20

Electrochemistry

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A transit bus fitted with hydrogen–oxygen fuel cells. The use of fuel cells could dramatically reduce urban air pollution. The conversion of chemical energy into electrical energy is one of the main subjects of this chapter.

A conventional gasoline-powered automobile is only about 25% efficient in converting chemical energy into kinetic energy (energy of motion). An electric-powered auto is about three times as efficient. Unfortunately, when automotive technology was first being developed, devices for converting chemical energy to electrical energy did not perform at their intrinsic efficiencies. This fact, together with the availability of high-quality gasoline at a low cost, resulted in the preeminence of the internal combustion automobile. Now, with concern about long-term energy supplies and environmental pollution, there is a renewed interest in electric-powered buses and automobiles.

In this chapter, we will see how chemical reactions can be used to produce electricity and how electricity can be used to cause chemical reactions. The practical applications of electrochemistry are countless, ranging from batteries and fuel cells as electric power sources to the manufacture of key chemicals, the refining of metals, and methods for controlling corrosion. Also important, however, are the theoretical implications. Because electricity involves a flow of electric charge, a study of the relationship

between chemistry and electricity gives us additional insight into reactions in which electrons are transferred—*oxidation–reduction reactions*.

20-1 Electrode Potentials and Their Measurement

The criteria for spontaneous change developed in Chapter 19 apply to reactions of all types—precipitation, acid–base, and oxidation–reduction (redox). We can devise an additional useful criterion for redox reactions, however.

Figure 20-1 shows that a redox reaction occurs between Cu(s) and $Ag^+(aq)$, but not between Cu(s) and $Zn^{2+}(aq)$. Specifically, we see that silver ions are reduced to silver atoms on a copper surface, whereas zinc ions are *not* reduced to zinc atoms on a copper surface. We can say that Ag^+ is more readily reduced than is Zn^{2+}. In this section, we will introduce the *electrode potential*, a property related to these reduction tendencies.

▶ The term *electrode* is sometimes used for the entire half-cell assembly.

When used in electrochemical studies, a strip of metal, M, is called an **electrode**. An electrode immersed in a solution containing ions of the same metal, M^{n+}, is called a **half-cell**. Two kinds of interactions are possible between metal atoms on the electrode and metal ions in solution (Fig. 20-2):

1. A metal ion M^{n+} from solution may collide with the electrode, gain n electrons from it, and be converted to a metal atom M. *The ion is reduced.*
2. A metal atom M on the surface may lose n electrons to the electrode and enter the solution as the ion M^{n+}. *The metal atom is oxidized.*

An equilibrium is quickly established between the metal and the solution, which can be represented as

$$M(s) \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} M^{n+}(aq) + ne^- \qquad (20.1)$$

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that although $M^{n+}(aq)$ and ne^- appear together on the right-hand side of this expression, only the ion M^{n+} enters the solution. The electrons remain on the electrode, M(s). Free electrons are never found in an aqueous solution.

However, any changes produced at the electrode or in the solution as a consequence of this equilibrium are too slight to measure. Instead, measurements must be based on a combination of *two different* half-cells. Specifically, we must measure the tendency for electrons to flow from the electrode of one half-cell to the electrode of the other. Electrodes are classified according to whether oxidation or reduction takes place there. If oxidation takes place, the electrode is called the **anode**. If reduction takes place, the electrode is called the **cathode**.



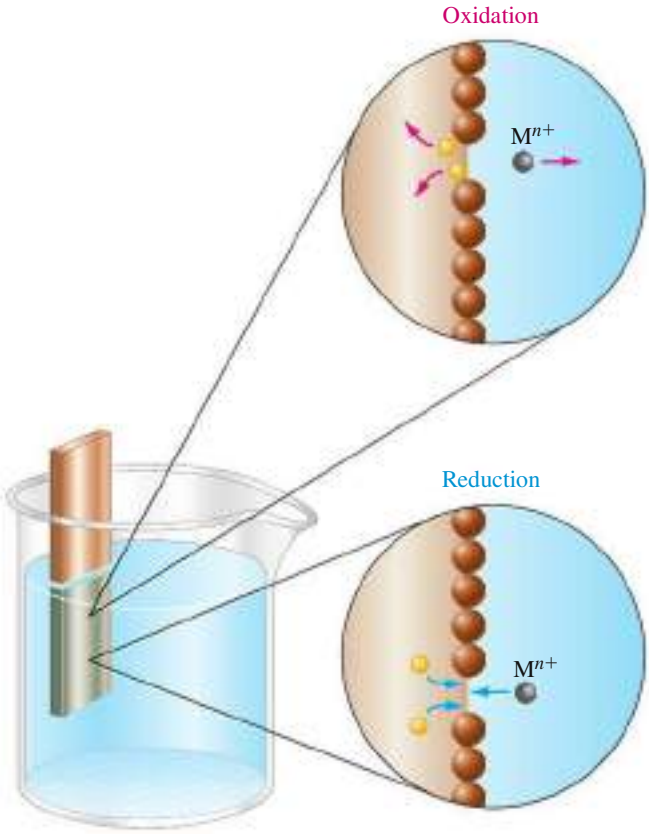
(a) (b)

▶ FIGURE 20-1
Behavior of $Ag^+(aq)$ and $Zn^+(aq)$ in the presence of copper
(a) Copper metal displaces silver ions from colorless $AgNO_3(aq)$ as a deposit of silver metal; the copper enters the solution as blue $Cu^{2+}(aq)$.

$$Cu(s) + 2\,Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2\,Ag(s)$$

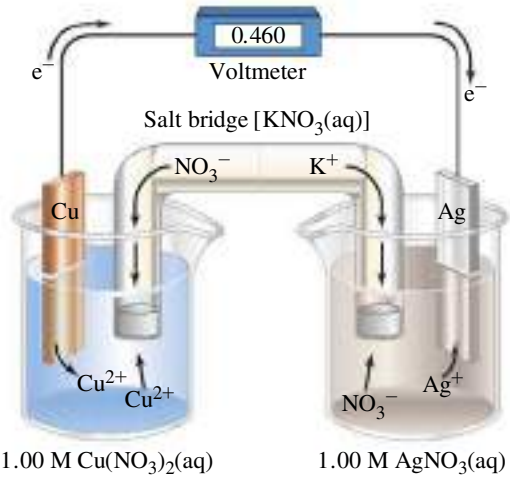
(b) Cu(s) *does not* displace colorless Zn^{2+} from $Zn(NO_3)_2(aq)$.

$$Cu(s) + Zn^{2+}(aq) \longrightarrow \text{no reaction}$$



◀ FIGURE 20-2
An electrochemical half-cell
The half-cell consists of a metal electrode, M, partially immersed in an aqueous solution of its ions, M^{n+}. (The anions required to maintain electrical neutrality in the solution are not shown.) The situation illustrated here is limited to metals that do not react with water.

Figure 20-3 depicts a combination of two half-cells, one with a Cu electrode in contact with $Cu^{2+}(aq)$, and the other with an Ag electrode in contact with $Ag^{+}(aq)$. The two electrodes are joined by wires to an electric meter—here, a *voltmeter*. To complete the electric circuit, the two solutions must also be connected electrically. However, because charge is carried through solutions by the migration of *ions*, a wire cannot be used for this connection. The solutions



▲ FIGURE 20-3
Measurement of the electromotive force of an electrochemical cell
An electrochemical cell consists of two half-cells with electrodes joined by a wire and solutions joined by a salt bridge. (The ends of the salt bridge are plugged with a porous material that allows ions to migrate but prevents the bulk flow of liquid.) Electrons flow from the Cu electrode, the anode, where oxidation occurs to the Ag electrode, the cathode, where reduction occurs. For precise measurements, the amount of electric current drawn from the cell must be kept very small by means of either a specially designed voltmeter or a device called a potentiometer.

◀ Anions migrate toward the anode, and cations toward the cathode.

must either be in direct contact through a porous barrier or joined by a third solution in a U-tube called a **salt bridge**. The properly connected combination of two half-cells is called an **electrochemical cell**.

Now, we will consider the changes that occur in the electrochemical cell in Figure 20-3. As the arrows suggest, Cu atoms release electrons at the anode and enter the $Cu(NO_3)_2(aq)$ as Cu^{2+} ions. Electrons lost by the Cu atoms pass through the wires and the voltmeter to the cathode, where they are gained by Ag^+ ions from the $AgNO_3(aq)$, producing a deposit of metallic silver. Simultaneously, anions (NO_3^-) from the salt bridge migrate into the copper half-cell and neutralize the positive charge of the excess Cu^{2+} ions; cations (K^+) migrate into the silver half-cell and neutralize the negative charge of the excess NO_3^- ions. Each copper atom loses two electrons to produce Cu^{2+}; each Ag^+ ion requires one electron to produce Ag(s); consequently, two silver atoms are produced for every Cu^{2+} ion formed. The overall reaction that occurs as the electrochemical cell spontaneously produces electric current is

$$\begin{aligned} &\textit{Oxidation:} && Cu(s) \longrightarrow Cu^{2+}(aq) + 2\,e^- \\ &\textit{Reduction:} && 2\{Ag^+(aq) + e^- \longrightarrow Ag(s)\} \\ &\textit{Overall:} && Cu(s) + 2\,Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2\,Ag(s) \end{aligned} \qquad \textbf{(20.2)}$$

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that the overall reaction occurring in the electrochemical cell is identical to what happens in the direct addition of Cu(s) to $Ag^+(aq)$ pictured in Figure 20-1(a).

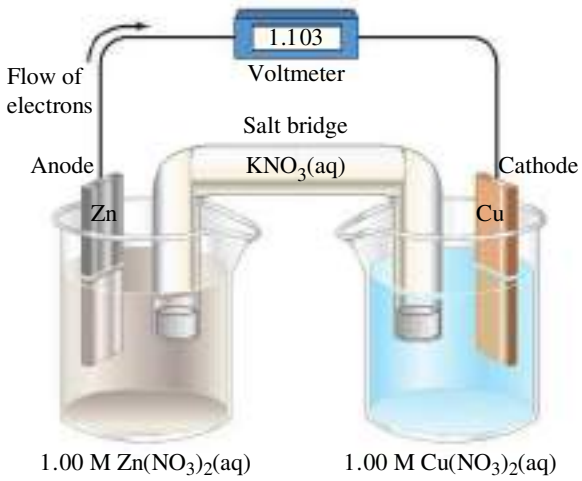
The reading on the voltmeter (0.460 V) is significant. It is the **cell voltage**, or the *potential difference* between the two half-cells. The unit of cell voltage, **volt (V)**, is the energy per unit charge. Thus, a potential difference of one volt signifies an energy of one joule for every coulomb of charge passing through an electric circuit: 1 V = 1 J/C. We can think of a voltage, or potential difference, as the driving force for electrons; the greater the voltage, the greater the driving force. The flow of water from a higher to a lower level is analogous to this situation. The greater the difference in water levels, the greater the force behind the flow of water. Cell voltage is also called **electromotive force (emf)**, or **cell potential**, and represented by the symbol E_{cell}.

▶ Such formulations as $Zn(s)/Zn^{2+}(aq)$ are called *couples* and are often used as abbreviations for half-cells.

Now let's return to the question raised by Figure 20-1: Why does copper *not* displace Zn^{2+} from solution? In an electrochemical cell consisting of a $Zn(s)/Zn^{2+}(aq)$ half-cell and a $Cu^{2+}(aq)/Cu(s)$ half-cell, electrons flow *from the Zn to the Cu*. The spontaneous reaction in the electrochemical cell in Figure 20-4 is

$$\begin{aligned} &\textit{Oxidation:} && Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^- \\ &\textit{Reduction:} && Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s) \\ &\textit{Overall:} && Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \end{aligned} \qquad \textbf{(20.3)}$$

Because reaction (20.3) is a spontaneous reaction, the displacement of $Zn^{2+}(aq)$ by Cu(s)—the *reverse* of reaction (20.3)—does *not* occur spontaneously. This is the observation made in Figure 20-1. In Section 20-3, we will discuss how to predict the direction of spontaneous change for oxidation–reduction reactions:



▶ FIGURE 20-4
The reaction $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$ in an electrochemical cell

Cell Diagrams and Terminology

Drawing sketches of electrochemical cells, as in Figures 20-3 and 20-4, is helpful, but more often a simpler representation is used. A **cell diagram** shows the components of an electrochemical cell in a symbolic way. We will use the following, generally accepted conventions in writing cell diagrams.

- The anode, the electrode at which *oxidation* occurs, is placed at the *left* side of the diagram.
- The cathode, the electrode at which *reduction* occurs, is placed at the *right* side of the diagram.
- A boundary between different phases (for example, an electrode and a solution) is represented by a *single vertical line* (|).
- The boundary between half-cell compartments, commonly a salt bridge, is represented by a *double vertical line* (||). Species in aqueous solution are placed on either side of the double vertical line. Different species within the same solution are separated from each other by a comma. Although IUPAC recommends the use of double dashed vertical lines to represent the salt bridge, the recommendation has not yet been universally adopted by chemists. In this text, we will continue to use the double vertical line (||) for a salt bridge.

◀ Several memory devices have been proposed for the oxidation/anode and reduction/cathode relationships. Perhaps the simplest is that in the oxidation/anode relationship, both terms begin with a vowel: *o*/*a*; in the reduction/cathode relationship, both begin with a consonant: *r*/*c*.

The cell diagram corresponding to both Figure 20-4 and reaction (20.3) is customarily written as

$$\text{anode} \longrightarrow \underbrace{\text{Zn(s)}\,|\,\text{Zn}^{2+}\text{(aq)}}_{\substack{\text{Half-cell}\\(\text{oxidation})}} \;\underbrace{\|}_{\substack{\text{Salt}\\\text{bridge}}}\; \underbrace{\text{Cu}^{2+}\text{(aq)}\,|\,\text{Cu(s)}}_{\substack{\text{Half-cell}\\(\text{reduction})}} \longleftarrow \text{cathode} \quad \underbrace{E_{\text{cell}} = 1.103\ \text{V}}_{\substack{\text{Cell voltage}}} \qquad \textbf{(20.4)}$$

The electrochemical cells of Figures 20-3 and 20-4 produce electricity as a result of spontaneous chemical reactions; as such, they are called **voltaic**, or **galvanic**, **cells**. In Section 20-7 we will consider *electrolytic cells*—electrochemical cells in which electricity is used to accomplish a nonspontaneous chemical change.

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that the spectator ions are not shown in a cell diagram, but they are present. They pass through the salt bridge to maintain electrical neutrality.

EXAMPLE 20-1 Representing a Redox Reaction by Means of a Cell Diagram

Aluminum metal displaces zinc(II) ion from aqueous solution.

