CHAPTER 1

INTRODUCTION

Electrochemical techniques are used for the production of aluminum and chlorine, the conversion of energy in batteries and fuel cells, sensors, electroplating, and the protection of metal structures against corrosion, to name just a few prominent applications. While applications such as fuel cells and electroplating may seem quite disparate, in this book we show that a few basic principles form the foundation for the design of all electrochemical processes.

The first practical electrochemical system was the Volta pile, invented by Alexander Volta in 1800. Volta's pile is still used today in batteries for a variety of industrial, medical, and military applications. Volta found that when he made a sandwich of a layer of zinc metal, paper soaked in salt water, and tarnished silver and then connected a wire from the zinc to the silver, he could obtain electricity (see Figure 1.1). What is happening when the wire is connected? Electrons have a chemical preference to be in the silver rather than the zinc, and this chemical preference is manifest as a voltage difference that drives the current. At each electrode, an electrochemical reaction is occurring: zinc reacts with hydroxide ions in solution to form free electrons, zinc oxide, and water, while silver oxide (tarnished silver) reacts with water and electrons to form silver and hydroxide ions. Hydroxide ions travel through the salt solution (the electrolyte) from the silver to the zinc, while electrons travel through the external wire from the zinc to the silver.

We see from this example that many phenomena interact in electrochemical systems. Driving forces for reaction are determined by the thermodynamic properties of the electrodes and electrolyte. The rate of the reaction at the interface in

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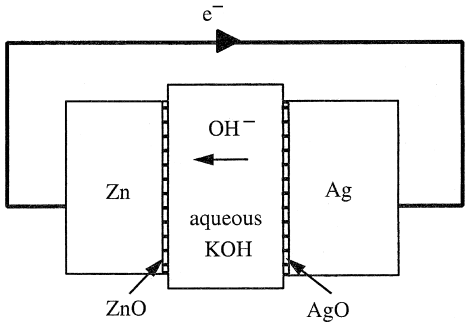

Figure 1.1 Volta's first battery, comprised of a sandwich of zinc with its oxide layer, salt solution, and silver with its oxide layer. While the original Volta pile used an electrolyte of NaCl in water, modern batteries use aqueous KOH to increase the conductivity and the concentration of OH^-.

response to this driving force depends on kinetic rate parameters. Finally, mass must be transported through the electrolyte to bring reactants to the interface, and electrons must travel through the electrodes. The total resistance is therefore a combination of the effects of reaction kinetics and mass and electron transfer. Each of these phenomena—thermodynamics, kinetics, and transport—is addressed separately in subsequent chapters. In this chapter, we define basic terminology and give an overview of the principal concepts that will be derived in subsequent chapters.

1.1 DEFINITIONS

Every electrochemical system must contain two electrodes separated by an electrolyte and connected via an external electronic conductor. Ions flow through the electrolyte from one electrode to the other, and the circuit is completed by electrons flowing through the external conductor.

An *electrode* is a material in which electrons are the mobile species and therefore can be used to sense (or control) the potential of electrons. It may be a metal or other electronic conductor such as carbon, an alloy or intermetallic compound, one of many transition-metal chalcogenides, or a semiconductor. In particular, in electrochemistry an electrode is considered to be an electronic conductor that carries out an electrochemical reaction or some similar interaction with an adjacent phase. Electronic conductivity generally decreases slightly with increasing temperature and is of the order 10^2 to 10^4 S/cm, where a siemen (S) is an inverse ohm.

An *electrolyte* is a material in which the mobile species are ions and free movement of electrons is blocked. Ionic conductors include molten salts, dissociated salts in solution, and some ionic solids. In an ionic conductor, neutral salts are found to be dissociated into their component ions. We use the term *species* to refer to ions as well as neutral molecular components that do not dissociate. Ionic conductivity

generally increases with increasing temperature and is of the order 10^{-4} to 10^{-1} S/cm, although it can be substantially lower.

In addition to these two classes of materials, some materials are *mixed conductors*, in which charge can be transported by both electrons and ions. Mixed conductors are occasionally used in electrodes, for example, in solid-oxide fuel cells.

Thus the key feature of an electrochemical cell is that it contains two electrodes that allow transport of electrons, separated by an electrolyte that allows movement of ions but blocks movement of electrons. To get from one electrode to the other, electrons must travel through an external conducting circuit, doing work or requiring work in the process.

The primary distinction between an electrochemical reaction and a chemical redox reaction is that, in an electrochemical reaction, reduction occurs at one electrode and oxidation occurs at the other, while in a chemical reaction, both reduction and oxidation occur in the same place. This distinction has several implications. In an electrochemical reaction, oxidation is spatially separated from reduction. Thus, the complete redox reaction is broken into two *half-cells*. The rate of these reactions can be controlled by externally applying a potential difference between the electrodes, for example, with an external power supply, a feature absent from the design of chemical reactors. Finally, electrochemical reactions are always heterogeneous; that is, they always occur at the interface between the electrolyte and an electrode (and possibly a third phase such as a gaseous or insulating reactant).

Even though the half-cell reactions occur at different electrodes, the rates of reaction are coupled by the principles of conservation of charge and *electroneutrality*. As we demonstrate in Section 3.1, a very large force is required to bring about a spatial separation of charge. Therefore, the flow of current is continuous: All of the current that leaves one electrode must enter the other. At the interface between the electrode and the electrolyte, the flow of current is still continuous, but the identity of the charge-carrying species changes from being an electron to being an ion. This change is brought about by a charge-transfer (i.e., electrochemical) reaction. In the electrolyte, electroneutrality requires that there be the same number of equivalents of cations as anions:

$$\sum_i z_i c_i = 0, \tag{1.1}$$

where the sum is over all species i in solution, and c_i and z_i are the concentration and the charge number of species i, respectively. For example, $z_{Zn^{2+}}$ is $+2$, z_{OH^-} is -1, and z_{H_2O} is 0.

Faraday's law relates the rate of reaction to the current. It states that the rate of production of a species is proportional to the current, and the total mass produced is proportional to the amount of charge passed multiplied by the equivalent weight of the species:

$$m_i = -\frac{s_i M_i I t}{nF}, \tag{1.2}$$

where m_i is the mass of species i produced by a reaction in which its *stoichiometric coefficient* is s_i and n electrons are transferred, M_i is the molecular weight, F is Faraday's constant, equal to 96,487 coulombs/equivalent, and the total amount of charge passed is equal to the current I multiplied by time t. The sign of the stoichiometric coefficient is determined by the convention of writing an electrochemical reaction in the form

$$\sum_i s_i M_i^{z_i} \rightleftharpoons n\mathrm{e}^-, \tag{1.3}$$

where here M_i is the symbol for the chemical formula of species i. For example, for the reaction

$$\mathrm{Zn} + 2\mathrm{OH}^- \rightleftharpoons \mathrm{ZnO} + 2\mathrm{e}^- + \mathrm{H_2O}, \tag{1.4}$$

s_{ZnO} is -1, s_{OH^-} is 2, and n is 2.

Following historical convention, current is defined as the flow of positive charge. Thus, electrons move in the direction opposite to that of the convention for current flow. *Current density* is the flux of charge, that is, the rate of flow of positive charge per unit area perpendicular to the direction of flow. The behavior of electrochemical systems is determined more by the current density than by the total current, which is the product of the current density and the cross-sectional area. In this text, the symbol i refers to current density unless otherwise specified.

Owing to the historical development of the field of electrochemistry, several terms are in common use. *Polarization* refers to the departure of the potential from equilibrium conditions caused by the passage of current. *Overpotential* refers to the magnitude of this potential drop caused by resistance to the passage of current. Below, we will discuss different types of resistances that cause overpotential.

