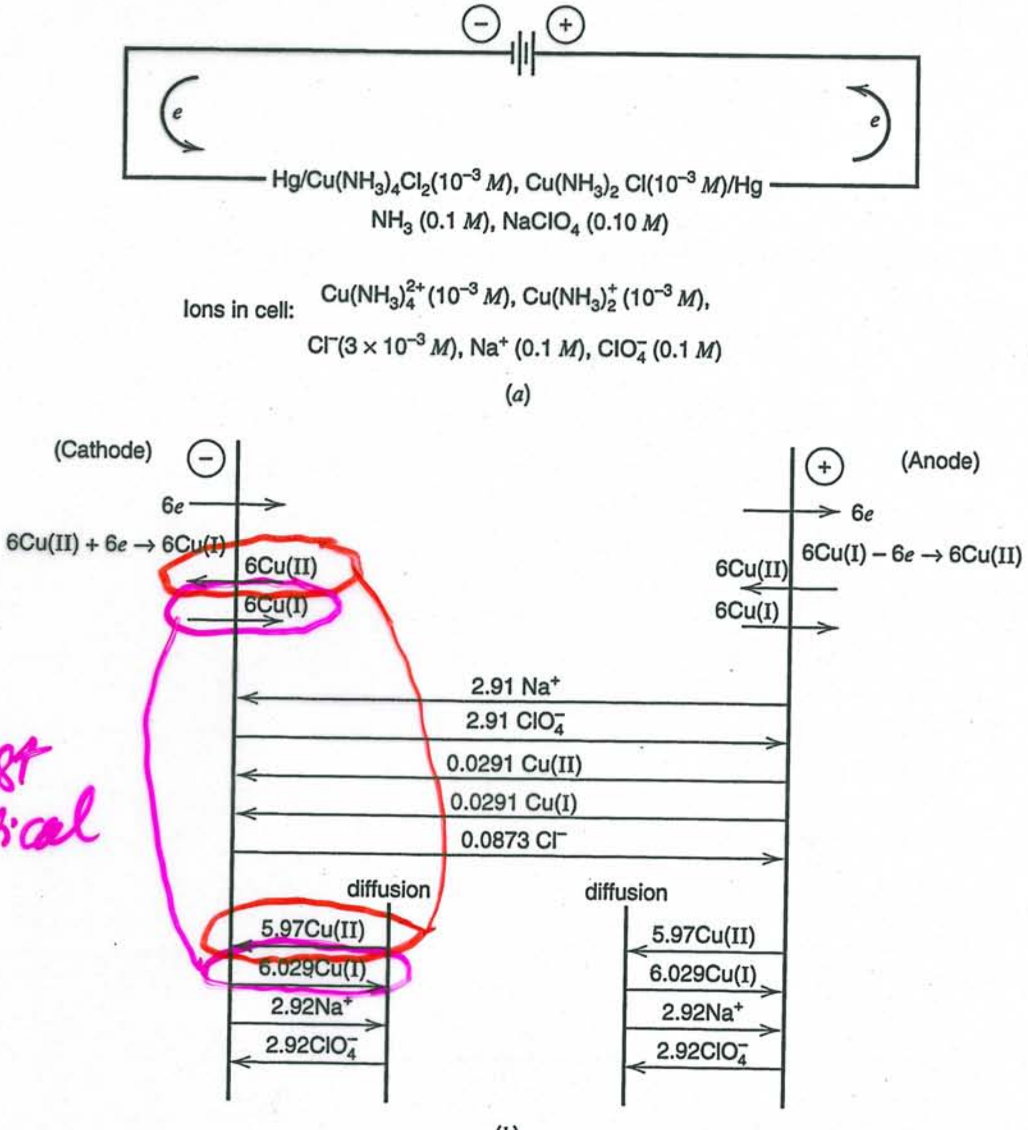
Example 4.3

Let us consider the same cell as in Example 4.2, except with the solution containing 0.10 *M* $NaClO_4$ as an excess electrolyte (Figure 4.3.4*a*). Assuming that $\lambda_{\mathrm{Na}^+} = \lambda_{\mathrm{ClO}_4^-} = \lambda$, we obtain the following transference numbers: $t_{\mathrm{Na}^+} = t_{\mathrm{ClO}_4^-}$, = 0.485, $t_{\mathrm{Cu(II)}} = 0.0097$, $t_{\mathrm{Cu(I)}} = 0.00485$, $t_{\mathrm{Cl}^-} = 0.0146$. The Na^+ and ClO_4^- do not participate in the electron-transfer reactions; but because their concentrations are high, they carry 97% of the current in the bulk solution. The balance sheet for this cell (Figure 4.3.4*b*) shows that most of the Cu(II) now reaches the cathode by diffusion, and only 0.5% of the total flux is by migration.

eqn 4.2.10

Thus, the addition of an excess of nonelectroactive ions (a *supporting electrolyte*) nearly eliminates the contribution of migration to the mass transfer of the electroactive species. In general, it simplifies the mathematical treatment of electrochemical systems by elimination of the $\nabla\phi$ or $\partial\phi/\partial x$ term in the mass transport equations (e.g., equations 4.1.10 and 4.1.11).

In addition to minimizing the contribution of migration, the supporting electrolyte serves other important functions. The presence of a high concentration of ions decreases

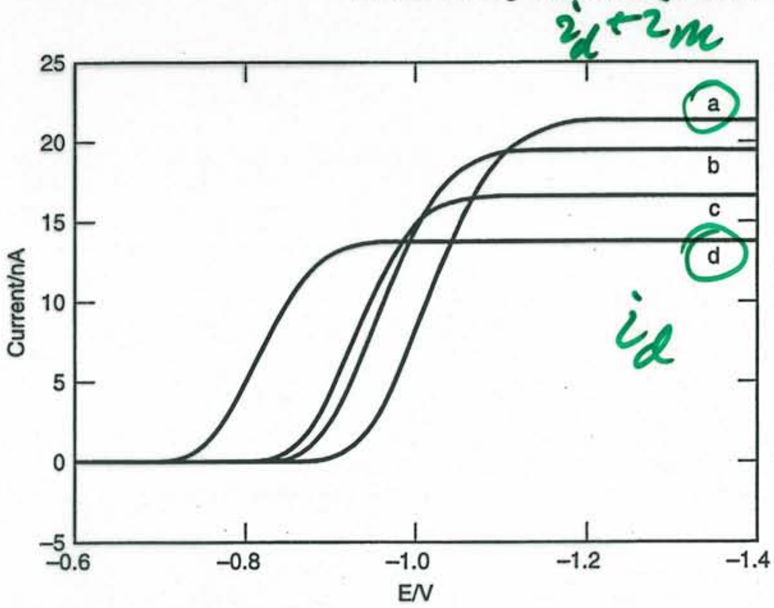


almost identical