(a) Write oxidation and reduction half-equations and an overall equation for this redox reaction.

(b) Write a cell diagram for a voltaic cell in which this reaction occurs.

Analyze

The term *displaces* means that aluminum goes into solution as $Al^{3+}(aq)$, forcing $Zn^{2+}(aq)$ out of solution as zinc metal. Al is oxidized to Al^{3+}, and Zn^{2+} is reduced to Zn. In combining the half-equations to produce the overall equation, we must take care to ensure that the *number of electrons involved in reduction equals the number involved in oxidation.* (This is the half-reaction method of balancing redox equations discussed in Section 5-5.) The cell diagram is written with the reduction half-equation as the right-hand electrode.

Solve

(a) The two half equations are

$$\textit{Oxidation:} \quad \text{Al(s)} \longrightarrow \text{Al}^{3+}\text{(aq)} + 3\,\text{e}^-$$

$$\textit{Reduction:} \quad \text{Zn}^{2+}\text{(aq)} + 2\,\text{e}^- \longrightarrow \text{Zn(s)}$$

On inspecting these half-equations, we see that the number of electrons involved in oxidation and reduction are different. In writing the overall equation, the coefficients must be adjusted so that equal numbers of electrons are involved in oxidation and in reduction.

$$\textit{Oxidation:} \quad 2\,\{\text{Al(s)} \longrightarrow \text{Al}^{3+}\text{(aq)} + 3\,\text{e}^-\}$$

$$\textit{Reduction:} \quad 3\,\{\text{Zn}^{2+}\text{(aq)} + 2\,\text{e}^- \longrightarrow \text{Zn(s)}\}$$

$$\textit{Overall:} \quad 2\,\text{Al(s)} + 3\,\text{Zn}^{2+}\text{(aq)} \longrightarrow 2\,\text{Al}^{3+}\text{(aq)} + 3\,\text{Zn(s)}$$

(continued)

(b) Al(s) is oxidized to $Al^{3+}(aq)$ in the anode half-cell (written on the left of the cell diagram), and $Zn^{2+}(aq)$ is reduced to Zn(s) in the cathode half-cell (written on the right of the cell diagram).

$$Al(s)\,|Al^{3+}(aq)\,||Zn^{2+}(aq)\,|Zn(s)$$

Assess

Whenever balancing redox equations, it is important to ensure that the number of electrons in the oxidation step equals the number of electrons in the reduction step. This is achieved by multiplying the entire half-reaction(s) by the appropriate factor(s).

PRACTICE EXAMPLE A: Write the overall equation for the redox reaction that occurs in the voltaic cell $Sc(s)\,|Sc^{3+}(aq)\,||Ag^{+}(aq)\,|Ag(s)$.

PRACTICE EXAMPLE B: Draw a voltaic cell in which silver ion is displaced from solution by aluminum metal. Label the cathode, the anode, and other features of the cell. Show the direction of flow of electrons. Also, indicate the direction of flow of cations and anions from a $KNO_3(aq)$ salt bridge. Write an equation for the half-reaction occurring at each electrode, write a balanced equation for the overall cell reaction, and write a cell diagram.

EXAMPLE 20-2 Deducing the Balanced Redox Reaction from a Cell Diagram

The cell diagram for an electrochemical cell is written as

$$Ni(s)\,|NiCl_2(aq)\,||Ce(ClO_4)_4(aq)\,,\,Ce(ClO_4)_3(aq)\,|Pt(s)$$

Write the equations for the half-reactions that occur at the electrodes. Balance the overall cell reaction.

Analyze

When inspecting a cell diagram, we first need to identify the species involved in oxidation and in reduction. Then we can write balanced half-cell equations. Finally, we can combine the half-cell equations to give the overall cell reaction. The new part to this example is the Ce^{4+}/Ce^{3+} couple in the presence of the inert platinum electrode at which the reduction takes place. Again, when balancing redox equations, it is important to ensure that the number of electrons in the oxidation step equals the number of electrons in the reduction step.

Solve

The cerium reduction reaction is

$$Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)$$

The nickel oxidation reaction is

$$Ni(s) \longrightarrow Ni^{2+}(aq) + 2\,e^-$$

In these half-equations the number of electrons involved in oxidation and reduction are different. In writing the overall equation, the coefficients must be adjusted so that equal numbers of electrons are involved in oxidation and in reduction.

$$\begin{array}{ll} \textit{Oxidation:} & Ni(s) \longrightarrow Ni^{2+}(aq) + 2\,e^- \\ \textit{Reduction:} & 2\,\{Ce^{4+}(aq) + e^- \longrightarrow Ce^{3+}(aq)\} \\ \textit{Overall:} & Ni(s) + 2\,Ce^{4+}(aq) \longrightarrow Ni^{2+}(aq) + 2\,Ce^{3+}(aq) \end{array}$$

Assess

We can see the importance of balancing each half-equation with respect to charge and mass.

PRACTICE EXAMPLE A: The cell diagram for an electrochemical cell is written as

$$Sn(s)\,|SnCl_2(aq)\,||AgNO_3(aq)\,|Ag(s)$$

Write the equations for the half-reactions that occur at the electrodes. Balance the overall cell reaction.

PRACTICE EXAMPLE B: The cell diagram for an electrochemical cell is written as

$$In(s)\,|In(ClO_4)_3(aq)\,||CdCl_2(aq)\,|Cd(s)$$

Write the equations for the half-reactions that occur at the electrodes. Balance the overall cell reaction.

20-1 CONCEPT ASSESSMENT

Add appropriate arrows to Figure 20-4 to show the direction of migration of ions through the electrochemical cell.

20-2 Standard Electrode Potentials

Cell voltages—*potential differences* between electrodes—are among the most precise scientific measurements possible. Potentials of individual electrodes, however, cannot be precisely established. If we could make such measurements, cell voltages could be obtained just by subtracting one electrode potential from another. The same result can be achieved by *arbitrarily* choosing a particular half-cell that is assigned an electrode potential of *zero*. Other half-cells can then be compared with this reference. The commonly accepted reference is the standard hydrogen electrode.

◀ This method is comparable to establishing standard enthalpies or Gibbs energies of formation on the basis of an arbitrary zero value.

The **standard hydrogen electrode (SHE)** is depicted in Figure 20-5. The SHE involves equilibrium established on the surface of an inert metal (such as platinum) between H_3O^+ ions from a solution in which they are at unit activity (that is, $a_{H_3O^+} = 1$) and H_2 molecules from the gaseous state at a pressure of 1 bar. The equilibrium reaction produces a particular potential on the metal surface, but this potential is arbitrarily taken to be *zero*.

$$2\,H^+(a = 1) + 2\,e^- \overset{\text{on Pt}}{\rightleftharpoons} H_2(g, 1\text{ bar}) \qquad E^\circ = 0\text{ volt (V)} \qquad \textbf{(20.5)}$$

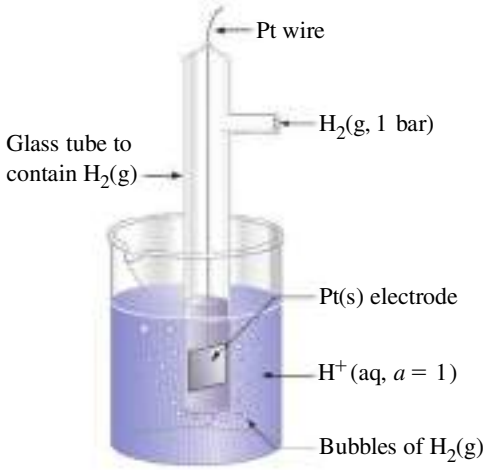
The diagram for this half-cell is

$$Pt|H_2(g, 1\text{ bar})|H^+(a = 1)$$

The two vertical lines signify that three phases are present: solid platinum, gaseous hydrogen, and aqueous hydrogen ion. For simplicity, we will usually write H^+ for H_3O^+, assume that unit activity ($a = 1$) exists at roughly $[H^+] = 1$ M, and replace a pressure of 1 bar by 1 atm.

◀ In this chapter, we shall use the units bar and atm interchangeably. The reason is that, although the current standard pressure is defined as 1 bar, the most extensive and authoritative tabulations of E° values are based on the old standard of 1 atm. Fortunately, the difference between 1 bar and 1 atm is small and so too are the differences between E° values based on the old and new standards.

By international agreement, a **standard electrode potential, E°**, measures the tendency for a *reduction* process to occur at an electrode. In all cases, the



▲ FIGURE 20-5
The standard hydrogen electrode (SHE)
Because hydrogen is a gas at room temperature, electrodes cannot be constructed from it. The standard hydrogen electrode consists of a piece of platinum dipped into a solution containing 1 M H^+(aq) with a stream of hydrogen passing over its surface. The platinum does not react but provides a surface for the reduction of $H_3O(aq)^+$ to $H_2(g)$ as well as the reverse oxidation half-reaction.

ionic species are present in aqueous solution at unit activity (approximately 1 M), and gases are at 1 bar pressure (approximately 1 atm). Where no metallic substance is indicated, the potential is established on an inert metallic electrode, such as platinum.

To emphasize that $E°$ refers to a reduction, we will write a reduction couple as a subscript to $E°$, as shown in half-reaction (20.6). The substance being reduced is written on the left of the slash sign (/), and the chief reduction product on the right.

$$Cu^{2+}(1\ M) + 2\,e^- \longrightarrow Cu(s) \qquad E°_{Cu^{2+}/Cu} = ? \tag{20.6}$$

To determine the value of $E°$ for a standard electrode such as that to which half-reaction (20.6) applies, we compare it with a standard hydrogen electrode (SHE). In this comparison, the SHE is always taken as the electrode on the *left* of the cell diagram—the anode—and the compared electrode is the electrode on the *right*—the cathode. In the following voltaic cell, the measured potential difference is 0.340 V, with electrons flowing from the H_2 to the Cu electrode.

$$\underset{\text{anode}}{Pt|H_2(g, 1\ atm)|H^+(1\ M)}||\underset{\text{cathode}}{Cu^{2+}(1\ M)|Cu(s)} \qquad E°_{cell} = 0.340\ V \tag{20.7}$$

A **standard cell potential, $E°_{cell}$**, is the potential difference, or voltage, of a cell formed from two *standard* electrodes. The *difference* is always taken in the following way:

$$E°_{cell} = \underset{\text{(cathode)}}{E°(\text{right})} - \underset{\text{(anode)}}{E°(\text{left})}$$

Applied to the cell diagram (20.7), we get

$$\begin{aligned} E°_{cell} &= E°_{Cu^{2+}/Cu} - E°_{H^+/H_2} = 0.340\ V \\ &= E°_{Cu^{2+}/Cu} - 0\ V = 0.340\ V \\ E°_{Cu^{2+}/Cu} &= 0.340\ V \end{aligned}$$

Thus, the standard *reduction* half-reaction can be written as

$$Cu^{2+}(1\ M) + 2\,e^- \longrightarrow Cu(s) \qquad E°_{Cu^{2+}/Cu} = +0.340\ V \tag{20.8}$$

The overall reaction occurring in the voltaic cell diagrammed in (20.7) can be represented as

$$H_2(g, 1\ atm) + Cu^{2+}(1\ M) \longrightarrow 2\,H^+(1\ M) + Cu(s) \qquad E°_{cell} = 0.340\ V \tag{20.9}$$

Cell reaction (20.9) indicates that $Cu^{2+}(1\ M)$ is more easily reduced than is $H^+(1\ M)$.

Suppose the standard copper electrode in cell diagram (20.7) is replaced by a standard zinc electrode, and the potential difference between the standard hydrogen and zinc electrodes is measured by using the same voltmeter connections as in (20.7). In this case, the voltage is found to be −0.763 V. The negative sign indicates that electrons flow in the direction *opposite* that in (20.7)—that is, *from* the zinc electrode to the hydrogen electrode. Here $H^+(1\ M)$ is more easily reduced than is $Zn^{2+}(1\ M)$. These findings are represented in the following cell diagram, in which the zinc electrode appears on the *right*.

$$Pt|H_2(g, 1\ atm)|H^+(1\ M)||Zn^{2+}(1\ M)|Zn(s) \qquad E°_{cell} = -0.763\ V \tag{20.10}$$

The standard electrode potential for the Zn^{2+}/Zn couple can be written as

$$\begin{aligned} E°_{cell} &= E°(\text{right}) - E°(\text{left}) \\ &= E°_{Zn^{2+}/Zn} - 0\ V = -0.763\ V \\ E°_{Zn^{2+}/Zn} &= -0.763\ V \end{aligned}$$

Thus, the standard *reduction* half-reaction is

$$Zn^{2+}(1\ M) + 2\,e^- \longrightarrow Zn(s) \qquad E°_{Zn^{2+}/Zn} = -0.763\ V \tag{20.11}$$

In summary, the potential of the standard hydrogen electrode is set at exactly 0 V. Any electrode at which a reduction half-reaction shows a *greater* tendency to occur than does the reduction of H^+ (1 M) to H_2 (g, 1 atm) has a *positive* value for its standard electrode potential, $E°$. Any electrode at which a reduction half-reaction shows a *lesser* tendency to occur than does the reduction of H^+(1 M) to H_2 (g, 1 atm) has a *negative* value for its standard reduction potential, $E°$. Comparisons of the standard copper and zinc electrodes to the standard hydrogen electrode are illustrated in Figure 20-6. Table 20.1 on the next page lists some common reduction half-reactions and their standard electrode potentials at 25 °C.

20-2 CONCEPT ASSESSMENT

For Figure 20-6, describe any changes in mass that might be detected at the Pt, Cu, and Zn electrodes as electric current passes through the electrochemical cells.

Standard reduction potentials are used throughout this chapter for many purposes. Our first objective will be to calculate standard cell potentials for redox reactions—$E°_{cell}$ values—from standard electrode potentials for half-cell reactions—$E°$ values. The procedure used is illustrated here for reaction (20.3) and cell diagram (20.4). Note that the first three equations are alternative ways of stating the same thing; we will generally not write all of them.