1.2 THERMODYNAMICS AND POTENTIAL

If one places a piece of tarnished silver in a basin of salt water and connects the silver to a piece of zinc, the silver spontaneously will become shiny, and the zinc will dissolve. Why? An electrochemical reaction is occurring in which silver oxide is reduced to silver metal while zinc metal is oxidized. It is the thermodynamic properties of silver, silver oxide, zinc, and zinc oxide that determine that silver oxide is reduced spontaneously at the expense of zinc (as opposed to reducing zinc oxide at the expense of the silver). These thermodynamic properties are the *electrochemical potentials*. Let us arbitrarily call one half-cell the right electrode and the other the left electrode. The energy change for the reaction is given by the change in Gibbs free energy for each half-cell reaction:

$$\Delta G = \left(\sum_i s_i \mu_i\right)_{\text{right}} - \left(\sum_i s_i \mu_i\right)_{\text{left}}, \tag{1.5}$$

where G is the Gibbs free energy, μ_i is the electrochemical potential of species i, and s_i is the stoichiometric coefficient of species i, as defined by equation 1.3. If ΔG for the reaction with our arbitrary choice of right and left electrodes is negative, then the electrons will want to flow spontaneously from the left electrode to the right electrode. The right electrode is then the more positive electrode, which is the electrode in which the electrons have a lower electrochemical potential. This is equivalent to saying that ΔG is equal to the free energy of the products minus the free energy of the reactants.

Now imagine that instead of connecting the silver directly to the zinc, we connect them via a high-impedance potentiostat, and we adjust the potential across the potentiostat until no current is flowing between the silver and the zinc. (A *potentiostat* is a device that can apply a potential, while a *galvanostat* is a device that can control the applied current. If the potentiostat has a high internal impedance (resistance), then it draws little current in measuring the potential.) The potential at which no current flows is called the *equilibrium* or *open-circuit* potential, denoted by the symbol U. This equilibrium potential is related to the Gibbs free energy by

$$\Delta G = -nFU. \tag{1.6}$$

The equilibrium potential is thus a function of the intrinsic nature of the species present, as well as their concentrations and, to a lesser extent, temperature.

While no net current is flowing at equilibrium, random thermal collisions among reactant and product species still cause reaction to occur, sometimes in the forward direction and sometimes in the backward direction. At equilibrium, the rate of the forward reaction is equal to the rate of the backward reaction. The potential of the electrode at equilibrium is a measure of the electrochemical potential (i.e., energy) of electrons in equilibrium with the reactant and product species. Electrochemical potential will be defined in more detail in Chapter 2. In brief, the electrochemical potential can be related to the molality m_i and activity coefficient γ_i by

$$\mu_i = \mu_i^\theta + RT \ln m_i \gamma_i, \tag{1.7}$$

where μ^θ is independent of concentration, R is the universal gas constant (8.3143 $\mathrm{J/mol \cdot K}$), and T is temperature in kelvin. If one assumes that all activity coefficients are equal to 1, then equation 1.5 reduces to the Nernst equation

$$U = U^\theta - \frac{RT}{nF} \ln \left(\prod_i m_i^{s_i} \right)_{\text{right}} + \frac{RT}{nF} \ln \left(\prod_i m_i^{s_i} \right)_{\text{left}}, \tag{1.8}$$

which relates the equilibrium potential to the concentrations of reactants and products. In many texts, one sees equation 1.8 without the "left" term. It is then implied that one is measuring the potential of the right electrode with respect to some unspecified left electrode.

By connecting an electrode to an external power supply, one can electrically control the electrochemical potential of electrons in the electrode, thereby

perturbing the equilibrium and driving a reaction. Applying a negative potential to an electrode increases the energy of electrons. Increasing the electrons' energy above the lowest unoccupied molecular orbital of a species in the adjacent electrolyte will cause reduction of that species (see Figure 1.2). This reduction current (flow of electrons into the electrode and from there into the reactant) is also called a *cathodic* current, and the electrode at which it occurs is called the *cathode*. Conversely, applying a positive potential to an electrode decreases the energy of electrons, causing electrons to be transferred from the reactants to the electrode. The electrode where such an oxidation reaction is occurring is called the *anode*. Thus, applying a positive potential relative to the equilibrium potential of the electrode will drive the reaction in the anodic direction; that is, electrons will be removed from the reactants. Applying a negative potential relative to the equilibrium potential will drive the reaction in the cathodic direction. Anodic currents are defined as positive (flow of positive charges into the solution from the electrode) while cathodic currents are negative. Common examples of cathodic reactions include deposition of a metal from its salt and evolution of H_2 gas, while common anodic reactions include corrosion of a metal and evolution of O_2 or Cl_2.

Note that one cannot control the potential of an electrode by itself. Potential must always be controlled relative to another electrode. Similarly, potentials can be measured only relative to some reference state. While it is common in the physics literature to use the potential of an electron in a vacuum as the reference state (see Chapter 3), electrochemists generally use a *reference electrode*, an electrode designed so that its potential is well-defined and reproducible. A potential is well-defined if both reactant and product species are present and the kinetics of the reaction is sufficiently fast that the species are present in their equilibrium concentrations. Since potential is measured with a high-impedance voltmeter, negligible current passes through a reference electrode. Chapter 5 discusses commonly used reference electrodes.

Electrochemical cells can be divided into two categories: *galvanic cells*, which spontaneously produce work, and *electrolytic cells*, which require an input of work

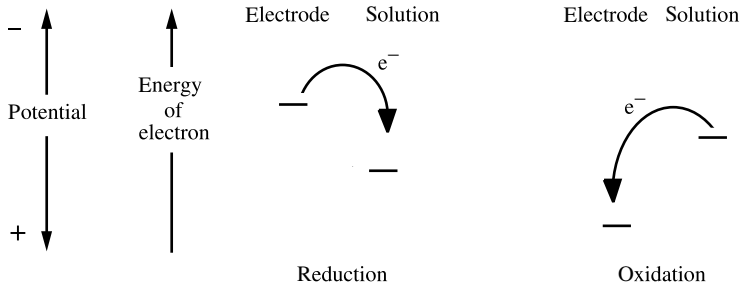

Figure 1.2 Schematic of the relative energy of the electron in reduction and oxidation reactions. During a reduction reaction, electrons are transferred from the electrode to the lowest unoccupied energy level of a reactant species. During oxidation, electrons are transferred from the highest occupied energy level of the reactant to the electrode.

to drive the reaction. Galvanic applications include discharge of batteries and fuel cells. Electrolytic applications include charging batteries, electroplating, electrowinning, and electrosynthesis. In a galvanic cell, connecting the positive and negative electrodes causes a driving force for charge transfer that decreases the potential of the positive electrode, driving its reaction in the cathodic direction, and increases the potential of the negative electrode, driving its reaction in the anodic direction. Conversely, in an electrolytic cell, a positive potential (positive with respect to the equilibrium potential of the positive electrode) is applied to the positive electrode to force the reaction in the anodic direction, while a negative potential is applied to the negative electrode to drive its reaction in the cathodic direction. Thus, the positive electrode is the anode in an electrolytic cell while it is the cathode in a galvanic cell, and the negative electrode is the cathode in an electrolytic cell and the anode in a galvanic cell.