Figure 4.3.4 Balance sheet for the system in Figure 4.3.3, but with excess NaClO$_4$ as a supporting electrolyte. (*a*) Cell schematic. (*b*) Various contributions to the current when 6*e* are passed in the external circuit per unit time ($i = 6, n = 1$). $t_{\mathrm{Cu(II)}} = [(2 \times 10^{-3})\lambda/(2 \times 10^{-3} + 10^{-3} + 3 \times 10^{-3} + 0.2)\lambda] = 0.0097$. For Cu(II) at the cathode, $|i_m| = (1/2)(0.0097)(6) = 0.03$, $i_d = 6 - 0.03 = 5.97$.

the solution resistance, and hence the uncompensated resistance drop, between the working and reference electrodes (Section 1.3.4). Consequently, the supporting electrolyte allows an improvement in the accuracy with which the working electrode's potential is controlled or measured (Chapter 15). Improved conductivity in the bulk of the solution also reduces the electrical power dissipated in the cell and can lead to important simplifications in apparatus (Chapters 11 and 15). Beyond these physical benefits are chemical contributions by the supporting electrolyte, for it frequently establishes the solution composition (pH, ionic strength, ligand concentration) that controls the reaction conditions (Chapters 5, 7, 11, and 12). In analytical applications, the presence of a high concentration of electrolyte, which is often also a buffer, serves to decrease or eliminate sample matrix effects. Finally, the supporting electrolyte ensures that the double layer remains thin with respect to the diffusion layer (Chapter 13), and it establishes a uniform ionic strength throughout the solution, even when ions are produced or consumed at the electrodes.