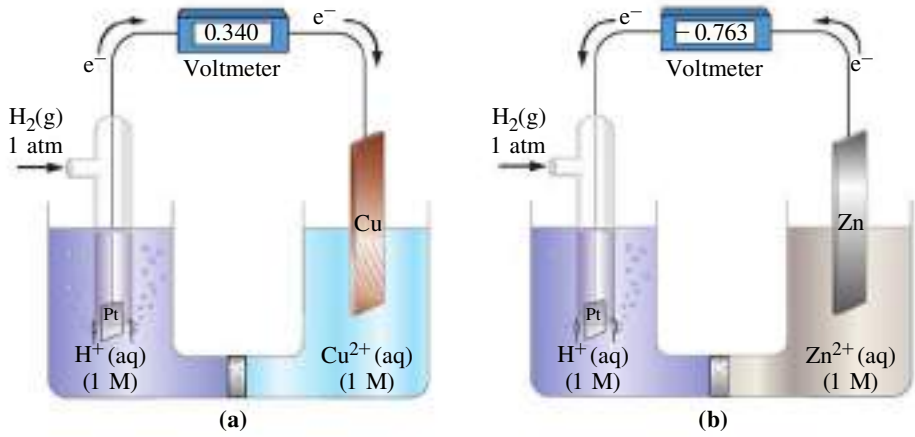
◀ Reaction (20.3) is shown on page 866 and diagram (20.4) on page 867.

$$\begin{aligned} E°_{cell} &= E°(\text{right}) - E°(\text{left}) \\ &= E°(\text{cathode}) - E°(\text{anode}) \\ &= E°(\text{reduction half-cell}) - E°(\text{oxidation half-cell}) \\ &= E°_{Cu^{2+}/Cu} - E°_{Zn^{2+}/Zn} \\ &= 0.340\ \text{V} - (-0.763\ \text{V}) = 1.103\ \text{V} \end{aligned}$$

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that the $E°$ values in this formulation are for a reduction half-reaction, regardless of whether oxidation or reduction occurs in the half-cell.

Example 20-3 predicts $E°_{cell}$ for a new battery system. Example 20-4 uses one known electrode potential and a measured $E°_{cell}$ value to determine an unknown $E°$.



▲ FIGURE 20-6
Measuring standard electrode potentials
(a) A standard hydrogen electrode is the anode, and copper is the cathode. Contact between the half-cells occurs through a porous plate that prevents bulk flow of the solutions while allowing ions to pass. **(b)** This cell has the same connections as that in part (a), but with zinc substituting for copper. However, the electron flow is opposite that in (a), as noted by the *negative* voltage. (Zinc is the anode.)

▶ A more extensive listing of reduction half-reactions and their potentials is given in Appendix D.

▶ The placement of *oxidizing agents* is as follows: strongest oxidizing agents ($F_2, O_3, \ldots$), *left* sides, *top* of the list; weakest oxidizing agents ($Li^+, K^+, \ldots$), *left* sides, *bottom* of list. The placement of *reducing agents* is as follows: strongest reducing agents (Li, K, . . .), *right* sides, *bottom* of list; weakest reducing agents ($F^-, O_2, \ldots$), *right* sides, *top* of list.

TABLE 20.1 Some Selected Standard Electrode (Reduction) Potentials at 25 °C

Reduction Half-Reaction	$E°$, V
Acidic solution	
$F_2(g) + 2\,e^- \longrightarrow 2\,F^-(aq)$	+2.866
$O_3(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow O_2(g) + H_2O(l)$	+2.075
$S_2O_8^{2-}(aq) + 2\,e^- \longrightarrow 2\,SO_4^{2-}(aq)$	+2.01
$H_2O_2(aq) + 2\,H^+(aq) + 2\,e^- \longrightarrow 2\,H_2O(l)$	+1.763
$MnO_4^-(aq) + 8\,H^+(aq) + 5\,e^- \longrightarrow Mn^{2+}(aq) + 4\,H_2O(l)$	+1.51
$PbO_2(s) + 4\,H^+(aq) + 2\,e^- \longrightarrow Pb^{2+}(aq) + 2\,H_2O(l)$	+1.455
$Cl_2(g) + 2\,e^- \longrightarrow 2\,Cl^-(aq)$	+1.358
$Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,e^- \longrightarrow 2\,Cr^{3+}(aq) + 7\,H_2O(l)$	+1.33
$MnO_2(s) + 4\,H^+(aq) + 2\,e^- \longrightarrow Mn^{2+}(aq) + 2\,H_2O(l)$	+1.23
$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l)$	+1.229
$2\,IO_3^-(aq) + 12\,H^+(aq) + 10\,e^- \longrightarrow I_2(s) + 6\,H_2O(l)$	+1.20
$Br_2(l) + 2\,e^- \longrightarrow 2\,Br^-(aq)$	+1.065
$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \longrightarrow NO(g) + 2\,H_2O(l)$	+0.956
$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+0.800
$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$	+0.771
$O_2(g) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2O_2(aq)$	+0.695
$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq)$	+0.535
$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$	+0.340
$SO_4^{2-}(aq) + 4\,H^+(aq) + 2\,e^- \longrightarrow 2\,H_2O(l) + SO_2(g)$	+0.17
$Sn^{4+}(aq) + 2\,e^- \longrightarrow Sn^{2+}(aq)$	+0.154
$S(s) + 2\,H^+(aq) + 2\,e^- \longrightarrow H_2S(g)$	+0.14
$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g)$	0
$Pb^{2+}(aq) + 2\,e^- \longrightarrow Pb(s)$	−0.125
$Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(s)$	−0.137
$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s)$	−0.440
$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$	−0.763
$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$	−1.676
$Mg^{2+}(aq) + 2\,e^- \longrightarrow Mg(s)$	−2.356
$Na^+(aq) + e^- \longrightarrow Na(s)$	−2.713
$Ca^{2+}(aq) + 2\,e^- \longrightarrow Ca(s)$	−2.84
$K^+(aq) + e^- \longrightarrow K(s)$	−2.924
$Li^+(aq) + e^- \longrightarrow Li(s)$	−3.040
Basic solution	
$O_3(g) + H_2O(l) + 2\,e^- \longrightarrow O_2(g) + 2\,OH^-(aq)$	+1.246
$OCl^-(aq) + H_2O(l) + 2\,e^- \longrightarrow Cl^-(aq) + 2\,OH^-(aq)$	+0.890
$O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq)$	+0.401
$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$	−0.828

EXAMPLE 20-3 Combining $E°$ Values into $E°_{cell}$ for a Reaction

A new battery system currently under study for possible use in electric vehicles is the zinc–chlorine battery. The overall reaction producing electricity in this cell is $Zn(s) + Cl_2(g) \longrightarrow ZnCl_2(aq)$. What is $E°_{cell}$ of this voltaic cell?

Analyze

First we identify the species that are oxidized and reduced. Then we obtain the standard reduction potentials for the cathode and anode from Table 20.1 or Appendix D and calculate E°_{cell}.

Solve

The oxidation state of zinc changes from 0 to +2 and therefore is oxidized; consequently, the chlorine is reduced. The half-reactions are indicated below and are combined into the overall equation (20.12).

$$\begin{aligned} &\textit{Oxidation:} && \mathrm{Zn(s)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{e^-} \\ &\textit{Reduction:} && \mathrm{Cl_2(g)} + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Cl^-(aq)} \\ &\textit{Overall:} && \mathrm{Zn(s)} + \mathrm{Cl_2(g)} \longrightarrow \mathrm{Zn^{2+}(aq)} + 2\,\mathrm{Cl^-(aq)} \end{aligned} \qquad \textbf{(20.12)}$$

$$\begin{aligned} E^\circ_{cell} &= E^\circ(\text{reduction half-cell}) - E^\circ(\text{oxidation half-cell}) \\ &= 1.358\ \mathrm{V} - (-0.763\ \mathrm{V}) = 2.121\ \mathrm{V} \end{aligned}$$

Assess

Once the oxidized and reduced species are identified, we can establish E°_{cell}.

PRACTICE EXAMPLE A: What is E°_{cell} for the reaction in which $Cl_2(g)$ oxidizes $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$?

$$2\,\mathrm{Fe^{2+}(aq)} + \mathrm{Cl_2(g)} \longrightarrow 2\,\mathrm{Fe^{3+}(aq)} + 2\,\mathrm{Cl^-(aq)} \qquad E^\circ_{cell} = ?$$

PRACTICE EXAMPLE B: Use data from Table 20.1 to determine E°_{cell} for the redox reaction in which $Fe^{2+}(aq)$ is oxidized to $Fe^{3+}(aq)$ by $MnO_4^-(aq)$ in acidic solution.

EXAMPLE 20-4 Determining an Unknown E° from an E°_{cell} Measurement

Cadmium is found in small quantities wherever zinc is found. Unlike zinc, which in trace amounts is an essential element, cadmium is an environmental poison. To determine cadmium ion concentrations by electrical measurements, we need the standard electrode potential for the Cd^{2+}/Cd electrode. The voltage of the following voltaic cell is measured.

$$\mathrm{Cd(s)\,|Cd^{2+}(1\ M)\,||Cu^{2+}(1\ M)\,|Cu(s)} \qquad E^\circ_{cell} = 0.743\ \mathrm{V}$$

What is the standard electrode potential for the Cd^{2+}/Cd electrode?

Analyze

We know one half-cell potential and E°_{cell} for the overall redox reaction. We can solve for the unknown standard electrode potential, $E^\circ_{Cd^{2+}/Cd}$.

Solve

$$\begin{aligned} E^\circ_{cell} &= E^\circ(\text{right}) - E^\circ(\text{left}) \\ 0.743\ \mathrm{V} &= E^\circ_{Cu^{2+}/Cu} - E^\circ_{Cd^{2+}/Cd} \\ &= 0.340\ \mathrm{V} - E^\circ_{Cd^{2+}/Cd} \\ E^\circ_{Cd^{2+}/Cd} &= 0.340\ \mathrm{V} - 0.743\ \mathrm{V} = -0.403\ \mathrm{V} \end{aligned}$$

Assess

Based on the entries in Table 20.1 we see that Cd(s) is a stronger reducing agent than Sn(s), but weaker than Fe(s). $Cd^{2+}(aq)$ is a weaker oxidizing agent than $Sn^{2+}(aq)$.

PRACTICE EXAMPLE A: In acidic solution, dichromate ion oxidizes oxalic acid, $H_2C_2O_4(aq)$, to $CO_2(g)$ in a reaction with $E^\circ_{cell} = 1.81$ V.

$$\mathrm{Cr_2O_7^{2-}(aq)} + 3\,\mathrm{H_2C_2O_4(aq)} + 8\,\mathrm{H^+(aq)} \longrightarrow 2\,\mathrm{Cr^{3+}(aq)} + 7\,\mathrm{H_2O} + 6\,\mathrm{CO_2(g)}$$

Use the value of E°_{cell} for this reaction, together with appropriate data from Table 20.1, to determine E° for the $CO_2(g)/H_2C_2O_4(aq)$ electrode.

PRACTICE EXAMPLE B: In an acidic solution, $O_2(g)$ oxidizes $Cr^{2+}(aq)$ to $Cr^{3+}(aq)$. The $O_2(g)$ is reduced to $H_2O(l)$. E°_{cell} for the reaction is 1.653 V. What is the standard electrode potential for the couple Cr^{3+}/Cr^{2+}?

20-3 CONCEPT ASSESSMENT

For the half-cell reaction $ClO_4^-(aq) + 8\,H^+(aq) + 7\,e^- \longrightarrow \frac{1}{2}Cl_2(g) + 4\,H_2O(l)$, what are the standard-state conditions for the reactants and products?

20-3 E_{cell}, ΔG, and K

When a reaction occurs in a voltaic cell, the cell does work—electrical work. Think of this as the work of moving electric charges. The total work done is the product of three terms: (a) E_{cell}; (b) z, the number of electrons transferred between the electrodes; and (c) the electric charge per mole of electrons, called the **Faraday constant** ***(F)***. The Faraday constant is equal to 96,485 coulombs per mole of electrons (96,485 C/mol). Because the product volt × coulomb = joule, the unit of w_{elec} is joules (J).

▶ It is quite common to see the symbol n used for the number of electrons; however, IUPAC recommends z to avoid confusion with the use of n as the amount of substance, such as the number of moles of gas in the ideal gas equation.

$$w_{elec} = zFE_{cell} \qquad \textbf{(20.13)}$$

Expression (20.13) applies only if the cell operates reversibly.* The last paragraph in Section 19-4 on page 836 described the amount of available energy (work) that can be derived from a process as equal to $-\Delta G$. Thus,

$$\Delta G = -zFE_{cell} \qquad \textbf{(20.14)}$$

In the special case in which the reactants and products are in their standard states,

$$\Delta G^\circ = -zFE^\circ_{cell} \qquad \textbf{(20.15)}$$



▲ **Michael Faraday (1791–1867)** Faraday, an assistant to Humphry Davy and often called "Davy's greatest discovery," made many contributions to both physics and chemistry, including systematic studies of electrolysis.

At this point we should clear up some issues of units and definitions. The symbol z in equations (20.14) and (20.15) is properly called the *electron number* of an electrochemical reaction and is occasionally referred to as the *charge number*. The electron number has no units; that is, it is simply a number. For any given cell reaction we can write the reaction with a charge number of one or two. Thus, the hydrogen electrode reaction can be written as either

$$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g) \quad \text{or} \quad H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$$

However, in considering an overall cell reaction, we must balance the electrons. Thus for the cell

$$Pt(s)\,|H_2(g)\,|H^+(aq, 1\,M)\,||Cu^{2+}(aq)\,|Cu(s)$$

the half-cell reactions can be written as

$$2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g) \quad \text{and} \quad 2\,e^- + Cu^{2+}(aq) \longrightarrow Cu(s)$$

Thus, the electron number is two and the overall electrochemical reaction is

$$H_2(g) + Cu^{2+}(aq) \longrightarrow 2\,H^+(aq) + Cu(s)$$

The standard reduction potential for this reaction is

$$E^\circ_{cell} = E^\circ(\text{right}) - E^\circ(\text{left})$$
$$= E^\circ_{Cu^{2+}/Cu} - 0\ V = 0.340\ V$$

The standard Gibbs energy is given by

$$\Delta G^\circ_{rxn} = -zFE^\circ_{cell} = 2 \times \frac{96485\ C}{mol} \times 0.340\ V$$
$$= -6.5610 \times 10^4\ J\ mol^{-1} = -65.6\ kJ\ mol^{-1}$$

*The meaning of a reversible process was illustrated by Figure 7-12 on page 258. The reversible operation of a voltaic cell requires that electric current be drawn from the cell only very, very slowly.