1.3 KINETICS AND RATES OF REACTION

Imagine that we have a system with three electrodes: a zinc negative electrode, a silver positive electrode, and another zinc electrode, all immersed in a beaker of aqueous KOH (see Figure 1.1). We pass current between the negative and positive electrodes. For the moment, let us just focus on one electrode, such as the zinc negative electrode. Since it is our electrode of interest, we call it the *working electrode*, and the other electrode through which current passes is termed the *counterelectrode*. The second zinc electrode will be placed in solution and connected to the working electrode through a high-impedance voltmeter. This second zinc electrode is in equilibrium with the electrolyte since no current is passing through it. We can therefore use this electrode as a reference electrode to probe changes in the potential in the electrolyte relative to the potential of the working electrode.

As mentioned above, a driving force is required to force an electrochemical reaction to occur. Imagine that we place our reference electrode in the solution adjacent to the working electrode. Recall that our working and reference electrodes are of the same material composition. Since no current is flowing at the reference electrode, and a potential has been applied to the working electrode to force current to flow, the difference in potential between the two electrodes must be the driving force for reaction. This driving force is termed the *surface overpotential* and is given the symbol η_s. The rate of reaction often can be related to the surface overpotential by the *Butler–Volmer equation*, which has the form

$$i = i_0\left[\exp\left(\frac{\alpha_a F}{RT}\eta_s\right) - \exp\left(-\frac{\alpha_c F}{RT}\eta_s\right)\right]. \tag{1.9}$$

A positive η_s produces a positive (anodic) current. The derivation and application of the Butler–Volmer equation, and its limitations, is discussed in Chapter 8. As mentioned above, random thermal collisions cause reactions to occur in both the

forward and backward directions. The first term in equation 1.9 is the rate of the anodic direction, while the second term is the rate of the cathodic direction. The difference between these rates gives the net rate of reaction. The parameter i_0 is called the *exchange current density* and is analogous to the rate constant used in chemical kinetics. In a reaction with a high exchange current density, both the forward and backward reactions occur rapidly. The net direction of reaction depends on the sign of the surface overpotential. The exchange current density depends on the concentrations of reactants and products, temperature, and also the nature of the electrode–electrolyte interface and impurities that may contaminate the surface. Each of these factors can change the value of i_0 by several orders of magnitude. i_0 can range from over 1 $\mathrm{mA/cm^2}$ to less than 10^{-7} $\mathrm{mA/cm^2}$. The parameters α_a and α_c, called *apparent transfer coefficients*, are additional kinetic parameters that relate how an applied potential favors one direction of reaction over the other. They usually have values between 0.2 and 2.

A reaction with a large value of i_0 is often called fast or reversible. For a large value of i_0, a large current density can be obtained with a small surface overpotential.

The relationship between current density and surface overpotential is graphed in Figures 1.3 and 1.4. In Figure 1.3, we see that the current density varies linearly with η_s for small values of η_s, and from the semilog graph given in Figure 1.4 we see that the current density varies exponentially with η_s for large values of η_s. The latter observation was made by Tafel in 1905, and Figure 1.4 is termed a *Tafel plot*. For large values of the surface overpotential, one of the terms in equation 1.9 is negligible, and the overall rate is given by either

$$i = i_0 \exp\left(\frac{\alpha_a F}{RT}\,\eta_s\right) \qquad (\text{for } \alpha_a F \eta_s \gg RT) \tag{1.10}$$

or

$$i = -i_0 \exp\left(-\frac{\alpha_c F}{RT}\,\eta_s\right) \qquad (\text{for } \alpha_c F \eta_s \ll -RT). \tag{1.11}$$

The *Tafel slope*, either $2.303RT/\alpha_a F$ or $2.303RT/\alpha_c F$, thus depends on the apparent transfer coefficient.

1.4 TRANSPORT

The previous section describes how applying a potential to an electrode creates a driving force for reaction. In addition, the imposition of a potential difference across an electronic conductor creates a driving force for the flow of electrons. The driving force is the *electric field* $\mathbf{E}$, related to the gradient in potential Φ by

$$\mathbf{E} = -\nabla\Phi. \tag{1.12}$$

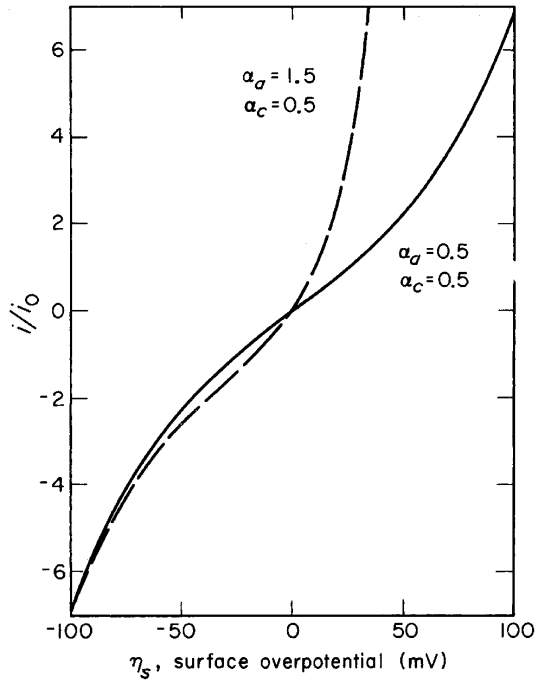

Figure 1.3 Dependence of current density on surface overpotential at 25°C.

Ohm's law relates the current density to the gradient in potential by

$$\mathbf{i} = -\sigma \nabla \Phi, \tag{1.13}$$

where σ is the *electronic conductivity*, equal to the inverse of the resistivity.

Similarly, applying an electric field across a solution of ions creates a driving force for ionic current. Current in solution is the net flux of charged species:

$$\mathbf{i} = \sum_i z_i F \mathbf{N}_i, \tag{1.14}$$

where $\mathbf{N}_i$ is the flux density of species i.

While electrons in a conductor flow only in response to an electric field, ions in an electrolyte move in response to an electric field (a process called *migration*) and also in response to concentration gradients (*diffusion*) and bulk fluid motion (*convection*). The net flux of an ion is therefore the sum of the migration, diffusion, and convection terms. In the following pages we look at each term individually. To simplify our discussion, let us consider a solution that contains a single salt in a single solvent, $CuSO_4$ in H_2O. An electrolyte that contains only one solvent and one salt is called a *binary electrolyte*.

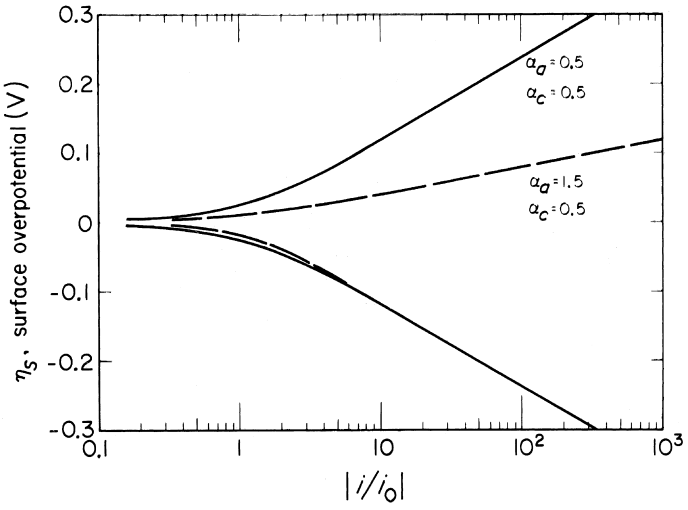

Figure 1.4 Tafel plot of the relationship between current density and surface overpotential at 25°C.