Supporting electrolytes also bring some disadvantages. Because they are used in such large concentrations, their impurities can present serious interferences, for example,



as Conc. $Tl^+ \uparrow$
$i_l \uparrow$

as Conc. $LiClO_4 \uparrow$
$i_l \downarrow$
even at constant
C_{Tl^+}

Figure 4.3.5 Voltammograms for reduction of 0.65 m*M* Tl_2SO_4 at a mercury film on a silver ultramicroelectrode (radius, 15 μm) in the presence of (*a*) 0, (*b*) 0.1, (*c*) 1, and (*d*) 100 m*M* $LiClO_4$. The potential was controlled *vs.* a Pt wire QRE whose potential was a function of solution composition. This variability is the basis for the shifts in wave position along the potential axis. [Reprinted with permission from M. Ciszkowska and J. G. Osteryoung, *Anal. Chem.*, **67**, 1125 (1995). Copyright 1995, American Chemical Society.]

by giving rise to faradaic responses of their own, by reacting with the intended product of an electrode process, or by adsorbing on the electrode surface and altering kinetics. Also, a supporting electrolyte significantly alters the medium in the cell, so that its properties differ from those of the pure solvent. The difference can complicate the comparison of results obtained in electrochemical experiments (e.g., thermodynamic data) with data from other kinds of experiments where pure solvents are typically employed.

Most electrochemical studies are carried out in the presence of a supporting electrolyte selected for the solvent and electrode process of interest. Many acids, bases, and salts are available for aqueous solutions. For organic solvents with high dielectric constants, like acetonitrile and N,N-dimethylformamide, normal practice is to employ tetra-*n*-alkylammonium salts, such as, Bu_4NBF_4 and Et_4NClO_4 (Bu = *n*-butyl, Et = ethyl). Studies in low-dielectric solvents like benzene inevitably involve solutions of high resistance, because most ionic salts do not dissolve in them to an appreciable extent. In solutions of salts that do dissolve in apolar media, such as Hx_4NClO_4 (where Hx = *n*-hexyl), ion pairing is extensive.

Studies in very resistive solutions require the use of UMEs, which usually pass low currents that do not give rise to appreciable resistive drops (see Section 5.9.2). The effect of supporting electrolyte concentration on the limiting steady-state current at UMEs has been treated (12–14). Typical results, shown in Figure 4.3.5, illustrate how the limiting current for reduction of Tl^+ to the amalgam at a mercury film decreases with an increase in $LiClO_4$ concentration (15). The current in the absence of $LiClO_4$, or at very low concentrations, is appreciably larger than at high concentrations, because migration of the positively charged Tl(I) species to the cathode enhances the current. At high $LiClO_4$ concentrations, Li^+ migration replaces that of Tl^+, and the observed current is essentially a pure diffusion current. A similar example involving the polarography of Pb(II) with KNO_3 supporting electrolyte was given in the first edition.[1]

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[1] First edition, p. 127.

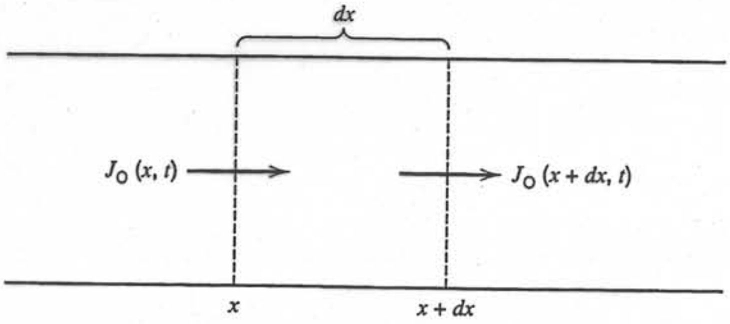

Figure 4.4.4 Fluxes into and out of an element at x.