That is, 65.6 kJ of energy is generated when 1 mole of Cu^{2+} ions is reduced or 2 moles of H^+ are produced. The process is accompanied by the passage of two moles of electrons around the outer circuit. We could also have written the reactions as

$$\begin{aligned}
&\textit{Oxidation:} && \tfrac{1}{2}H_2(g) \longrightarrow H^+(aq) + e^- \\
&\textit{Reduction:} && \tfrac{1}{2}Cu^{2+}(aq) + e^- \longrightarrow \tfrac{1}{2}Cu(s) \\
&\textit{Overall:} && \tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cu^{2+}(aq) \longrightarrow \tfrac{1}{2}Cu(s) + H^+(aq)
\end{aligned}$$

This reaction is represented by the same cell diagram given above, but the electron number is one; consequently, the Gibbs energy is one-half of that previously calculated, but the value of E°_{cell} is the same. This result supports the fact that the standard reduction potential is an intensive property but the Gibbs energy is an extensive property. Finally, the reaction tells us that when 0.5 mole of Cu^{2+} is reduced, 32.8 kJ of energy is released and one mole of electrons passes from the anode to the cathode.

Our primary interest is not in calculating quantities of work but in using expression (20.15) as a means of evaluating Gibbs energy changes from measured cell potentials, as illustrated in Example 20-5.

EXAMPLE 20-5 Determining a Gibbs Energy Change from a Cell Potential

Use E° data to determine ΔG° for the reaction

$$Zn(s) + Cl_2(g, 1\text{ atm}) \longrightarrow ZnCl_2(aq, 1\text{ M})$$

Solution

This reaction is cell reaction (20.12) occurring in the voltaic cell described in Example 20-3. In this type of problem, the overall equation generally needs to be separated into two half-equations. Then the value of E°_{cell} and the number of moles of electrons (n) involved in the cell reaction can be determined. Refer to Example 20-3 to see that $E^\circ_{cell} = 2.121$ V and $z = 2$ mol e^-. Now use equation (20.15).

$$\begin{aligned}
\Delta G^\circ &= -zFE^\circ_{cell} = -\left(2\text{ mol e}^- \times \frac{96{,}485\text{ C}}{1\text{ mol e}^-} \times 2.121\text{ V}\right) \\
&= -4.093 \times 10^5\text{ J} = -409.3\text{ kJ mol}^{-1}
\end{aligned}$$

PRACTICE EXAMPLE A: Use electrode potential data to determine ΔG° for the reaction

$$2\,Al(s) + 3\,Br_2(l) \longrightarrow 2\,Al^{3+}(aq, 1\text{ M}) + 6\,Br^-(aq, 1\text{ M}) \qquad \Delta G^\circ = ?$$

PRACTICE EXAMPLE B: The hydrogen–oxygen fuel cell is a voltaic cell with a cell reaction of $2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l)$. Calculate E°_{cell} for this reaction. [*Hint:* Use thermodynamic data from Appendix D (Table D-2).]

Combining Reduction Half-Equations

Not only can equation (20.15) be used to determine ΔG° from E°_{cell}, as in Example 20-5, but the calculation can be reversed and an E°_{cell} value determined from ΔG°. Moreover, equation (20.15) can be applied to half-cell reactions and half-cell potentials—that is, to standard electrode potentials, E°. That is what we must do, for example, to determine E° for the half-reaction

$$Fe^{3+}(aq) + 3\,e^- \longrightarrow Fe(s)$$

Both in Table 20.1 and in Appendix D, the only entries that deal with Fe(s) and its ions are

$$Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s), E^\circ = -0.440\text{ V} \quad \text{and} \quad Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq), E^\circ = 0.771\text{ V}$$

The half-equation we are seeking is simply the sum of these two half-equations, but the $E°$ value we are seeking is *not* the sum of −0.440 V and 0.771 V. What we *can* add together, though, are the $\Delta G°$ values for the two known half-reactions.

KEEP IN MIND

that Gibbs energy changes are functions of state and therefore ΔG values can be combined to determine Gibbs energy changes for new reactions.

$$\begin{aligned} &Fe^{2+}(aq) + 2\,e^- \longrightarrow Fe(s); && \Delta G° = -2 \times F \times (-0.440\ V) \\ &Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq); && \Delta G° = -1 \times F \times (0.771\ V) \\ \hline &Fe^{3+}(aq) + 3\,e^- \longrightarrow Fe(s); && \Delta G° = (0.880F)\ V - (0.771F)\ V = (0.109F)\ V \end{aligned}$$

Now, to get $E°_{Fe^{3+}/Fe}$, we can again use equation (20.15) and solve for $E°_{Fe^{3+}/Fe}$.

$$\Delta G° = -zFE°_{Fe^{3+}/Fe} = -3FE°_{Fe^{3+}/Fe} = (0.109F)\ V$$
$$E°_{Fe^{3+}/Fe} = (-0.109F/3F)\ V = -0.0363\ V$$

20-1 ARE YOU WONDERING...

How the procedure for combining two $E°$ values to obtain an unknown $E°_{cell}$ relates to combining two $E°$ values to obtain an unknown $E°$?

We have just seen how to obtain an unknown $E°$ from two known values of $E°$ by working through the expression $\Delta G = -zFE°$. As shown below for a hypothetical displacement reaction, we can similarly calculate an unknown $E°_{cell}$ through the expression $\Delta G° = -zFE°_{cell}$. (Note that for the oxidation half-reaction, $\Delta G°_{ox}$ is simply the negative of the value for the reverse half-reaction, $\Delta G°_{red}$.)

$$\begin{aligned} &\textit{Reduction:}\quad M^{z+}(aq) + z\,e^- \longrightarrow M(s) && \Delta G°_{red} = -zFE°_{M^{2+}/M} \\ &\textit{Oxidation:}\quad N(s) \longrightarrow N^{z+}(aq) + z\,e^- \\ &\qquad\qquad \Delta G°_{ox} = -(\Delta G°_{red}) = -(-zFE°_{N^{z+}/N}) = zFE°_{N^{2+}/N} \\ &\textit{Overall:}\quad M^{z+}(aq) + N(s) \longrightarrow M(s) + N^{z+}(aq) \\ &\qquad\qquad \Delta G° = \Delta G°_{red} + \Delta G°_{ox} = -zFE°_{cell} = -zFE°_{M^{2+}/M} + zFE°_{N^{2+}/N} \end{aligned}$$

Dividing through the above equation by the term $-zF$, we obtain $E°_{cell}$ as the familiar difference in two electrode potentials.

$$E°_{cell} = E°_{M^{z+}/M} - E°_{N^{z+}/N}$$

We have been able to skip this calculation based on $\Delta G°$ values and proceed straight to the expression

$$E°_{cell} = E°(\text{reduction}) - E°(\text{oxidation})$$

because the term $-zF$ always cancels out. That is, z, the number of electrons, must have the same value for the oxidation and reduction half-reactions and the overall reaction. By contrast, when obtaining an unknown $E°$ from the known $E°$ values, the value for z will not be the same in all three places where it appears, and so we do have to work through the $\Delta G°$ expressions.

Spontaneous Change in Oxidation–Reduction Reactions

Our main criterion for spontaneous change is that $\Delta G < 0$. According to equation (20.14), however, redox reactions have the property that, if $\Delta G < 0$, then $E_{cell} > 0$. That is, E_{cell} must be *positive* if ΔG is to be negative. Predicting the direction of spontaneous change in a redox reaction is a relatively simple matter by using the following ideas:

- If E_{cell} is *positive*, a reaction occurs spontaneously in the *forward* direction for the stated conditions. If E_{cell} is *negative*, the reaction occurs spontaneously in the *reverse* direction for the stated conditions. If $E_{cell} = 0$, the reaction is at equilibrium for the stated conditions.
- If a cell reaction is *reversed*, E_{cell} changes sign.

EXAMPLE 20-6 Applying the Criterion for Spontaneous Change in a Redox Reaction

Will aluminum metal displace Cu^{2+} ion from aqueous solution? That is, will a spontaneous reaction occur in the forward direction for the following reaction?

$$2\,Al(s) + 3\,Cu^{2+}(1\,M) \longrightarrow 3\,Cu(s) + 2\,Al^{3+}(1\,M)$$

Analyze

We need to identify the species reduced in the reaction as it is written. We then calculate E°_{cell}. If E°_{cell} is positive, then the reaction will occur spontaneously.

Solve

The cell diagram corresponding to the reaction is $Al(s)\,|Al^{3+}(aq)\,||Cu^{2+}(aq)\,|Cu(s)$, and E°_{cell} is

$$\begin{aligned} E^\circ_{cell} &= E^\circ(\text{cathode}) - E^\circ(\text{anode}) \\ &= E^\circ_{Cu^{2+}/Cu} - E^\circ_{Al^{3+}/Al} \\ &= 0.340\text{ V} - (-1.676\text{ V}) = 2.016\text{ V} \end{aligned}$$

Because E°_{cell} is positive, the direction of spontaneous change is that of the forward reaction. Al(s) will displace Cu^{2+} from aqueous solution under standard-state conditions.

Assess

The positive value of E°_{cell} means that the Gibbs energy change for the reaction is negative; hence, the reaction as written is spontaneous. Keep in mind that both E° and E°_{cell} are *intensive* properties. They do not depend on the quantities of materials involved, which means that their values are not affected by the choice of coefficients used to balance the equation for the cell reaction. We could just as well have written:

$$Al(s) + \frac{3}{2}Cu^{2+}(1\,M) \longrightarrow \frac{3}{2}Cu(s) + Al^{3+}(1\,M) \text{ or}$$

$$\frac{2}{3}Al(s) + Cu^{2+}(1\,M) \longrightarrow Cu(s) + \frac{2}{3}Al^{3+}(1\,M)$$

PRACTICE EXAMPLE A: Name one metal ion that Cu(s) will displace from aqueous solution, and determine E°_{cell} for the reaction.

PRACTICE EXAMPLE B: When sodium metal is added to seawater, which has $[Mg^{2+}] = 0.0512$ M, no magnesium metal is obtained. According to E° values, should this displacement reaction occur? What reaction does occur?

In the special case in which reactants and products are in their standard states, we work with ΔG° and E°_{cell} values, as illustrated in Examples 20-6 and 20-7.

Even though we used electrode potentials and cell voltage to predict a spontaneous reaction in Example 20-6, we do not have to carry out the reaction in a voltaic cell. This is an important point to keep in mind. Thus, Cu^{2+} is displaced from aqueous solution simply by adding aluminum metal, as shown in Figure 20-7. Another point, illustrated by Example 20-7, is that qualitative answers to questions concerning redox reactions can be found without going through a complete calculation of E°_{cell}.



▲ FIGURE 20-7
Reaction of Al(s) and Cu^{2+}(aq)
Notice the holes in the foil where Al(s) has dissolved. Notice also the dark deposit of Cu(s) at the bottom of the beaker.

The Behavior of Metals Toward Acids

In the discussion of redox reactions in Chapter 5, it was noted that most metals react with an acid, such as HCl, but that a few do not. This observation can now be explained. When a metal, M, reacts with an acid, such as HCl, the metal is oxidized to the metal ion, such as M^{2+}. The reduction involves H^+ being reduced to $H_2(g)$. These ideas can be expressed as

$$\begin{aligned} &\textit{Oxidation:} && M(s) \longrightarrow M^{2+}(aq) + 2\,e^- \\ &\textit{Reduction:} && 2\,H^+(aq) + 2\,e^- \longrightarrow H_2(g) \\ &\textit{Overall:} && M(s) + 2\,H^+(aq) \longrightarrow M^{2+}(aq) + H_2(g) \end{aligned}$$

$$E^\circ_{cell} = E^\circ_{H^+/H_2} - E^\circ_{M^{2+}/M} = 0\text{ V} - E^\circ_{M^{2+}/M} = -E^\circ_{M^{2+}/M}$$

EXAMPLE 20-7 Making Qualitative Predictions with Electrode Potential Data

Peroxodisulfate salts, such as $Na_2S_2O_8$, are oxidizing agents used in bleaching. Dichromates such as $K_2Cr_2O_7$ have been used as laboratory oxidizing agents. Which is the better oxidizing agent in acidic solution under standard conditions, $S_2O_8^{2-}$ or $Cr_2O_7^{2-}$?

Analyze

In a redox reaction, the oxidizing agent is reduced; the greater the tendency for this reduction to occur, the better the oxidizing agent. The reduction tendency, in turn, is measured by the $E°$ value.

Solve

Because the $E°$ value for the reduction of $S_2O_8^{2-}(aq)$ to $SO_4^{2-}(aq)$ (2.01 V) is larger than that for the reduction of $Cr_2O_7^{2-}(aq)$ to $Cr^{3+}(aq)$ (1.33 V), $S_2O_8^{2-}(aq)$ should be the better oxidizing agent.

Assess

Inspection of standard reduction potentials enables us to qualitatively assess the spontaneity of a particular redox reaction.

PRACTICE EXAMPLE A: An inexpensive way to produce peroxodisulfates would be to pass $O_2(g)$ through an acidic solution containing sulfate ion. Is this method feasible under standard conditions? [*Hint:* What would be the reduction half-reaction?]

PRACTICE EXAMPLE B: Consider the following observations: (1) Aqueous solutions of Sn^{2+} are difficult to maintain because atmospheric oxygen easily oxidizes Sn^{2+} to Sn^{4+}. (2) One way to preserve the $Sn^{2+}(aq)$ solutions is to add some metallic tin. *Without doing detailed calculations,* explain these two statements by using $E°$ data.

Metals with *negative* standard electrode potentials yield *positive* values of $E°_{cell}$ in the above expression. These are the metals that should displace $H_2(g)$ from acidic solutions. Thus, all the metals listed *below* hydrogen in Table 20.1 (Pb through Li) should react with acids.

In acids, such as HCl, HBr, and HI, the oxidizing agent is H^+ (that is, H_3O^+). Certain metals that will not react with HCl will react with an acid in the presence of an *anion* that is a better oxidizing agent than H^+. Nitrate ion is a good oxidizing agent in acidic solution, and silver metal, which does not react with $HCl(aq)$, readily reacts with nitric acid, $HNO_3(aq)$.

$$3\,Ag(s) + NO_3^-(aq) + 4\,H^+(aq) \longrightarrow 3\,Ag^+(aq) + NO(g) + 2\,H_2O \quad E°_{cell} = 0.156\ V$$

The Relationship Between $E°_{cell}$ and K

▶ Note that any electrochemical cell, if left in a completed circuit, will eventually die as the redox reaction goes to completion. This means that the cell potential will eventually drop to zero. In Chapter 19, the relationship between Gibbs energy and equilibrium was established in a similar way.

$\Delta G°$ and $E°_{cell}$ were related through equation (20.15). In Chapter 19, $\Delta G°$ and K were related through equation (19.12). The three quantities are thus related in this way.

$$\Delta G° = -RT \ln K = -zFE°_{cell}$$

and therefore,

$$E°_{cell} = \frac{RT}{zF} \ln K \qquad \textbf{(20.16)}$$

▶ Equation 20.16 gives the expected result that reactions with equilibrium constants larger than one have a positive standard cell potential.