To give the reader a quantitative sense of the effect of different transport processes on the performance of an electrochemical system, we give calculations in the following sections for the specific system shown in Figure 1.5. This example consists of two concentric copper cylinders, of inner radius r_i, outer radius r_o, and height H, and with the annulus between filled with electrolyte. Since both cylinders are copper, at rest the open-circuit potential is zero. If we apply a potential between the inner and outer cylinders, copper will dissolve at the positive electrode to form Cu^{2+}, which will be deposited as Cu metal at the negative electrode. This type of process is widely used in industry for the electroplating and electrorefining of metals. While the annulus between concentric cylinders is not a practical geometry for many industrial applications, it is convenient for analytical applications.

Migration

Imagine that we place electrodes in the solution and apply an electric field between the electrodes. For the moment, let us imagine that the solution remains at a uniform concentration. We discuss the influence of concentration gradients in the next section. The electric field creates a driving force for the motion of charged species. It drives cations toward the cathode and anions toward the anode, that is, cations move in the direction opposite to the gradient in potential. The velocity of the ion in response to an electric field is its migration velocity, given by

$$v_{i,\text{migration}} = -z_i u_i F \nabla\Phi, \tag{1.15}$$

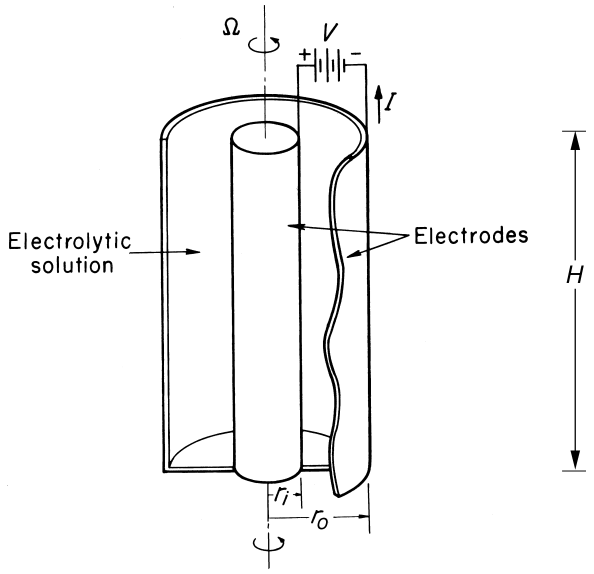

Figure 1.5 Two concentric copper electrodes, with the annulus filled with electrolyte. The inner electrode can be rotated.

where Φ is the potential in the solution (a concept that will be discussed in detail in Chapters 2, 3, and 6) and u_i, called the *mobility*, is a proportionality factor that relates how fast the ion moves in response to an electric field. It has units of $\mathrm{cm}^2 \cdot \mathrm{mol}/\mathrm{J} \cdot \mathrm{s}$.

The *flux density* of a species is equal to its velocity multiplied by its concentration. Thus the migrational flux density is given by

$$\mathbf{N}_{i,\text{migration}} = -z_i u_i F c_i \nabla\Phi. \tag{1.16}$$

Summing the migrational fluxes according to equation 1.14 for a binary electrolyte, we see that the current density due to migration is given by

$$\mathbf{i} = -F^2\left(z_+^2 u_+ c_+ + z_-^2 u_- c_-\right)\nabla\Phi. \tag{1.17}$$

The *ionic conductivity* κ is defined as

$$\kappa = F^2\left(z_+^2 u_+ c_+ + z_-^2 u_- c_-\right). \tag{1.18}$$

Thus, the movement of charged species in a uniform solution under the influence of an electric field is also given by Ohm's law:

$$\mathbf{i} = -\kappa \nabla \Phi. \tag{1.19}$$

We use κ instead of σ to indicate that the mobile charge carriers in electrolytes are ions, as opposed to electrons as in metals.

One can use this expression to obtain the potential profile and total ionic resistance for a cell of a given geometry, for example, our system of concentric cylinders. If the ends are insulators perpendicular to the cylinders, then the current flows only in the radial direction and is uniform in the angular and axial directions. The gradient in equation 1.19 is then simply given by

$$\mathbf{i} = -\kappa \frac{d\Phi}{dr}. \tag{1.20}$$

If a total current I is applied between the two cylinders, then the current density i in solution will vary with radial position by

$$i(r) = \frac{I}{2\pi r H}, \tag{1.21}$$

where H is the height of the cylinder. Substitution of equation 1.21 into equation 1.20 followed by integration gives the potential distribution in solution,

$$\Phi(r) - \Phi(r_i) = -\frac{I}{2\pi H \kappa} \ln \frac{r}{r_i}, \tag{1.22}$$

and the total potential drop between the electrodes is

$$\Phi(r_o) - \Phi(r_i) = -\frac{I}{2\pi H \kappa} \ln \frac{r_o}{r_i}. \tag{1.23}$$

The potential profile in solution is sketched in Figure 1.6. The potential changes more steeply closer to the smaller electrode, and the potential in solution at any given point is easily calculated from equation 1.22. As mentioned above, the *current distribution* on each electrode is uniform (although it is different on the two electrodes, being larger on the smaller electrode). Infinite parallel plates and concentric spheres are two other geometries that have uniform current distributions.

The reader may be familiar with the integrated form of Ohm's law commonly used in the field of electrostatics:

$$\Delta\Phi = IR, \tag{1.24}$$

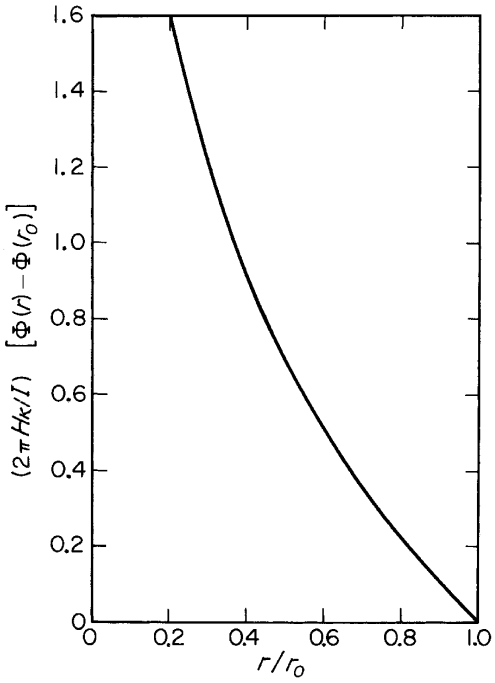

Figure 1.6 Distribution of the potential in solution between cylindrical electrodes.

where R is the total electrical resistance of the system in ohms. For our concentric cylinders we see that

$$R = \frac{\ln (r_o/r_i)}{2\pi H\kappa}. \tag{1.25}$$

For 0.1 M $CuSO_4$ in water, $\kappa = 0.00872$ S/cm. For H = 10 cm, r_o = 3 cm, and r_i = 2 cm, equation 1.25 gives the ohmic resistance of the system to be 0.74 Ω.

This analysis of the total resistance of the solution applies only in the absence of concentration gradients.

Diffusion

The application of an electric field creates a driving force for the motion of all ions in solution by migration. Thus for our system of aqueous copper sulfate, the current is caused by fluxes of both Cu^{2+} and SO_4^{2-}, with the cation migrating in the direction opposite to the anion. The *transference number* of an ion is defined as the fraction of the current that is carried by that ion in a solution of uniform composition:

$$t_i = \frac{z_i F N_i}{i}. \tag{1.26}$$

For example, for 0.1 M $CuSO_4$ in water at 25°C, $t_{Cu^{2+}} = 0.363$ and $t_{SO_4^{2-}} = 0.637$. However, in our system of copper electrodes, only the Cu^{2+} is reacting at the electrodes. Movement of sulfate ions toward the anode will therefore cause changes in concentration across the solution. In general, if the transference number of the reacting ion is less than unity, then there will be fluxes of the other ions in solution that will cause concentration gradients to form. These concentration gradients drive mass transport by the process of diffusion, which occurs in addition to the process of migration described above. The component of the flux density of a species due to diffusion is

$$\mathbf{N}_{i,\text{diffusion}} = -D_i \nabla c_i, \tag{1.27}$$

where D_i is the diffusion coefficient of species i. In aqueous systems at room temperature, diffusion coefficients are generally of order 10^{-5} cm^2/s.