and from equation 4.4.9 we obtain

$$-\frac{\partial J(x, t)}{\partial x} = \frac{\partial}{\partial x} D_O \frac{\partial C_O(x, t)}{\partial x} \tag{4.4.15}$$

Combination of equations 4.4.13 to 4.4.15 yields

$$\frac{\partial C_O(x, t)}{\partial t} = \left(\frac{\partial}{\partial x}\right)\left[D_O\left(\frac{\partial C_O(x, t)}{\partial x}\right)\right] \tag{4.4.16}$$

When D_O is not a function of x, (4.4.12) results.

In most electrochemical systems, the changes in solution composition caused by electrolysis are sufficiently small that variations in the diffusion coefficient with x can be neglected. However when the electroactive component is present at a high concentration, large changes in solution properties, such as the local viscosity, can occur during electrolysis. For such systems, (4.4.12) is no longer appropriate, and more complicated treatments are necessary (24, 25). Under these conditions, migrational effects can also become important.

We will have many occasions in future chapters to solve (4.4.12) under a variety of boundary conditions. Solutions of this equation yield *concentration profiles*, $C_O(x, t)$.

The general formulation of Fick's second law for any geometry is

$$\boxed{\frac{\partial C_O}{\partial t} = D_O \nabla^2 C_O} \tag{4.4.17}$$

where ∇^2 is the Laplacian operator. Forms of ∇^2 for different geometries are given in Table 4.4.2. Thus, for problems involving a planar electrode (Figure 4.4.5*a*), the linear diffusion equation, (4.4.12), is appropriate. For problems involving a spherical electrode

TABLE 4.4.2 Forms of the Laplacian Operator for Different Geometries[a]

Type	Variables	∇^2	Example
Linear	x	$\partial^2/\partial x^2$	Shielded disk electrode
Spherical	r	$\partial^2/\partial r^2 + (2/r)(\partial/\partial r)$	Hanging drop electrode
Cylindrical (axial)	r	$\partial^2/\partial r^2 + (1/r)(\partial/\partial r)$	Wire electrode
Disk	r, z	$\partial^2/\partial r^2 + (1/r)(\partial/\partial r) + \partial^2/\partial z^2$	Inlaid disk ultramicroelectrode[b]
Band	x, z	$\partial^2/\partial x^2 + \partial^2/\partial z^2$	Inlaid band electrode[c]

[a] See also J. Crank, "The Mathematics of Diffusion," Clarendon, Oxford, 1976.

[b] r = radial distance measured from the center of the disk; z = distance normal to the disk surface.

[c] x = distance in the plane of the band; z = distance normal to the band surface.

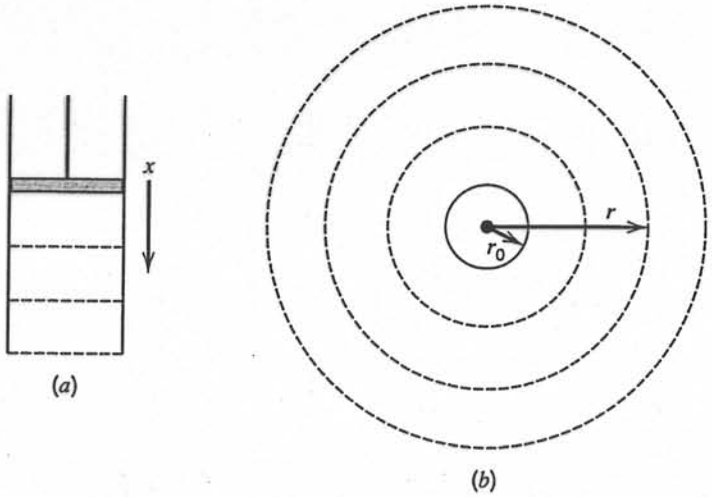

Figure 4.4.5 Types of diffusion occurring at different electrodes. (*a*) Linear diffusion to a planar electrode. (*b*) Spherical diffusion to a hanging drop electrode.