In equation (20.16), R has a value of 8.3145 J mol^{-1} K^{-1} and z represents the number of electrons involved in the reaction. If we then specify a temperature of 25 °C = 298.15 K (the temperature at which electrode potentials are generally determined), the combined terms "RT/F" in equation (20.16) can be replaced by a single constant. This constant has the value 0.025693 J/C = 0.025693 V.

$$E°_{cell} = \frac{RT}{zF} \ln K = \frac{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298.15\ \text{K}}{z \times 96485\ \text{C mol}^{-1}} \ln K$$

$$E^\circ_{cell} = \frac{0.025693\ V}{z} \ln K \qquad \textbf{(20.17)}$$

The relationship between E°_{cell} and K is illustrated in Example 20-8. Also, Figure 20-8 summarizes several important relationships from thermodynamics, equilibrium, and electrochemistry.

EXAMPLE 20-8 Relating K to E°_{cell} for a Redox Reaction

What is the value of the equilibrium constant K for the reaction between copper metal and iron(III) ions in aqueous solution at 25 °C?

$$Cu(s) + 2\,Fe^{3+}(aq) \longrightarrow Cu^{2+}(aq) + 2\,Fe^{2+}(aq) \qquad K = ?$$

Analyze

We first identify the reactant that is reduced and the reactant that is oxidized. We then use the data in Table 20.1 to obtain the standard reduction potentials and hence the cell potential. Finally, we use equation (20.17) to obtain K from E°_{cell}.

Solve

First, we use data from Table 20.1 to determine E°_{cell}.

$$\begin{aligned} E^\circ_{cell} &= E^\circ(\text{reduction half-cell}) - E^\circ(\text{oxidation half-cell}) \\ &= E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{Cu^{2+}/Cu} \\ &= 0.771\ V - 0.340\ V = 0.431\ V \end{aligned}$$

The charge number (z) for the cell reaction is 2.

$$E^\circ_{cell} = 0.431\ V = \frac{0.02569\ V}{2} \ln K$$

$$\ln K = \frac{2 \times 0.431\ V}{0.02569\ V} = 33.6$$

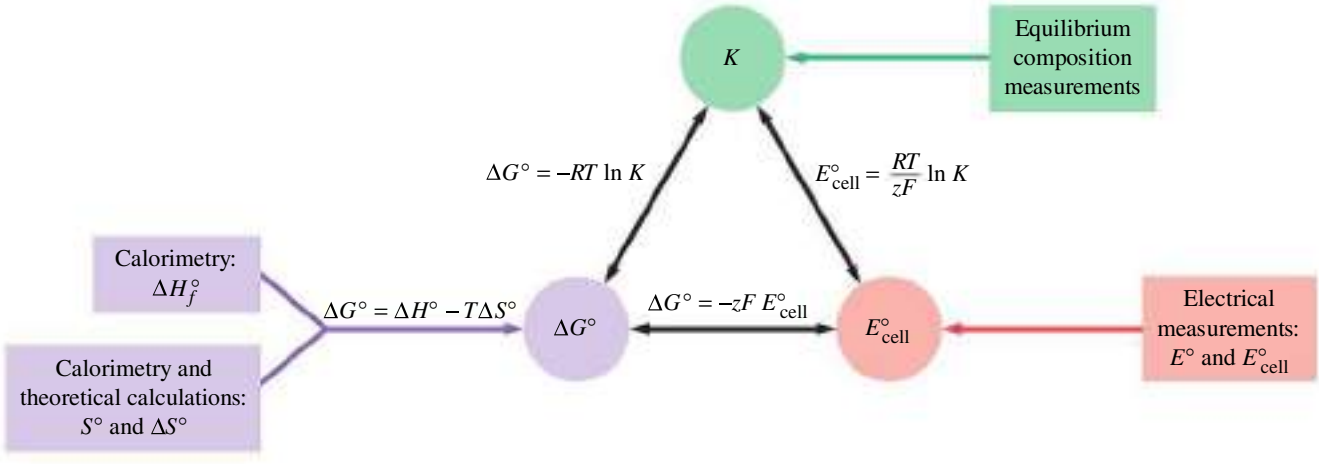
$$K = e^{33.6} = 4 \times 10^{14}$$

Assess

The positive value of the cell potential means that the equilibrium constant is greater than one. The value of the equilibrium constant is very large, and so we can expect this reaction to go to completion.

PRACTICE EXAMPLE A: Should the displacement of Cu^{2+} from aqueous solution by Al(s) go to completion? [*Hint:* Base your assessment on the value of K for the displacement reaction. We determined E°_{cell} for this reaction in Example 20-6.]

PRACTICE EXAMPLE B: Should the reaction of Sn(s) and $Pb^{2+}(aq)$ go to completion? Explain.

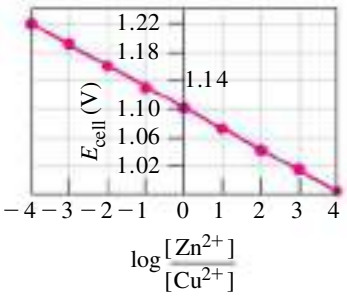


▲ FIGURE 20-8
A summary of important thermodynamic, equilibrium, and electrochemical relationships under standard conditions

20-4 CONCEPT ASSESSMENT

When two cell reactions with reactants and products in their standard states are compared, one is found to have a negative value of E°_{cell} and the other a positive value. Which cell reaction will proceed toward the formation of more products to establish equilibrium? Will a net cell reaction occur in the other case? If so, how will the equilibrium concentrations compare with the initial concentrations?

20-4 E_{cell} as a Function of Concentrations



▲ FIGURE 20-9
Variation of E_{cell} with ion concentrations
The cell reaction is Zn(s) + Cu^{2+}(aq) ⟶ Zn^{2+}(aq) + Cu(s) and has E°_{cell} = 1.103 V.

When we combine standard electrode potentials, we obtain a standard E°_{cell}, such as E°_{cell} = 1.103 V for the voltaic cell of Figure 20-4. For the following cell reaction at *nonstandard* conditions, however, the measured E_{cell} is not 1.103 V.

$$Zn(s) + Cu^{2+}(2.0\ M) \longrightarrow Zn^{2+}(0.10\ M) + Cu(s) \qquad E_{cell} = 1.142\ V$$

Experimental measurements of cell potentials are often made for nonstandard conditions; these measurements have great significance, especially for performing chemical analyses.

From Le Châtelier's principle, it would seem that *increasing* the concentration of a reactant (Cu^{2+}) while *decreasing* the concentration of a product (Zn^{2+}) should favor the forward reaction. Zn(s) should displace Cu^{2+}(aq) even more readily than for standard-state conditions and $E_{cell} > 1.103$ V. E_{cell} is found to vary linearly with log ($[Zn^{2+}]/[Cu^{2+}]$), as illustrated in Figure 20-9.

It is not difficult to establish the relationship between the cell potential, E_{cell}, and the concentrations of reactants and products. From Chapter 19 we can write equation (19.11).

$$\Delta G = \Delta G^\circ + RT \ln Q$$

For ΔG and ΔG°, we can substitute $-zFE_{cell}$ and $-zFE^\circ_{cell}$, respectively.

$$-zFE_{cell} = -zFE^\circ_{cell} + RT \ln Q$$

Dividing through by $-zF$ gives

$$E_{cell} = E^\circ_{cell} - \frac{RT}{zF} \ln Q$$



▲ **Walther Nernst (1864–1941)**
Nernst was only 25 years old when he formulated his equation relating cell voltages and concentrations. He is also credited with proposing the solubility product concept in the same year. In 1906, he announced his "heat theorem," which we now know as the third law of thermodynamics.

This equation was first proposed by Walther Nernst in 1889. It is commonly used by analytical chemists in the form in which Nernst expressed it. The **Nernst equation** can be obtained by switching from natural to common logarithms ($\ln Q = 2.3026 \log Q$).

$$E_{cell} = E^\circ_{cell} - \frac{2.3026\ RT}{zF} \log Q$$

By specifying a temperature of 298.15 K and replacing RT/F by 0.025693 V, as in the development of equation (20.17), we find that the term $2.3026\ RT/F = 2.3026 \times 0.025693\ V = 0.059161$ V, usually rounded off to 0.0592 V. The final form of the Nernst equation is

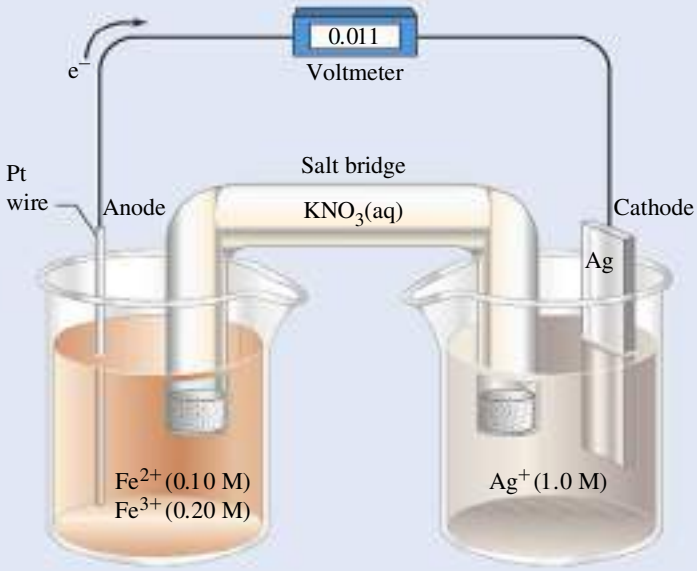
$$E_{cell} = E^\circ_{cell} - \frac{0.0592\ V}{z} \log Q \qquad \textbf{(20.18)}$$

In the Nernst equation, we make the usual substitutions into Q: $a = 1$ for the activities of pure solids and liquids, partial pressures (atm) for the activities of gases, and molarities for the activities of solution components. Example 20-9 demonstrates that the Nernst equation makes it possible to calculate E_{cell} for any chosen concentrations, not just for standard conditions.

EXAMPLE 20-9 Applying the Nernst Equation for Determining E_{cell}

What is the value of E_{cell} for the voltaic cell pictured in Figure 20-10 and diagrammed as follows?

$$Pt|Fe^{2+}(0.10\ M), Fe^{3+}(0.20\ M)||Ag^{+}(1.0\ M)|Ag(s) \qquad E_{cell} = ?$$



▲ FIGURE 20-10
A voltaic cell with nonstandard conditions—Example 20-9 illustrated

Analyze

To use the Nernst equation we need to establish E°_{cell} and the reaction to which the cell diagram corresponds so that the form of the reaction quotient (Q) can be revealed (see Example 20-2). Once we have determined the form of the Nernst equation, we can insert the concentration of the species.

Solve

Two steps are required when using the Nernst equation. First, to determine E°_{cell}, use data from Table 20.1 to write

$$\begin{aligned} E^{\circ}_{cell} &= E^{\circ}(\text{cathode}) - E^{\circ}(\text{anode}) \\ &= E^{\circ}_{Ag^+/Ag} - E^{\circ}_{Fe^{3+}/Fe^{2+}} \\ &= 0.800\ V - 0.771\ V = 0.029\ V \end{aligned} \qquad \textbf{(20.19)}$$

Now, to determine E_{cell} for the reaction

$$Fe^{2+}(0.10\ M) + Ag^{+}(1.0\ M) \longrightarrow Fe^{3+}(0.20\ M) + Ag(s) \qquad E_{cell} = ? \qquad \textbf{(20.20)}$$

substitute appropriate values into the Nernst equation (20.18), starting with $E^{\circ}_{cell} = 0.029$ V and $z = 1$,

$$E_{cell} = 0.029\ V - \frac{0.0592\ V}{1}\log\frac{[Fe^{3+}]}{[Fe^{2+}][Ag^{+}]}$$

and for concentrations $[Fe^{2+}] = 0.10$ M; $[Fe^{3+}] = 0.20$ M; $[Ag^{+}] = 1.0$ M.

$$\begin{aligned} E_{cell} &= 0.029\ V - 0.0592\ V \times \log\frac{0.20}{0.10 \times 1.0} \\ &= 0.029\ V - 0.0592\ V \times \log 2 = 0.029\ V - 0.018\ V \\ &= 0.011\ V \end{aligned}$$

Assess

The E_{cell} is positive so that the reaction is spontaneous in the direction of the reduction of silver.

PRACTICE EXAMPLE A: Calculate E_{cell} for the following voltaic cell.

$$Al(s)|Al^{3+}(0.36\ M)||Sn^{4+}(0.086\ M), Sn^{2+}(0.54\ M)|Pt$$

PRACTICE EXAMPLE B: Calculate E_{cell} for the following voltaic cell.

$$Pt(s)|Cl_2(1\ atm)|Cl^{-}(1.0\ M)||Pb^{2+}(0.050\ M), H^{+}(0.10\ M)|PbO_2(s)$$

20-5 CONCEPT ASSESSMENT

Describe *two* sets of conditions under which the measured E_{cell} for a reaction is equal to E°_{cell}.

In Section 20-3, we developed a criterion for spontaneous change ($E_{cell} > 0$), but we used the criterion only with E° data from Table 20.1 Qualitative conclusions reached with E°_{cell} values often hold over a broad range of nonstandard conditions as well. However, when E°_{cell} is within a few hundredths of a volt of zero, it is sometimes necessary to determine E_{cell} for nonstandard conditions in order to apply the criterion for spontaneity of redox reactions, as illustrated in Example 20-10.

EXAMPLE 20-10 Predicting Spontaneous Reactions for Nonstandard Conditions

Will the cell reaction proceed spontaneously as written for the following cell?

$$\mathrm{Ag(s)\,|Ag^+(0.075\ M)\,||Hg^{2+}(0.85\ M)\,|Hg(l)}$$

Analyze

To decide whether a reaction is spontaneous, we need to calculate E_{cell} by using equation (20.18) with the concentrations given. We then identify the oxidized and reduced species and look up the appropriate standard half-cell potentials. Then we construct the chemical equation that corresponds to the cell diagram, choosing an appropriate electron number (z).