If the sulfate ion is not reacting electrochemically, how does it carry current? At steady state, of course, it does not. The flux of sulfate in one direction by migration, proportional to its transference number, must be counterbalanced by the flux of sulfate in the opposite direction by diffusion. Thus, concentration gradients will develop until diffusion of sulfate exactly counterbalances migration of sulfate. At steady state,

$$\mathbf{N}_{-,\text{migration}} = -z_- u_- F c_- \nabla\Phi = -\mathbf{N}_{-,\text{diffusion}} = D_- \nabla c_-. \tag{1.28}$$

Before the concentration gradients have reached their steady-state magnitudes, the sulfate ion *is* effectively carrying current because salt accumulates at the anode side of the cell and decreases at the cathode side of the cell. While migration and diffusion of the sulfate ions oppose each other, migration and diffusion act in the same direction for the cupric ion, which carries all of the current at steady state.

A low transference number means that little of the current is carried by migration of that ion. If the ion is the reacting species, then more diffusion is needed to transport the ion for a lower t_i, and therefore a larger concentration gradient forms.

The magnitude of these concentration gradients is given by a combination of both the transference number and the salt diffusion coefficient, as will be discussed in Chapters 11 and 12. The salt diffusion coefficient D for a binary electrolyte is an average of the individual ionic diffusivities:

$$D = \frac{z_+ u_+ D_- - z_- u_- D_+}{z_+ u_+ - z_- u_-}. \tag{1.29}$$

For a binary electrolyte, the transference number is related to the mobilities by

$$t_+ = \frac{z_+ u_+}{z_+ u_+ - z_- u_-}. \tag{1.30}$$

The treatment of transport in electrolytic solutions is thus more complicated than the treatment of solutions of neutral molecules. In a solution with a single neutral solute, the magnitude of the concentration gradient depends on only one transport property, the diffusion coefficient. In contrast, transport in a solution of a dissociated salt is determined by a total of three transport properties. The magnitude of the concentration gradient is determined by D and t_+, while κ determines the ohmic resistance.

Convection

Convection is the bulk movement of a fluid. The equations describing fluid velocity and convection will be detailed in Chapter 15. The flux density of a species by convection is given by

$$\mathbf{N}_{i,\text{convection}} = c_i \mathbf{v}, \tag{1.31}$$

where $\mathbf{v}$ is the velocity of the bulk fluid. Convection includes natural convection (caused by density gradients) and forced convection (caused by mechanical stirring or a pressure gradient). Convection can be laminar, meaning that the fluid flows in a smooth fashion, or turbulent, in which the motion is chaotic.

Substitution into equation 1.14 for the current gives

$$\mathbf{i}_{\text{convection}} = \sum_i z_i c_i F \mathbf{v}. \tag{1.32}$$

By electroneutrality, $\sum_i z_i c_i = 0$. Therefore, in an electrically neutral solution, bulk convection alone does not cause a net current. However, convection can cause mixing of the solution, and while it alone cannot cause a current, fluid motion can affect concentration profiles and serve as an effective means to bring reactants to the electrode surface.

The net flux density of an ion is given by the combination of equations 1.16, 1.27, and 1.31:

$$\mathbf{N}_i = -z_i u_i F c_i \nabla\Phi - D_i \nabla c_i + c_i \mathbf{v}. \tag{1.33}$$

To understand how the different components interact, consider Figure 1.7, which shows the concentration profile between the two copper cylinders at steady state for two cases. The dashed curve shows the case in which there is no convection. The slope of this curve is determined by the transference number, salt diffusion coefficient, and the current density, as mentioned previously. The cation migrates toward the negative electrode (here the outer electrode), and the concentration profile shows that this migration is augmented by diffusion down the concentration gradient. Conversely, migration of the unreacting sulfate ion toward the anode is counterbalanced by diffusion acting in the opposite direction.

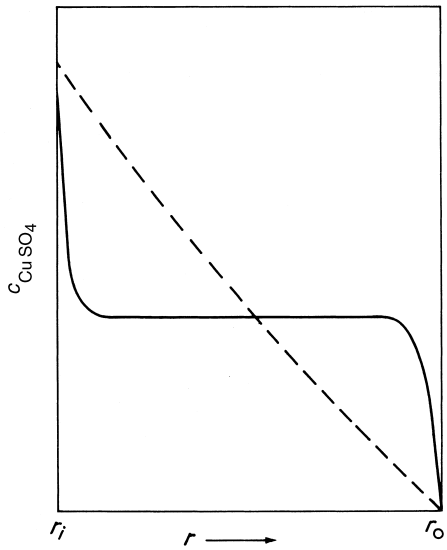

Figure 1.7 Concentration profile in the annular space between the electrodes. The dashed curve refers to the absence of a radial component of velocity. The solid curve refers to the presence of turbulent mixing.

If one increases the current density, the slope of the dashed curve in Figure 1.7 increases. At some current density, the concentration of cupric ion at the cathode will reach zero. Experimentally, one observes a large increase in the cell voltage if one tries to increase the current density beyond this value. This current is called the *limiting current* and is the highest current that can be carried by the cupric ion in this solution and geometry. A higher current can be passed only if another reaction, such as hydrogen evolution, starts occurring to carry the extra current.

The concentration profile in solution can be modified by convection. For example, one could flow electrolyte axially through the annulus, causing the concentration to vary with both radial position and distance from the inlet. Conversely, laminar angular flow of the solution in the annulus, such as would be caused by slow rotation of one of the cylinders, would have no impact on the concentration profile since the fluid velocity would be always perpendicular to the concentration gradients.

The solid curve in Figure 1.7 shows the concentration profile for the case when the inner cylinder is rotated at a high speed, causing turbulent convection in the bulk of the solution. At the solid-solution interface, the "no-slip" condition applies, which damps the fluid velocity. Diffusion and migration therefore dominate convection immediately adjacent to the electrodes. The mixing causes the solution to be more or less uniform in all regions except narrow boundary layers adjacent to the electrode surfaces. These boundary regions are called *diffusion layers*. They become thinner as the rate of mixing increases. Because the mixing evens out the concentration in the

bulk of the electrolyte, the concentration gradients can now be steeper in these boundary regions, leading to much higher rates of mass transport than would be possible without the stirring. Thus, stirring increases the limiting current. For example, for the system shown in Figure 1.5 with $r_o = 3$ cm, $r_i = 2$ cm, and 0.1 M aqueous $CuSO_4$, the limiting current given by diffusion and migration in the absence of convection is 0.37 mA/cm^2. If one rotates the inner cylinder at 900 rpm to cause turbulent mixing, the system can carry a much higher limiting current of 79 mA/cm^2.

Convection can occur even in the absence of mechanical stirring. At the cathode, cupric ions are consumed, and the concentration of salt in solution decreases. Conversely, at the anode, the concentration of salt increases. Since the density of the electrolyte changes appreciably with salt concentration, these concentration gradients cause density gradients that lead to natural convection. The less dense fluid near the cathode will flow up, and the denser fluid near the anode will flow down. The resulting pattern of streamlines is shown in Figure 1.8. A limiting current, corresponding to a zero concentration of cupric ions along the cathode surface, still can develop in this system. The corresponding current distribution on the cathode now will be nonuniform, tending to be higher near the bottom and decreasing farther up the cathode as the solution becomes depleted while flowing along the electrode surface. The stirring caused by this natural convection increases the limiting current, from a calculated value of 0.37 mA/cm^2 in the case of no convection to 9.1 mA/cm^2 with natural convection.