(Figure 4.4.5*b*), such as the hanging mercury drop electrode (HMDE), the spherical form of the diffusion equation must be employed:

$$\boxed{\frac{\partial C_{\mathrm{O}}(r,t)}{\partial t} = D_{\mathrm{O}}\left(\frac{\partial^2 C_{\mathrm{O}}(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial C_{\mathrm{O}}(r,t)}{\partial r}\right)} \tag{4.4.18}$$

The difference between the linear and spherical equations arises because spherical diffusion takes place through an increasing area as *r* increases.

Consider the situation where O is an electroactive species transported purely by diffusion to an electrode, where it undergoes the electrode reaction

$$\mathrm{O} + ne \rightleftarrows \mathrm{R} \tag{4.4.19}$$

If no other electrode reactions occur, then the current is related to the flux of O at the electrode surface ($x = 0$), $J_{\mathrm{O}}(0, t)$, by the equation

$$\boxed{-J_{\mathrm{O}}(0,t) = \frac{i}{nFA} = D_{\mathrm{O}}\left[\frac{\partial C_{\mathrm{O}}(x,t)}{\partial x}\right]_{x=0}} \tag{4.4.20}$$

because the total number of electrons transferred at the electrode in a unit time must be proportional to the quantity of O reaching the electrode in that time period. This is an extremely important relationship in electrochemistry, because it is the link between the evolving concentration profile near the electrode and the current flowing in an electrochemical experiment. We will draw upon it many times in subsequent chapters.

If several electroactive species exist in the solution, the current is related to the sum of their fluxes at the electrode surface. Thus, for *q* reducible species,

$$\frac{i}{FA} = -\sum_{\mathrm{k}=1}^{\mathrm{q}} n_{\mathrm{k}} J_{\mathrm{k}}(0,t) = \sum_{\mathrm{k}=1}^{\mathrm{q}} n_{\mathrm{k}} D_{\mathrm{k}}\left[\frac{\partial C_{\mathrm{k}}(x,t)}{\partial x}\right]_{x=0} \tag{4.4.21}$$

4.4.3 Boundary Conditions in Electrochemical Problems

In solving the mass-transfer part of an electrochemical problem, a diffusion equation (or, in general, a mass-transfer equation) is written for each dissolved species (O, R, . . .). The solution of these equations, that is, the discovery of an equation expressing C_{O}, C_{R}, . . . as functions of *x* and *t*, requires that an initial condition (the concentration profile at

$t = 0$) and two boundary conditions (functions applicable at certain values of x) be given for each diffusing species. Typical initial and boundary conditions include the following.

(a) Initial Conditions

These are usually of the form

$$C_{\rm O}(x, 0) = f(x) \tag{4.4.22}$$

For example, if O is uniformly distributed throughout the solution at a bulk concentration $C_{\rm O}^*$ at the start of the experiment, the initial condition is

$$C_{\rm O}(x, 0) = C_{\rm O}^* \qquad \text{(for all } x) \tag{4.4.23}$$

If R is initially absent from the solution, then

$$C_{\rm R}(x, 0) = 0 \qquad \text{(for all } x) \tag{4.4.24}$$

(b) Semi-infinite Boundary Conditions

The electrolysis cell is usually large compared to the length of diffusion; hence the solution at the walls of the cell is not altered by the process at the electrode (see Section 5.2.1). One can normally assume that at large distances from the electrode ($x \rightarrow \infty$) the concentration reaches a constant value, typically the initial concentration, so that, for example,

$$\lim_{x\rightarrow\infty} C_{\rm O}(x, t) = C_{\rm O}^* \qquad \text{(at all } t) \tag{4.4.25}$$

$$\lim_{x\rightarrow\infty} C_{\rm R}(x, t) = 0 \qquad \text{(at all } t) \tag{4.4.26}$$

For thin-layer electrochemical cells (Section 11.7), where the cell wall is at a distance, l, of the order of the diffusion length, one must use boundary conditions at $x = l$ instead of those for $x \rightarrow \infty$.