Solve

To determine E°_{cell} from E° data we write

$$\begin{aligned} &\textit{Oxidation:} && 2\,\mathrm{Ag(s)} \longrightarrow 2\,\mathrm{Ag^+(aq)} + 2\,\mathrm{e^-} \\ &\textit{Reduction:} && \mathrm{Hg^{2+}(aq)} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Hg(l)} \\ &\textit{Overall:} && 2\,\mathrm{Ag(s)} + \mathrm{Hg^{2+}(aq)} \longrightarrow 2\,\mathrm{Ag^+(aq)} + \mathrm{Hg(l)} \end{aligned}$$

$$\begin{aligned} E^\circ_{cell} &= E^\circ(\text{reduction half-cell}) - E^\circ(\text{oxidation half-cell}) \\ &= 0.854\ \mathrm{V} - (0.800\ \mathrm{V}) = 0.054\ \mathrm{V} \end{aligned}$$

The overall reaction that we have written has an electron number, $z = 2$, so that the Nernst equation is

$$E_{cell} = 0.054\ \mathrm{V} - \frac{0.0592\ \mathrm{V}}{2} \log \frac{[\mathrm{Ag^+}]^2}{[\mathrm{Hg^{2+}}]}$$

By using the concentrations $[\mathrm{Ag^+}] = 0.075$ M and $[\mathrm{Hg^{2+}}] = 0.85$ M provided, we obtain

$$\begin{aligned} E_{cell} &= 0.054\ \mathrm{V} - 0.0296\ \mathrm{V} \log \frac{[0.075]^2}{[0.85]} \\ &= 0.054\ \mathrm{V} - 0.0296\ \mathrm{V} \log(0.0066) = 0.054 - 0.0296 \times (-2.179)\ \mathrm{V} \\ &= 0.054 + 0.065\ \mathrm{V} = -0.119\ \mathrm{V} \end{aligned}$$

Because $E_{cell} > 0$, we conclude that the reaction as written is spontaneous.

Assess

If we had used an electron number of $z = 1$, the overall reaction would have been

$$\textit{Overall}\ (z = 1)\text{: } \mathrm{Ag(s)} + \frac{1}{2}\mathrm{Hg^{2+}(aq)} \longrightarrow \mathrm{Ag^+(aq)} + \frac{1}{2}\mathrm{Hg(l)}$$

The corresponding Nernst equation is

$$E_{cell} = 0.054\ \mathrm{V} - \frac{0.0592\ \mathrm{V}}{1} \log \frac{[\mathrm{Ag^+}]}{[\mathrm{Hg^{2+}}]^{1/2}}$$

By rearranging slightly and using a property of logarithms,

$$E_{cell} = 0.054\ V - \frac{0.0592\ V}{1}\log\left(\frac{[Ag^+]^2}{[Hg^{2+}]}\right)^{1/2} = 0.054\ V - \frac{0.0592\ V}{2}\log\frac{[Ag^+]^2}{[Hg^{2+}]}$$

we have recovered the Nernst equation for the cell reaction by using an electron number (z) of 2. We conclude that as long as we balance charge and the electron number correctly, we will always get the correct result.

PRACTICE EXAMPLE A: Will the cell reaction proceed spontaneously as written for the following cell?

$$Cu(s)\,|Cu^{2+}(0.15\ M)\,||Fe^{3+}(0.35\ M),\,Fe^{2+}(0.25\ M)\,|Pt(s)$$

PRACTICE EXAMPLE B: For what ratio of $[Ag^+]^2/[Hg^{2+}]$ will the cell reaction in Example 20-10 not be spontaneous in either direction?

20-6 CONCEPT ASSESSMENT

The following cell is set up under standard-state conditions.

$$Pb(s)\,|Pb^{2+}||Cu^{2+}|Cu(s) \qquad E^\circ_{cell} = 0.47\ V$$

When sodium sulfate is added to the anode half-cell, formation of a white precipitate is observed, accompanied by a change in the value of E_{cell}. Explain these observations, and predict whether the new E_{cell} is greater or less than E°_{cell}.

Concentration Cells

The voltaic cell in Figure 20-11 consists of two hydrogen electrodes. One is a standard hydrogen electrode (SHE), and the other is a hydrogen electrode immersed in a solution of unknown $[H^+]$, less than 1 M. The cell diagram is

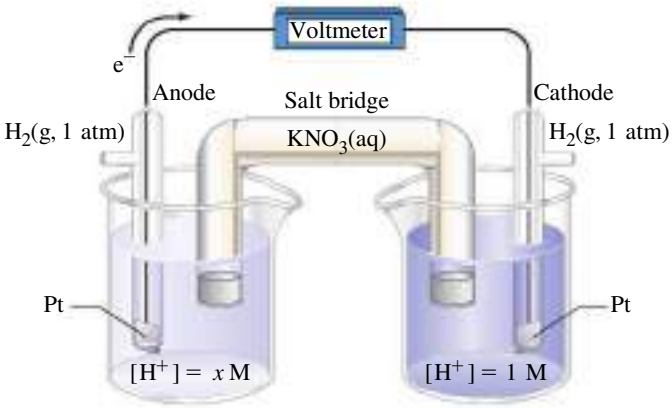
$$Pt|H_2(g, 1\ atm)\,|H^+(x\ M)\,||H^+(1\ M)\,|H_2(g, 1\ atm)\,|Pt$$

The reaction occurring in this cell is

$$\begin{aligned} &\textit{Reduction:} && 2\,H^+(1\ M) + 2\,e^- \longrightarrow H_2(g, 1\ atm) \\ &\textit{Oxidation:} && H_2(g, 1\ atm) \longrightarrow 2\,H^+(x\ M) + 2\,e^- \\ &\textit{Overall:} && 2\,H^+(1\ M) \longrightarrow 2\,H^+(x\ M) \end{aligned} \qquad \textbf{(20.21)}$$

$$E^\circ_{cell} = E^\circ_{H^+/H_2} - E^\circ_{H^+/H_2} = 0\ V$$

The voltaic cell in Figure 20-11 is called a concentration cell. A **concentration cell** consists of two half-cells with *identical electrodes* but different ion concentrations. Because the electrodes are identical, the standard electrode potentials are numerically equal and subtracting one from the other leads to the value $E^\circ_{cell} = 0$. However, because the ion concentrations differ, there is a potential



◀ FIGURE 20-11
A concentration cell
The cell consists of two hydrogen electrodes. The electrode on the right is a SHE. Oxidation occurs at the anode on the left, where $[H^+]$ is less than 1 M. The reading on the voltmeter is directly proportional to the pH of the solution in the anode compartment.

difference between the two half-cells. The spontaneous change in a concentration cell always occurs such that the concentrated solution becomes more dilute, and the dilute solution becomes more concentrated. The final result is as if the solutions were simply mixed. In a concentration cell, however, the natural tendency for entropy to increase in a mixing process is used as a means of producing electricity.

The Nernst equation for reaction (20.21) takes the form

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592\ \text{V}}{2}\log\frac{x^2}{1^2}$$

which simplifies to

$$E_{\text{cell}} = 0 - \frac{0.0592\ \text{V}}{2} \times 2\log\frac{x}{1} = -0.0592\ \text{V}\log x$$

Because x is $[\text{H}^+]$ in the unknown solution and $-\log x = -\log[\text{H}^+] = \text{pH}$, the final result is

$$E_{\text{cell}} = (0.0592\ \text{pH})\ \text{V} \qquad \textbf{(20.22)}$$

where the pH is that of the unknown solution. If an unknown solution has a pH of 3.50, for example, the measured cell voltage in Figure 20-11 will be $E_{\text{cell}} = (0.0592 \times 3.50)\ \text{V} = 0.207\ \text{V}$.

Constructing and using a hydrogen electrode is difficult. The Pt metal surface must be specially prepared and maintained, gas pressure must be controlled, and the electrode cannot be used in the presence of strong oxidizing or reducing agents. The solution to these problems is discussed later in this chapter.

20-7 CONCEPT ASSESSMENT

Write a cell diagram for a possible voltaic cell in which the cell reaction is $\text{Cl}^-(0.50\ \text{M}) \longrightarrow \text{Cl}^-(0.10\ \text{M})$. What would be E_{cell} for this reaction?

Measurement of K_{sp}

The difference in concentration of ions in the two half-cells of a concentration cell accounts for the observed E_{cell}. It also provides a basis for determining K_{sp} values for sparingly soluble ionic compounds. Consider the following concentration cell.

$$\text{Ag(s)}\,|\,\text{Ag}^+(\text{satd AgI})\,||\,\text{Ag}^+(0.100\ \text{M})\,|\,\text{Ag} \qquad E_{\text{cell}} = 0.417\ \text{V}$$

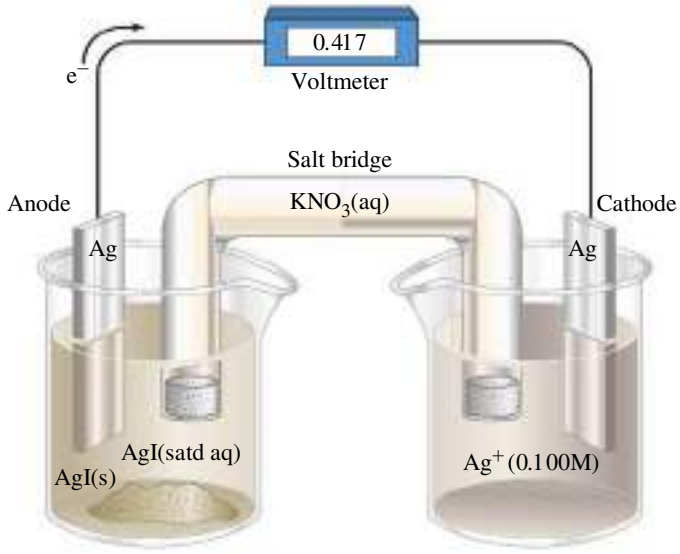
At the anode, a silver electrode is placed in a saturated aqueous solution of silver iodide. At the cathode, a second silver electrode is placed in a solution with $[\text{Ag}^+] = 0.100\ \text{M}$. The two half-cells are connected by a salt bridge, and the measured cell voltage is 0.417 V (Fig. 20-12). The cell reaction occurring in this *concentration cell* is

$$\begin{aligned} &\textit{Reduction:} && \text{Ag}^+(0.100\ \text{M}) + \text{e}^- \longrightarrow \text{Ag(s)} \\ &\textit{Oxidation:} && \text{Ag(s)} \longrightarrow \text{Ag}^+(\text{satd AgI}) \\ &\textit{Overall:} && \text{Ag}^+(0.100\ \text{M}) \longrightarrow \text{Ag}^+(\text{satd AgI}) \end{aligned} \qquad \textbf{(20.23)}$$

The calculation of K_{sp} of silver iodide is completed in Example 20-11.

Alternative Standard Electrodes

The standard hydrogen electrode is not the most convenient to use because it requires highly flammable hydrogen gas to be bubbled over the platinum electrode. Other electrodes can be used as secondary standard electrodes, such as the



▲ FIGURE 20-12
A concentration cell for determining K_{sp} of AgI
The silver electrode in the anode compartment is in contact with a saturated solution of AgI. In the cathode compartment, $[Ag^+] = 0.100$ M.

EXAMPLE 20-11 Using a Voltaic Cell to Determine K_{sp} of a Slightly Soluble Solute

With the data given for reaction (20.23), calculate K_{sp} for AgI.

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq) \qquad K_{sp} = ?$$

Analyze

Once we have determined the concentration of Ag^+ ions from the Nernst equation for the cell, we can calculate the equilibrium constant by using the expression for the solubility product.

Solve

$[Ag^+]$ in saturated silver iodide solution can be represented as x. The Nernst equation is then applied to reaction (20.23). (To simplify the equations that follow, we have dropped the unit V, which would otherwise appear in several places.)

$$E_{cell} = E^\circ_{cell} - \frac{0.0592}{z}\log\frac{[Ag^+]_{satd\ AgI}}{[Ag^+]_{0.100\ M\ soln}}$$

$$= E^\circ_{cell} - \frac{0.0592}{1}\log\frac{x}{0.100}$$

$$0.417 = 0 - 0.0592(\log x - \log 0.100)$$

Divide both sides of the equation by 0.0592.

$$\frac{0.417}{0.0592} = -\log x + \log 0.100$$

$$\log x = \log 0.100 - \frac{0.417}{0.0592} = -1.00 - 7.04 = -8.04$$

$$x = [Ag^+] = 10^{-8.04} = 9.1 \times 10^{-9}\ M$$

Because in saturated AgI the concentrations of Ag^+ and I^- are equal,

$$K_{sp} = [Ag^+][I^-] = (9.1 \times 10^{-9})(9.1 \times 10^{-9}) = 8.3 \times 10^{-17}$$

Assess

Apart from the use of the Nernst equation, the other essential aspect is the realization that the only source of Ag^+ and I^- is from the AgI present; the saturated AgI(s) electrode has $[Ag^+] = [I^-]$.

PRACTICE EXAMPLE A: K_{sp} for AgCl $= 1.8 \times 10^{-10}$. What would be the measured E_{cell} for the voltaic cell in Example 20-11 if the contents of the anode half-cell were saturated AgCl(aq) and AgCl(s)?

PRACTICE EXAMPLE B: Calculate the K_{sp} for PbI_2 given the following concentration cell information.

$$Pb(s)\,|Pb^{2+}(satd\ PbI_2)\,||Pb^{2+}(0.100\ M)\,|Pb(s) \qquad E_{cell} = 0.0567\ V$$

silver–silver chloride electrode, in which a silver wire is covered with a layer of insoluble solid silver chloride. The silver-chloride-coated silver wire is immersed in a 1 M potassium chloride solution (see Fig. 20-13a), giving the electrode

$$\mathrm{Ag(s)|AgCl(s)|Cl^-(1.0\ M)}$$

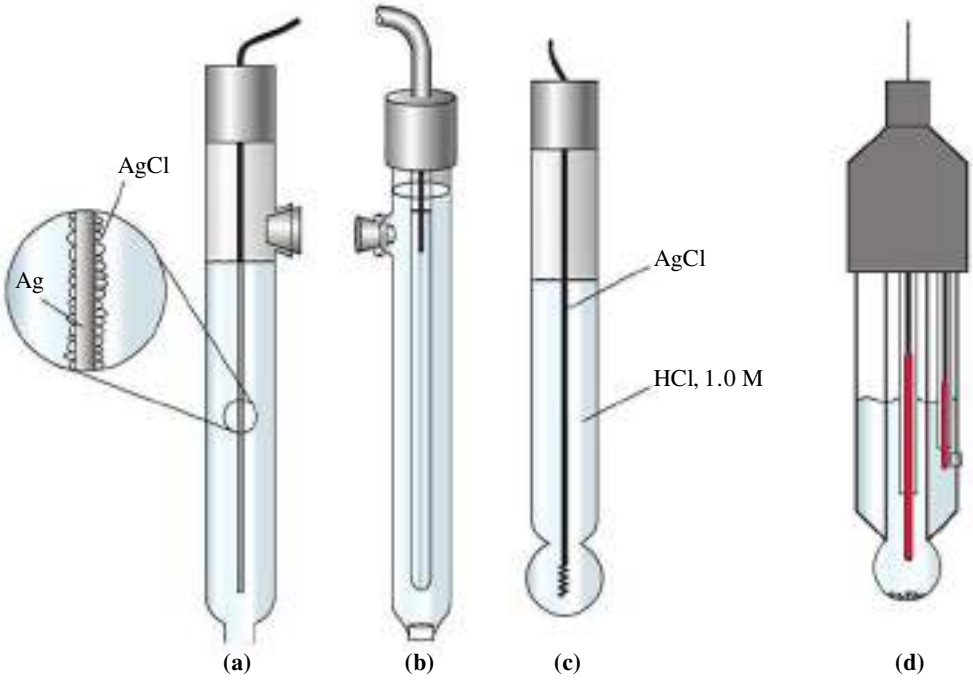
with a half-cell reaction of

$$\mathrm{AgCl(s) + e^- \longrightarrow Ag(s) + Cl^-(aq)}$$

This electrode has been measured against the standard hydrogen electrode, and the electrode potential has been found to be 0.22233 V at 25 °C. Since all components of this electrode are in their standard states, the standard electrode potential of the silver–silver chloride electrode is 0.22233 V at 25 °C.