In the field of electrochemical engineering, we are often concerned with trying to figure out the distribution of the current over the surface of an electrode, how this distribution changes with changes in the size, shape, and material properties of a system, and how changes in the current distribution affect the performance of the

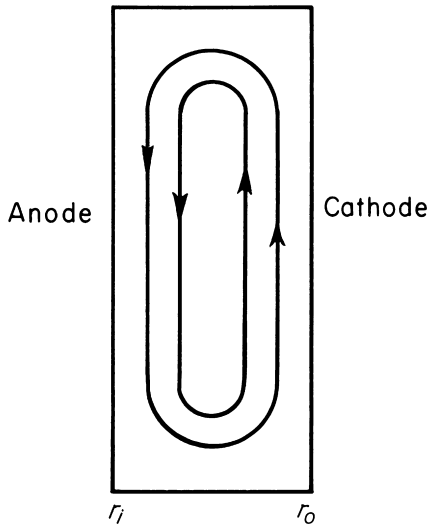

Figure 1.8 Streamlines for free convection in the annular space between two cylindrical electrodes.

system. Often, the engineer seeks to construct the geometry and system parameters in such a way as to ensure a uniform current distribution. For example, one way to avoid the natural convection mentioned above is to use a horizontal, planar cell configuration with the anode on the bottom.

In many applications, such as metal electrodeposition and some instances of analytical electrochemistry, it is common to add a *supporting electrolyte*, which is a salt, acid, or base that increases the conductivity of the solution without participating in any electrode reactions. For example, one might add sulfuric acid to the solution of copper sulfate. Adding sulfuric acid as supporting electrolyte has several interrelated effects on the behavior of the system. First, the conductivity κ is increased, thereby reducing the electric field in solution for a given applied current density. In addition, the transference number of the cupric ion is reduced. These two effects mean that the role of migration in the transport of cupric ion is greatly reduced. The effect of adding supporting electrolyte is thus to reduce the ohmic potential drop in solution and to increase the importance of diffusion in the transport of the reacting ion. Since migration is reduced, a supporting electrolyte has the effect of decreasing the limiting current. For example, adding 1.53 M H_2SO_4 to our 0.1 M solution of $CuSO_4$ will increase the ionic conductivity from 0.00872 S/cm to 0.548 S/cm, thus substantially decreasing the ohmic resistance of the system. The resultant decrease in the electric field for a given applied current and lowering of $t_{Cu^{2+}}$ cause a decrease in the limiting current from 79 mA/cm^2 with no supporting electrolyte to 48 mA/cm^2 with supporting electrolyte (with turbulent mixing).

The conductivity of the solution could also have been increased by adding more cupric sulfate. However, in refining a precious metal, it is desirable to maintain the inventory in the system at a low level. Furthermore, the solubility of cupric sulfate is only 1.4 M. To avoid supersaturation at the anode, we might set an upper limit of 0.7 M, at which concentration the conductivity is still only 0.037 S/cm. An excess of supporting electrolyte is usually used in electroanalytical chemistry and in studies of electrode kinetics or of mass transfer, not only because the potential variations in the solution are kept small but also because activity coefficients, transport properties, and even the properties of the interface change little with small changes of the reactant concentration.

The above discussion describes transport under a framework called dilute-solution theory in which migration is considered independently from diffusion. Chapter 12 describes how to unify the treatment of migration and diffusion under the framework of concentrated-solution theory.

1.5 CONCENTRATION OVERPOTENTIAL AND THE DIFFUSION POTENTIAL

We already have described two sources of resistance: the surface overpotential, which represents the resistance to electrochemical reaction, and the ohmic resistance, which is the resistance to ionic or electronic current. In this section, we discuss how the presence of concentration gradients creates another source of overpotential.

Consider the following scenario shown in Figure 1.9. A solution of 0.1 *M* $CuSO_4$ is connected to a solution of 0.05 *M* $CuSO_4$ via a porous glass disk. The disk prevents rapid mixing between the solutions, but it does allow the flow of current and slow diffusion between the solutions. Into each solution we dip an identical copper electrode.

In Section 1.2, we discussed the dependence of the open-circuit potential on concentration. Thus, from equation 1.8, we can predict that there will be a potential difference between the two electrodes placed in solutions of differing reactant concentrations. Because of the concentration differences, there is a tendency for cupric ions to plate out from the 0.1 *M* solution and for copper to dissolve into the 0.05 *M* solution. This manifests itself in a potential difference between the electrodes in order to prevent the flow of current, the electrode in the more concentrated solution being positive relative to the other electrode. If these electrodes were connected through an external resistor, current would flow through the resistor from the positive to the negative electrode and through the solution from the negative to the positive.

Even if a potential is applied to prevent the flow of current between the electrodes, the situation depicted in Figure 1.9 is not at equilibrium. Diffusion may be restricted by the glass disk, but it will still occur until eventually the two sides of the cell reach the equilibrium condition of equal concentrations. Therefore, the potential difference between the electrodes includes transport properties as well as thermodynamic properties. The meaning of potential in a solution of nonuniform concentration and the calculation of potential differences across nonuniform solutions are treated in detail in Chapters 2 and 12. For the particular case given by Figure 1.9, the potential of the cell is given approximately by

$$\Phi_{\mathrm{I}} - \Phi_{\mathrm{II}} = U_{\mathrm{conc}} = (1 - t_+)\frac{RT}{F}\ln\frac{c_{\mathrm{I}}}{c_{\mathrm{II}}}. \tag{1.34}$$

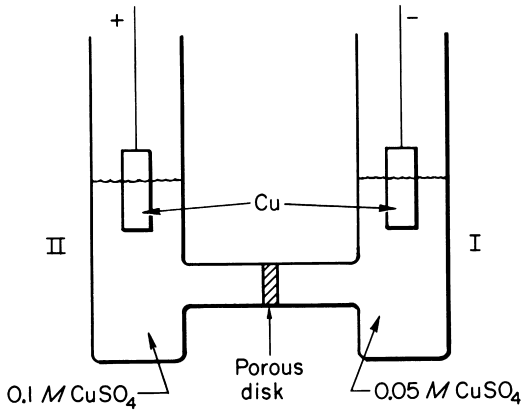

Figure 1.9 Concentration cell.

Notice the difference between this equation and equation 1.8. Equation 1.8 describes how the open-circuit potential depends on the concentrations of reactants and products at equilibrium whereas equation 1.34 includes in addition the diffusion potential caused by the presence of concentration gradients.

If we have a solution with a concentration gradient across it, instead of two solutions separated by a porous disk, the potential between any two points in solution still depends on the concentration differences in a manner described by equation 1.34. This potential difference caused by a concentration gradient can be referred to as a *concentration overpotential*.

Let us consider the concentration overpotentials in our system of concentric copper cylinders. We rotate one cylinder to create turbulent mixing, so that the concentration profile is uniform in the middle of the annulus (see Figure 1.7). This arrangement allows us to isolate the concentration overpotentials at each electrode.

We place three copper reference electrodes in the solution as shown in Figure 1.10. Reference electrode 1 is adjacent to the anode, reference 2 is adjacent to the cathode, and reference 3 is in the middle of the cell where the concentration is uniform. These reference electrodes can sense the potential in a solution carrying current, even though they themselves carry no current. One tries to situate the reference electrodes in such a position that they do not alter conditions significantly from those prevailing in their absence. We can do that here by using very small copper wires.