(c) Electrode Surface Boundary Conditions

Additional boundary conditions usually relate to concentrations or concentration gradients at the electrode surface. For example, if the potential is controlled in an experiment, one might have

$$C_{\rm O}(0, t) = f(E) \tag{4.4.27}$$

$$\frac{C_{\rm O}(0, t)}{C_{\rm R}(0, t)} = f(E) \tag{4.4.28}$$

where $f(E)$ is some function of the electrode potential derived from the general current-potential characteristic or one of its special cases (e.g., the Nernst equation).

If the current is the controlled quantity, the boundary condition is expressed in terms of the flux at $x = 0$; for example,

$$-J_{\rm O}(0, t) = \frac{i}{nFA} = D_{\rm O}\left[\frac{\partial C_{\rm O}(x, t)}{\partial x}\right]_{x=0} = f(t) \tag{4.4.29}$$

The conservation of matter in an electrode reaction is also important. For example, when O is converted to R at the electrode and both O and R are soluble in the solution phase, then for each O that undergoes electron transfer at the electrode, an R must be produced. Consequently, $J_{\rm O}(0, t) = -J_{\rm R}(0, t)$, and

$$D_{\rm O}\left[\frac{\partial C_{\rm O}(x, t)}{\partial x}\right]_{x=0} + D_{\rm R}\left[\frac{\partial C_{\rm R}(x, t)}{\partial x}\right]_{x=0} = 0 \tag{4.4.30}$$

4.4.4 Solution of Diffusion Equations

In the chapters that follow, we will examine the solution of the diffusion equations under a variety of conditions. The analytical mathematical methods for attacking these problems are discussed briefly in Appendix A. Numerical methods, including digital simulations (Appendix B), are also frequently employed.

Sometimes one is interested only in the steady-state solution (e.g., with rotating disk electrodes or ultramicroelectrodes). Since $\partial C_{\mathrm{O}}/\partial t = 0$ in such a situation, the diffusion equation simply becomes

$$\nabla^2 C_{\mathrm{O}} = 0 \tag{4.4.31}$$

Occasionally, solutions can be found by searching the literature concerning analogous problems. For example, the conduction of heat involves equations of the same form as the diffusion equation (26, 27);

$$\partial T/\partial t = \alpha_{\mathrm{i}} \nabla^2 T \tag{4.4.32}$$

where T is the temperature, and $\alpha_{\mathrm{i}} = \kappa/\rho s$ (κ = thermal conductivity, ρ = density, and s = specific heat). If one can find the solution of a problem of interest in terms of the temperature distribution, such as, $T(x, t)$, or heat flux, one can easily transpose the results to give concentration profiles and currents.

Electrical analogies also exist. For example, the steady-state diffusion equation, (4.4.31), is of the same form as that for the potential distribution in a region of space not occupied by electrically charged bodies (Laplace's equation),

$$\nabla^2 \phi = 0 \tag{4.4.33}$$

If one can solve an electrical problem in terms of the current density, j, where

$$-j = \kappa \nabla \phi \tag{4.4.34}$$

(where κ is the conductivity), one can write the solution to an analogous diffusion problem (as the function C_{O}) and find the flux from equation 4.4.20 or from the more general form,

$$-J = D_{\mathrm{O}} \nabla C_{\mathrm{O}} \tag{4.4.35}$$

This approach has been employed, for example, in determining the steady-state uncompensated resistance at an ultramicroelectrode (28) and the solution resistance between an ion-selective electrode tip and a surface in a scanning electrochemical microscope (29, 30). It also is sometimes possible to model the mass transport and kinetics in an electrochemical system by a network of electrical components (31, 32). Since there are a number of computer programs (e.g., SPICE) for the analysis of electric circuits, this approach can be convenient for certain electrochemical problems.

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