An alternative electrode is the calomel electrode, illustrated in Figure 20-13(b). In this electrode, mercurous chloride (calomel, Hg_2Cl_2) is mixed with mercury to form a paste, which is in contact with liquid mercury, Hg(l), and the whole setup is immersed in either a 1.0 M solution of potassium chloride or a saturated solution of potassium chloride. The electrode is

$$\mathrm{Hg(l)|Hg_2Cl_2(s)|Cl^-(1.0\ M)}$$



▲ FIGURE 20-13
Schematic diagrams of some common electrodes
(a) The silver–silver chloride electrode. Silver wire is coated with silver chloride and immersed in a 1 M aqueous solution of KCl. At the bottom of the tube is a fritted (porous) disc to allow contact with a solution of interest. **(b)** The standard calomel electrode is a tube containing a paste of calomel and mercury, immersed in a 1.0 M solution of KCl. Contact with an external circuit is made with a Pt wire inserted in the inner tube; the inner tube makes contact with the outer 1.0 M solution of KCl through a small hole in the bottom of the inner tube. **(c)** A glass electrode consists of tube with a very thin glass bulb at the end and a Ag–AgCl electrode immersed in a 1.0 M HCl solution. When the glass electrode is dipped into a solution, ions interact with the membrane. The potential established on the silver wire depends on the solution being tested. **(d)** A modern pH electrode consists of a glass electrode and an internal Ag–AgCl reference electrode. There is a small sintered disc in the side of the outer tube that acts as a salt bridge between the electrode and the unknown solution.

and the half-cell reaction is

$$\frac{1}{2}Hg_2Cl_2(s) + e^- \longrightarrow Hg(l) + Cl^-(aq)$$

The standard electrode potential at 25 °C is 0.2680 V. If, however, a saturated solution of KCl is used, as opposed to one of 1 M, the reduction potential is 0.2412 V. This electrode is known as the saturated calomel electrode (SCE) and is often used as a reference.

In practice a variety of reference electrodes are used; therefore, it is necessary to quote reduction potentials with respect to a specific reference.

20-8 CONCEPT ASSESSMENT

Why do the calomel standard reduction potential and the saturated calomel electrode have different potentials?

The Glass Electrode and the Electrochemical Measurement of pH

To measure the pH of a solution electrochemically, we need an electrode that responds to changes in $[H^+(aq)]$. We noted that the standard hydrogen electrode is difficult to use for this purpose, and so, for routine use, a simpler and safer electrode is needed. Such an electrode is the *glass electrode*, which consists of a very thin walled glass bulb (see Fig. 20-13c) at the end of a tube that contains a silver–silver chloride electrode and a HCl solution of known composition (e.g., 1 M). When the bulb is placed in a solution of unknown pH, a potential develops because of the concentration difference across the membrane, analogous to a concentration cell. To measure this potential difference, a reference electrode is used, which can be either a saturated calomel electrode or a second silver–silver chloride electrode, as in the combination electrode shown in Figure 20-13(d). The overall cell can be represented as

$$Ag(s)\,|AgCl(s)\,|Cl^-(1.0\ M),\,H^+(1.0\ M)\,|glass\ membrane|H^+(unknown)\,||Cl^-(1.0\ M)\,|AgCl(s)\,|Ag(s)$$

where the two electrodes are connected by a salt bridge. The half-reactions are

$$\begin{aligned} Ag(s) + Cl^-(aq) &\longrightarrow AgCl(s) + e^- \\ H^+(1.0\ M) &\longrightarrow H^+(unknown) \\ AgCl(s) + e^- &\longrightarrow Ag(s) + Cl^-(aq) \end{aligned}$$

The half-cell potentials of the two half-reactions for the silver–silver chloride electrodes cancel each other out and make no contribution to the cell potential. The Gibbs energy change corresponding to the dilution of protons from a known concentration of 1.0 M to the unknown solution is the source of the potential difference across the glass membrane. The Gibbs energy difference across the membrane, using $G = G^\circ + RT \ln[H^+]$, is

$$\begin{aligned} \Delta G &= G(unknown) - G(1.0\ M) \\ &= G^\circ + RT \ln[unknown] - G^\circ - RT \ln 1.0 \\ &= RT \ln[unknown] \end{aligned}$$

Converting this to a potential by dividing by $-zF$, $z = 1$, and assuming $T = 25$ °C, we obtain

$$E_{cell} = 0.0592\ pH$$

after converting the logarithm to base 10 and using the definition of $pH = -\log_{10}[unknown]$. The cell potential is measured with a pH meter, a voltage measuring device that electronically converts E_{cell} to pH and displays the result in pH units.

The glass electrode was devised in 1906 by German biologist Max Cremer, and it was the prototype for a large number of membrane electrodes that are selective for a particular ion, such as the ions K^+, NH_4^+, Cl^-, and many others. Such electrodes are known collectively as *ion-selective electrodes*, and they have many applications in environmental chemistry and biochemistry.

20-5 Batteries: Producing Electricity Through Chemical Reactions

▶ Batteries are vitally important to modern society. Annual production in developed nations has been estimated at more than 10 batteries per person per year.

A **battery** is a device that stores chemical energy for later release as electricity. Some batteries consist of a single voltaic cell with two electrodes and the appropriate electrolyte(s); an example is a flashlight cell. Other batteries consist of two or more voltaic cells joined in series fashion—plus to minus—to increase the total voltage; an example is an automobile battery. In this section, we will consider three types of voltaic cells and the batteries based on them.

- **Primary cells.** The cell reaction in a primary cell is not reversible. When the reactants have been mostly converted to products, no more electricity is produced and a battery employing a primary cell(s) is dead.
- **Secondary cells.** The cell reaction in a secondary cell *can* be reversed by passing electricity through the cell (charging). A battery employing secondary cells can be used through several hundred or more cycles of discharging followed by charging.
- **Flow batteries** and **fuel cells.** Materials (reactants, products, and electrolytes) pass through the battery, which is simply a converter of chemical energy to electric energy. These types of batteries can be run indefinitely as long as they are supplied by electrolytes.

▶ Cell phones, laptop computers, and many other devices rely heavily on rechargeable batteries. Advances in electrochemistry and engineering are leading to the development of batteries that weigh less, last longer, and provide more power for portable electronic devices.

The Leclanché (Dry) Cell

The most common form of voltaic cell is the *Leclanché cell*, invented by the French chemist Georges Leclanché (1839–1882) in the 1860s. Popularly called a *dry cell*, because no free liquid is present, or *flashlight battery*, the Leclanché cell is diagrammed in Figure 20-14. In this cell, oxidation occurs at a zinc anode and reduction at an inert carbon (graphite) cathode. The electrolyte is a moist paste of MnO_2, $ZnCl_2$, NH_4Cl, and carbon black (soot). The maximum cell voltage is 1.55 V. The anode (oxidation) half-reaction is simple.

$$\textit{Oxidation:}\quad Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$$

The reduction is more complex. Essentially, it involves the reduction of MnO_2 to compounds having Mn in a +3 oxidation state, for example,

$$\textit{Reduction:}\quad 2\,MnO_2(s) + H_2O(l) + 2\,e^- \longrightarrow Mn_2O_3(s) + 2\,OH^-(aq)$$

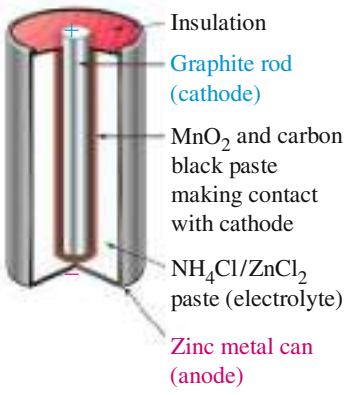
An acid–base reaction occurs between NH_4^+ (from NH_4Cl) and OH^-.

$$NH_4^+(aq) + OH^-(aq) \longrightarrow NH_3(g) + H_2O(l)$$

A buildup of $NH_3(g)$ around the cathode would disrupt the current because the $NH_3(g)$ adheres to the cathode. That buildup is prevented by a reaction between Zn^{2+} and $NH_3(g)$ to form the complex ion $[Zn(NH_3)_2]^{2+}$, which crystallizes as the chloride salt.

$$Zn^{2+}(aq) + 2\,NH_3(g) + 2\,Cl^-(aq) \longrightarrow [Zn(NH_3)_2]Cl_2(s)$$

The Leclanché cell is a *primary cell*; it cannot be recharged. This cell is cheap to make, but it has some drawbacks. When current is drawn rapidly from the cell, products, such as NH_3, build up on the electrodes, causing the voltage to drop. Also, because the electrolyte medium is acidic, zinc metal slowly dissolves.



▲ FIGURE 20-14
The Leclanché (dry) cell
The chief components of the cell are a graphite (carbon) rod serving as the cathode, a zinc container serving as the anode, and an electrolyte.

A superior form of the Leclanché cell is the *alkaline cell*, which uses NaOH or KOH in place of NH_4Cl as the electrolyte. The reduction half-reaction is the same as that shown above, but the oxidation half-reaction involves the formation of $Zn(OH)_2(s)$, which can be thought of as occurring in two steps.

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$$
$$Zn^{2+}(aq) + 2\,OH^-(aq) \longrightarrow Zn(OH)_2(s)$$
$$Zn(s) + 2\,OH^-(aq) \longrightarrow Zn(OH)_2(s) + 2\,e^-$$

The advantages of the alkaline cell are that zinc does not dissolve as readily in a basic (alkaline) medium as in an acidic medium, and the cell does a better job of maintaining its voltage as current is drawn from it.



▲ **E°_{cell} is an intensive property** The voltage of a dry cell battery does not depend on the size of the battery—all of those pictured here are 1.5 V batteries. Although these batteries deliver the same voltage, the total energy output of each battery is different.

The Lead–Acid (Storage) Battery

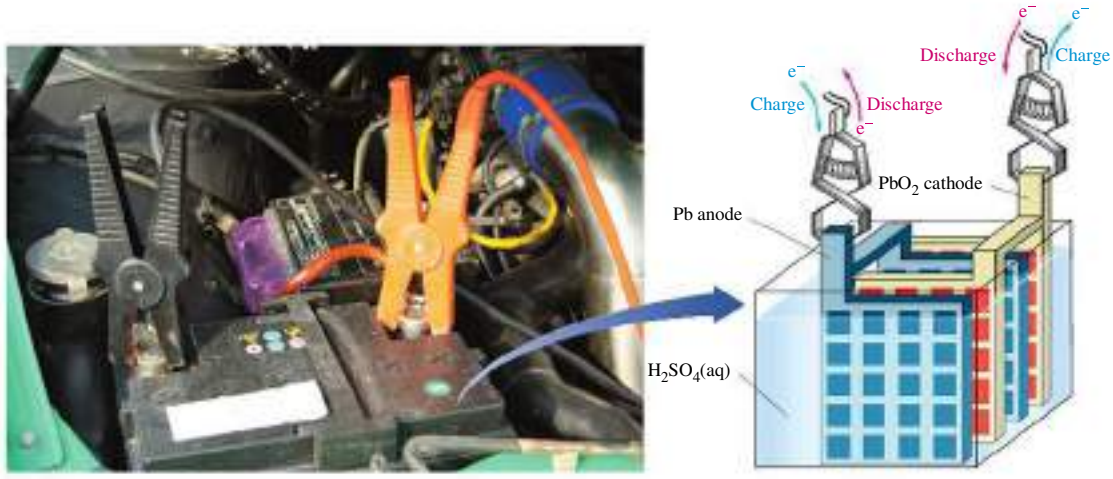
Secondary cells are commonly encountered joined together in series in the *lead–acid battery*, or *storage battery*, which has been used in automobiles since about 1915 (Fig. 20-15). A storage battery is capable of repeated use because its chemical reactions are reversible. That is, the discharged energy can be restored by supplying electric current to recharge the cells in the battery.

The reactants in a lead–acid cell are spongy lead packed into a lead grid at the anode, red-brown lead(IV) oxide packed into a lead grid at the cathode, and an electrolyte solution consisting of dilute sulfuric acid (about 35% H_2SO_4, by mass). In this strongly acidic medium, the ionization of H_2SO_4 does not go to completion. Both $HSO_4^-(aq)$ and $SO_4^{2-}(aq)$ are present, but $HSO_4^-(aq)$ predominates. The half-reactions and overall reaction are

$$\textit{Reduction:}\quad PbO_2(s) + 3\,H^+(aq) + HSO_4^-(aq) + 2\,e^- \longrightarrow PbSO_4(s) + 2\,H_2O(l)$$
$$\textit{Oxidation:}\quad Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2\,e^-$$
$$\textit{Overall:}\quad PbO_2(s) + Pb(s) + 2\,H^+(aq) + 2\,HSO_4^-(aq) \longrightarrow 2\,PbSO_4(s) + 2\,H_2O(l)$$

$$E_{cell} = E_{PbO_2/PbSO_4} - E_{PbSO_4/Pb} = 1.74\text{ V} - (-0.28\text{ V}) = 2.02\text{ V} \qquad \textbf{(20.24)}$$

◀ You can think of the half-reactions as occurring in two steps: (1) oxidation of Pb(s) to $Pb^{2+}(aq)$ and reduction of $PbO_2(s)$ to $Pb^{2+}(aq)$, followed by (2) precipitation of $PbSO_4(s)$ at each electrode.