$\Phi_1 - \Phi_2$ is the potential difference in the solution. It consists of two components, the ohmic potential drop and a concentration overpotential:

$$\Phi_1 - \Phi_2 = U_{\text{conc}} + \int_1^2 \frac{\mathbf{i} \cdot d\mathbf{r}}{\kappa}, \tag{1.35}$$

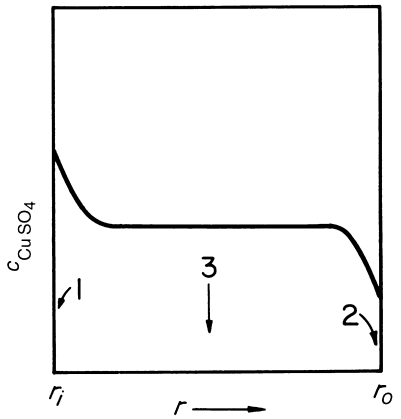

Figure 1.10 Placement of reference electrodes (1, 2, and 3) in the solution between cylindrical electrodes. The concentration profile shown corresponds to turbulent mixing at a current somewhat below the limiting current.

where we have included κ inside the integral because it may vary with concentration and U_{conc} is given approximately by equation 1.34 (the term concentration overpotential is redefined in equation 1.36). The ohmic portion is proportional to the current and will disappear immediately if the current is interrupted. This provides a means for distinguishing between the two. The total potential difference between the two reference electrodes is measured with the current flowing. The contribution of concentration variations is that value measured just after the current is interrupted but before the concentration distribution can change by diffusion or convection. The difference between these two measurements is the ohmic contribution. (It should be pointed out that, in many geometries, internal current redistribution may occur after the external current is turned off. In these cases, ohmic resistance is still present for some time after the current is interrupted.)

We can use the third reference electrode to separate the concentration overpotential into contributions from the anode and cathode. The concentration overpotential at the anode is then $\Phi_1 - \Phi_3$, and the cathodic concentration overpotential is $\Phi_2 - \Phi_3$, just after the current is interrupted. This decomposition of the concentration overpotential depends on the concept of thin diffusion layers near the electrodes and the existence of a bulk solution where the concentration does not vary significantly. Then the anodic and cathodic concentration overpotentials are independent of the precise location of the third reference electrode, since it is in a region of uniform concentration and there is no current flow.

Alternatively, we can define the concentration overpotential by

$$\eta_c = U_{\text{conc}} + \int_0^{\text{bulk}} \left(\frac{1}{\kappa} - \frac{1}{\kappa_{\text{bulk}}} \right) i_y \, dy, \tag{1.36}$$

where y is the distance from the electrode and bulk represents the solution properties in the uniform region of the annulus. Then $\Phi_1 - \Phi_2 = \eta_c + \Delta\Phi_{\text{ohm}}$, where $\Delta\Phi_{\text{ohm}}$ is the potential difference that would be measured in the hypothetical scenario of the same current distribution but with no concentration gradients. $\Delta\Phi_{\text{ohm}}$ can be calculated using the procedure given in Section 1.4 with constant conductivity. This definition of concentration overpotential means that η_c accounts for all potential changes induced by concentration effects. Figure 1.11 shows how the cathodic overpotential depends on current density for current densities up to the limiting current.

1.6 OVERALL CELL POTENTIAL

The potential difference across a cell will depend on all four components described above: the open-circuit potential U, the surface overpotential, the ohmic potential drop, and the concentration overpotential. These potential drops are interrelated, making the calculation of the total potential of the cell more complicated than that given by the ohmic potential drop alone. It is these interrelationships that make electrochemical engineering both a challenging and an interesting field.

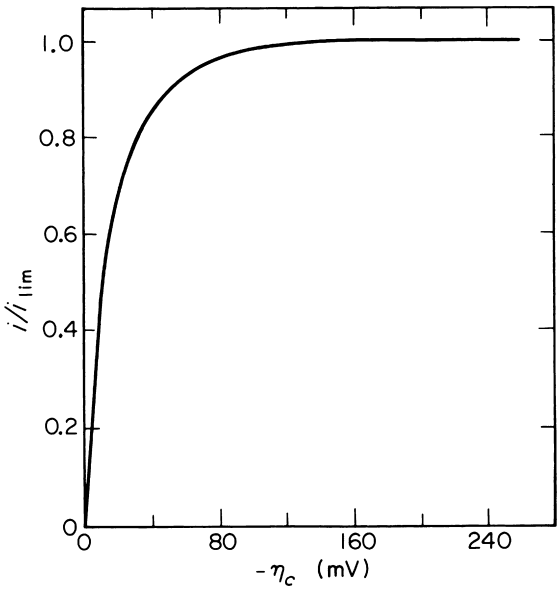

Figure 1.11 Concentration overpotentials at a cathode in 0.1 *M* $CuSO_4$.

The open-circuit potential U represents the maximum work that can be obtained from the system. We use the symbol V to denote the cell potential, which is often called the cell voltage. The cell potential V may differ from the open-circuit potential U, both during and shortly after the passage of current, because the passage of current has induced overpotentials. All of the overpotentials represent dissipative losses. Thus, for a galvanic cell, the actual cell potential during passage of current will always be less than U (the rate of work output of the cell, IV, is less than IU), while for an electrolytic cell the actual cell potential will be greater (the work that one must put into the cell is greater than the reversible work). The cell potential will approach the reversible potential as the current becomes infinitely small.

As described in Section 1.3, the potential drop due to kinetic resistance at the anode is $\eta_{s,\text{anode}} = \Phi_{\text{anode}} - \Phi_1$, where Φ_{anode} and Φ_1 are measured by electrodes made of the same compounds, and likewise the surface overpotential at the cathode is $\eta_{s,\text{cathode}} = \Phi_{\text{cathode}} - \Phi_2$, where Φ_{cathode} and Φ_2 are measured by electrodes made of the same compounds. $\eta_{s,\text{anode}}$ is positive while $\eta_{s,\text{cathode}}$ is negative.

The cell potential is given by

$$\begin{aligned} V &= \Phi_{\text{anode}} - \Phi_{\text{cathode}} \\ &= (\Phi_{\text{anode}} - \Phi_1) + (\Phi_1 - \Phi_2) - (\Phi_{\text{cathode}} - \Phi_2) \\ &= \eta_{s,\text{anode}} + (\eta_{c,\text{anode}} + U + \Delta\Phi_{\text{ohm}} - \eta_{c,\text{cathode}}) - \eta_{s,\text{cathode}}, \end{aligned} \tag{1.37}$$

where each η_s is obtained from an equation of the form of equation 1.9, $\Delta\Phi_{\text{ohm}}$ is given by equation 1.23, calculated using a constant conductivity, and η_c is obtained from equation 1.36, which includes the variation of conductivity with concentration as well as the diffusion potential. For generality, we have included the possibility that the cathode and anode may be made of different metals, such as zinc and silver, respectively. Then we would use a silver electrode for reference 1 and a zinc electrode for reference 2 in order to measure the surface overpotentials. To isolate the concentration overpotentials, we could use two reference electrodes, for example, a silver and a zinc, placed side by side at position 3. Call $\Phi_{3,a}$ the potential measured by the reference electrode of the same kind as the anode and $\Phi_{3,c}$ that measured by the reference electrode of the same kind as the cathode. $\Phi_{3,a} - \Phi_{3,c}$ is then U, the equilibrium potential difference between the anode and cathode electrodes in a region of uniform concentration. For the case in which all of the electrodes are the same, for example, all copper metal, U is zero. The terms η_c and η_s for the cathode enter with negative signs because of the conventions that have been adopted. Since they are negative, they make a positive contribution to the cell potential of this electrolytic cell. Thus, all of the overpotentials represent resistive losses.

Figure 1.12 indicates what we should expect for the response of the current I to the applied potential V. At low currents, most of the applied potential is consumed by ohmic losses, which increase linearly with the applied current. At low currents the surface overpotential increases linearly with current, and changes with the logarithm of current at moderate currents. As the concentration of reactants at the

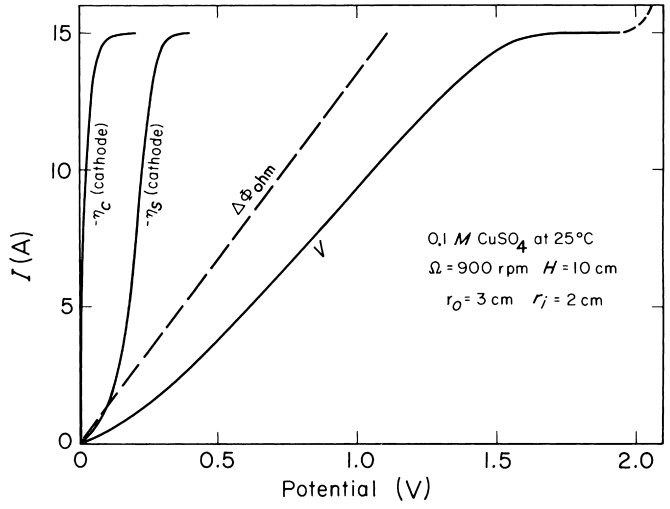

Figure 1.12 The dependence of the cell potential and its component overpotentials on current for concentric cylinders, the inner of which rotates. The overpotentials for the anode are small for this particular system and are not shown.

cathode is depleted near the limiting current, the exchange current density becomes very small and the surface overpotential increases substantially. The concentration polarization at the cathode increases dramatically as the limiting current is approached. At sufficiently large voltages, a second reaction such as hydrogen evolution may occur at the cathode, as indicated by the dashed line on the figure. $\eta_{s,\text{anode}}$ and $\eta_{c,\text{anode}}$ are not shown on the figure because, for this particular cell, they are small. $\eta_{s,\text{anode}}$ is less than $\eta_{s,\text{cathode}}$ because a different value of the apparent transfer coefficient was used (see Figure 1.3). $\eta_{c,\text{anode}}$ is smaller than $\eta_{c,\text{cathode}}$ because the order of magnitude of increase in the logarithm of the concentration of Cu^{2+} at the anode is much less than the order of magnitude of decrease in the logarithm of the concentration at the cathode, where the concentration is driven to zero.

Figure 1.13 shows how the current–potential relationships change when sulfuric acid is added as supporting electrolyte. The ohmic potential drop is reduced relative to Figure 1.12, and the concentration and surface overpotentials now constitute a larger fraction of the applied potential. The magnitude of the limiting current is also reduced.

The *energy efficiency* for a galvanic cell is given by the net work out ($\int IVdt$) divided by the reversible work ($\int IUdt$), that is, the work that could be obtained if the cell potential were always equal to its equilibrium potential. For an electrolytic cell, the energy efficiency is the reversible work divided by work input required to drive the reaction. One can also speak in terms of current efficiency for cells in which multiple reactions may occur in the same potential range. For example, if a metal's reduction potential is close to that of hydrogen evolution, then one may evolve hydrogen while trying to electrodeposit the metal.

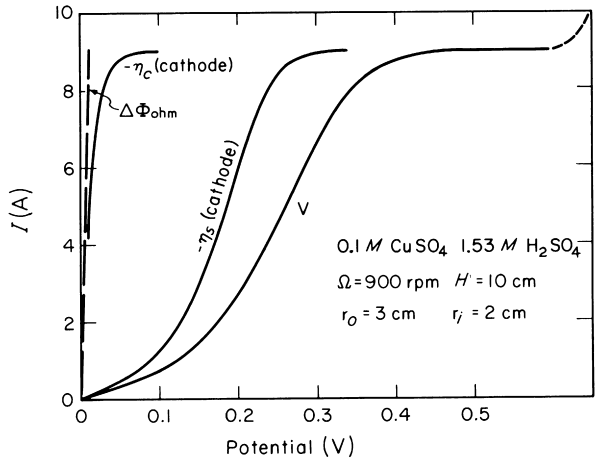

Figure 1.13 Current–potential relations with sulfuric acid added as a supporting electrolyte.

Current efficiency is the ratio of the charge consumed by the desired reaction to the total charge passed in the cell.

In conclusion, kinetics, thermodynamics, and transport are closely interrelated in electrochemical systems. In Parts A, B, and C, we describe the fundamentals of each in turn. However, it is impossible to discuss each aspect in complete isolation since all three phenomena are interdependent. In Part D, we describe applications that illustrate how to treat the coupled phenomena, and we discuss when simplifying assumptions may be used to reduce the complexity of the analysis of electrochemical systems.

PROBLEMS

1.1. Starting with equation 1.36, derive the following equation for the concentration overpotential in a binary salt solution:

$$\eta_c = \frac{RT}{F}\left[\ln\frac{c_o}{c_b} + t_+\left(1 - \frac{c_o}{c_b}\right)\right].$$

Assume that the concentration profile is linear within the diffusion layer and uniform outside this layer, which can be taken to be of finite thickness. In addition to the relationships expressed in this chapter, it is necessary to use the Nernst–Einstein relation between the mobility and the diffusion coefficient of species i:

$$D_i = RTu_i.$$

Use equation 1.18 for the variation of conductivity with concentration. c_o is the concentration at the electode surface and c_b is the concentration outside the diffusion layer. (See Section 20.2.)

NOTATION

c_i	concentration of species i, mol/cm^3
c_b	concentration in bulk solution, mol/cm^3
c_0	concentration at electrode surface, mol/cm^3
D	diffusion coefficient of electrolyte, cm^2/s
D_i	diffusion coefficient of species i, cm^2/s
F	Faraday's constant, 96,487 C/equiv
G	Gibbs free energy, J/mol
H	depth of solution, cm
i	current density, A/cm^2
i_0	exchange current density, A/cm^2
I	total current, A
ℓ	distance, cm

m	molality of species i, mol/kg
n	number of electrons involved in electrode reaction
$\mathbf{N}_i$	flux density of species i, $\text{mol/cm}^2 \cdot \text{s}$
r	radial position, cm
r_i	radius of inner electrode, cm
r_o	radius of outer electrode, cm
R	resistance, Ω
R	universal gas constant, $8.3143\ \text{J/mol} \cdot \text{K}$
s_i	stoichiometric coefficient of species i
t_+	cation transference number
T	absolute temperature, K
u_i	mobility of species i, $\text{cm}^2 \cdot \text{mol/J} \cdot \text{s}$
U	cell potential at open circuit, V
$\mathbf{v}$	fluid velocity, cm/s
$\mathbf{v}_i$	average velocity of species i, cm/s
V	cell potential, V
y	distance from electrode, cm
z_i	charge number of species i
$\alpha_a,\ \alpha_c$	anodic and cathodic transfer coefficients
η_c	concentration overpotential, V
η_s	surface overpotential, V
κ	ionic conductivity, S/cm
μ_i	electrochemical potential of species i, J/mol
Φ	potential, V
$\Delta\Phi_{\text{ohm}}$	ohmic potential drop, V
Ω	rotation speed, rad/s
σ	electronic conductivity, S/cm