▲ FIGURE 20-15
A lead–acid (storage) cell
The composition of the electrodes is described in the text. The cell reaction that occurs as the cell is discharged is given in equation (20.24). The voltage of the cell is 2.02 V. In this figure, two anode plates are connected in parallel fashion, as are two cathode plates. The battery shown in this figure is the good battery used to charge a dead battery.

▶ In spite of its usefulness and ability to deliver a strong current, the lead storage battery is also a pollution hazard. All batteries should be disposed of properly and should not be dumped in land fills or garbage disposal sites.

When an automobile engine is started, the battery is at first discharged. Once the car is in motion, an alternator powered by the engine constantly recharges the battery. At times, the plates of the battery become coated with $PbSO_4(s)$ and the electrolyte becomes sufficiently diluted with water that the battery must be recharged by connecting it to an external electric source. This forces the reverse of reaction (20.24), a nonspontaneous reaction.

$$2\,PbSO_4(s) + 2\,H_2O(l) \longrightarrow Pb(s) + PbO_2(s) + 2\,H^+(aq) + 2\,HSO_4^-(aq)$$
$$E_{cell} = -2.02\ V$$

▶ Lead-acid storage batteries are also used to power golf carts, wheelchairs, and passenger carts in airport terminals.

To prevent the anode and cathode from coming into contact with each other, causing a *short circuit*, sheets of an insulating material are used to separate alternating anode and cathode plates. A group of anodes is connected together electrically, as is a group of cathodes. This parallel connection increases the electrode area in contact with the electrolyte solution and increases the current-delivering capacity of the cell. Cells are then joined in a series fashion, positive to negative, to produce a battery. The typical 12 V battery consists of six cells, each cell with a potential of about 2 V.

The Silver–Zinc Cell: A Button Battery

▶ Rechargeable silver oxide batteries have been developed and provide alternatives to lithium-ion batteries.

The cell diagram of a *silver–zinc cell* (Fig. 20-16) is

$$Zn(s), ZnO(s)\,|\,KOH(satd)\,|\,Ag_2O(s), Ag(s)$$

The half-reactions on discharging are

$$\begin{aligned} &\textit{Reduction:} && Ag_2O(s) + H_2O(l) + 2\,e^- \longrightarrow 2\,Ag(s) + 2\,OH^-(aq) \\ &\textit{Oxidation:} && Zn(s) + 2\,OH^-(aq) \longrightarrow ZnO(s) + H_2O(l) + 2\,e^- \\ &\textit{Overall:} && Zn(s) + Ag_2O(s) \longrightarrow ZnO(s) + 2\,Ag(s) \end{aligned} \qquad \textbf{(20.25)}$$

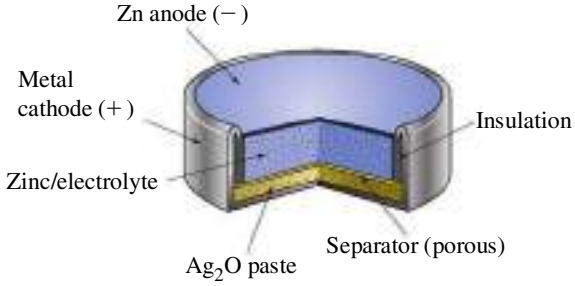
Because no solution species is involved in the cell reaction, the quantity of electrolyte is very small and the electrodes can be maintained very close together. The cell voltage is 1.8 V, and its storage capacity is six times greater than that of a lead–acid battery of the same size. These characteristics make batteries, such as the silver–zinc cell, useful in button batteries. These miniature batteries are used in watches, hearing aids, and cameras. In addition, silver–zinc batteries fulfill the requirements of spacecraft, satellites, missiles, rockets, space launch vehicles, torpedoes, underwater vehicles, and life-support systems. On the Mars *Pathfinder* mission, the rover and the cruise system were powered by solar cells. The energy storage requirements of the lander were met by modified silver–zinc batteries with about three times the storage capacity of the standard nickel–cadmium rechargeable battery.

The Nickel–Cadmium Cell: A Rechargeable Battery

The *nickel–cadmium cell* (or *nicad battery*) is commonly used in cordless electric devices, such as electric shavers and handheld calculators. The anode in this cell is cadmium metal, and the cathode is the Ni(III) compound NiO(OH)



▲ A rechargeable nickel–cadmium cell, or nicad battery.



▶ FIGURE 20-16
A silver–zinc button (miniature) cell

supported on nickel metal. The half-cell reactions for a nickel–cadmium battery during discharge are

$$\begin{aligned}
&\textit{Reduction:} && 2\,NiO(OH)(s) + 2\,H_2O(l) + 2\,e^- \longrightarrow 2\,Ni(OH)_2(s) + 2\,OH^-(aq)\\
&\textit{Oxidation:} && Cd(s) + 2\,OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2\,e^-\\
&\textit{Overall:} && Cd(s) + 2\,NiO(OH)(s) + 2\,H_2O(l) \longrightarrow 2\,Ni(OH)_2(s) + Cd(OH)_2(s)
\end{aligned}$$

This cell gives a fairly constant voltage of 1.4 V. When the cell is recharged by connection to an external voltage source, the reactions above are reversed. Nickel–cadmium batteries can be recharged many times because the solid products adhere to the surface of the electrodes.

In primary cells the positive and negative electrodes are known as the cathode, where reduction takes place, and the anode, where oxidation takes place. In rechargeable systems, however, we have either a charging mode or a discharging mode, and so depending whether electrons are flowing out of the cell or flowing into the cell, the notion of the anode and the cathode changes. On the discharge of a nicad battery, the NiO(OH) electrode is the cathode because reduction is taking place, but on the charge, it is the anode because oxidation is taking place (the reverse reaction). In discharge mode the NiO(OH) electrode electrons are removed from the electrode because of the reduction process, and so this electrode is positively charged. In the charging mode electrons are being removed from this electrode by the oxidation process; this is the anode and it is positively charged. Therefore, regardless of charging or discharging, the NiO(OH) electrode is positive.

The negative electrode, the cadmium electrode in a nicad battery, is the anode on discharging (oxidation) and the cathode (reduction) on charging. In both charging and discharging, the anode is the electrode from which electrons exit the battery, and the cathode is the electrode at which electrons enter the battery.

In summary, when dealing with rechargeable batteries, it is better to speak of the positive and negative electrodes and avoid the terms *cathode* and *anode*.

The Lithium-Ion Battery

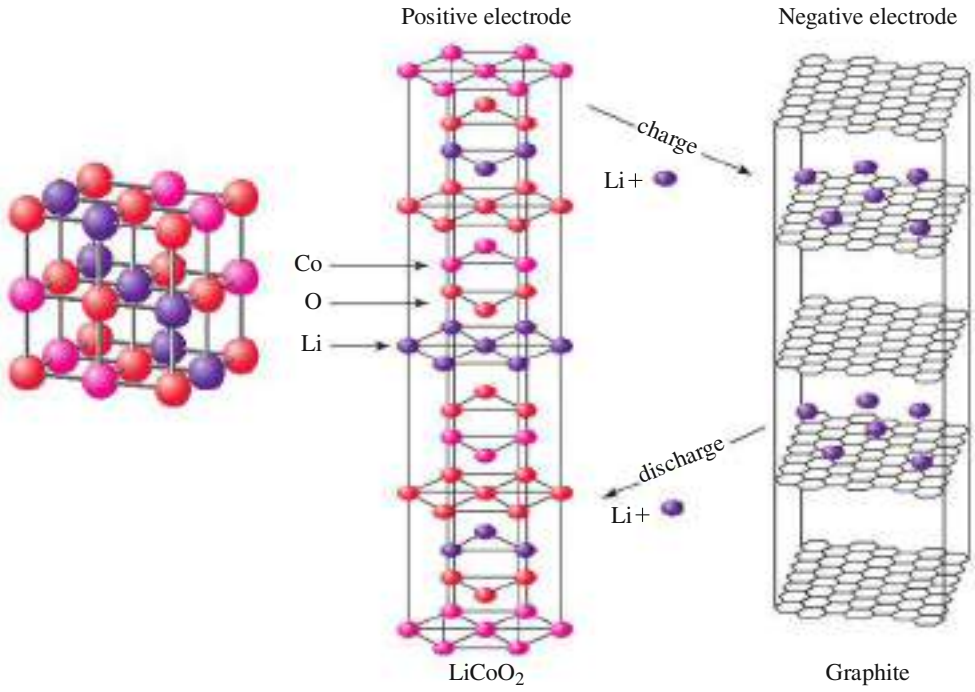
Lithium-ion batteries are a type of rechargeable battery now commonly used in consumer electronics, such as cell phones, laptop computers, and MP3 players. In a lithium-ion battery, the lithium ion moves between the positive and negative electrodes. The positive electrode consists of lithium cobalt(III) oxide, $LiCoO_2$, and the negative electrode is highly crystallized graphite. To complete the battery an electrolyte is needed, which can consist of an organic solvent and ions, such as $LiPF_6$. The structure of $LiCoO_2$ and graphite electrodes is illustrated in Figure 20-17. In the charging cycle at the positive electrode, lithium ions are released into the electrolyte solution as electrons are removed from the electrode. To maintain a charge balance, one cobalt(III) ion is oxidized to cobalt(IV) for each lithium ion released:

$$LiCoO_2(s) \longrightarrow Li_{(1-x)}CoO_2(s) + x\,Li^+(solvent) + x\,e^-$$

At the negative electrode, lithium ions enter between the graphite layers and are reduced to lithium metal. This insertion of a guest atom into a host solid is called *intercalation*, and the resulting product is called an *intercalation compound*:

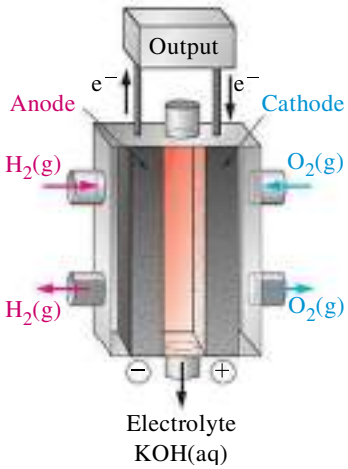
$$C(s) + x\,Li^+(solvent) + x\,e^- \longrightarrow Li_xC(s)$$

In the operation of a lithium-ion battery the source of the electrons is the oxidation of the Co(III) to Co(IV). The lithium ion takes these electrons to the graphite electrode during charging and returns them to the positive electrode during discharge.



▲ FIGURE 20-17
The electrodes of a lithium-ion battery
The layered graphite electrode is shown with lithium ions (violet) intercalated. The $LiCoO_2$ is shown as a face-centered cubic lattice, with the oxygen atoms (red) occupying the corners and the faces, the cobalt atoms (pink) occupying half of the edges, and the lithium atoms occupying half of the edges and the central octahedral hole. This arrangement leads to planes of oxygen, cobalt, oxygen, lithium, oxygen, cobalt, and oxygen atoms, as indicated in the figure.

Many other lithium batteries exist that use many different materials for the positive electrode, while graphite is the most common negative electrode. A major development is in the use of conducting polymers as the electrolyte, which has led to a whole range of *lithium-ion polymer batteries*. The development of new batteries based on lithium ions is currently an area of great interest.



▲ FIGURE 20-18
A hydrogen–oxygen fuel cell
A key requirement in fuel cells is porous electrodes that allow for easy access of the gaseous reactants to the electrolyte. The electrodes chosen should also catalyze the electrode reactions.

Fuel Cells

The three types of cells considered in the remainder of this section fall into the third category mentioned on page 888; they are found in flow batteries.

For most of the twentieth century, scientists explored the possibility of converting the chemical energy of fuels directly to electricity. The essential process in a fuel cell is *fuel + oxygen* ⟶ *oxidation products*. The first fuel cells were based on the reaction of hydrogen and oxygen. Figure 20-18 represents such a fuel cell. The overall change is that $H_2(g)$ and $O_2(g)$ in an alkaline medium produce $H_2O(l)$.

$$\begin{aligned} &\textit{Reduction:} && O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq) \\ &\textit{Oxidation:} && 2\{H_2(g) + 2\,OH^-(aq) \longrightarrow 2\,H_2O(l) + 2\,e^-\} \\ &\textit{Overall:} && 2\,H_2(g) + O_2(g) \longrightarrow 2\,H_2O(l) \end{aligned} \qquad \textbf{(20.26)}$$

$$E^\circ_{cell} = E^\circ_{O_2/OH^-} - E^\circ_{H_2O/H_2} = 0.401\ V - (-0.828\ V) = 1.229\ V$$

The theoretical maximum energy available as electric energy in any electrochemical cell is the Gibbs energy change for the cell reaction, $\Delta G°$. The maximum energy release when a fuel is burned is the enthalpy change, $\Delta H°$. One of the measures used to evaluate a fuel cell is the *efficiency value*, $\varepsilon = \Delta G°/\Delta H°$. For the hydrogen–oxygen fuel cell, $\varepsilon = -474.4\ kJ/-571.6\ kJ = 0.83$.

The day is fast approaching when fuel cells based on the direct oxidation of common fuels will become a reality. For example, the half-reaction and cell reaction for a fuel cell using methane (natural gas) are

$$\begin{aligned}
&\textit{Reduction:} && 2\{O_2(g) + 4H^+ + 4e^- \longrightarrow 2H_2O(l)\}\\
&\textit{Oxidation:} && CH_4(g) + 2H_2O(l) \longrightarrow CO_2(g) + 8H^+ + 8e^-\\
&\textit{Overall:} && CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)
\end{aligned}$$

$$\Delta H^\circ = -890\ \text{kJ} \qquad \Delta G^\circ = -818\ \text{kJ} \qquad \varepsilon = 0.92 \qquad \textbf{(20.27)}$$



▲ This Toyota prototype is a fuel-cell-powered electric car producing hydrogen from gasoline.

◀ Fuel cells are environmentally friendly. Oxygen and hydrogen are readily available. Hydrogen, although dangerous, can now be transported safely by the use of special materials that can adsorb large volumes.

Although methane fuel cells are still in the research stage, an automobile engine is currently under development in which (1) a liquid hydrocarbon is vaporized; (2) the vaporized fuel is partially oxidized to CO(g); (3) in the presence of a catalyst, steam converts the CO(g) to $CO_2(g)$ and $H_2(g)$; and (4) $H_2(g)$ and air are fed through a fuel cell, producing electric energy.

A fuel cell should actually be called an *energy converter* rather than a battery. As long as fuel and $O_2(g)$ are available, the cell will produce electricity. It does not have the limited capacity of a primary battery or the fixed storage capacity of a secondary battery. Fuel cells based on reaction (20.26) have had their most notable successes as energy sources in space vehicles. (Water produced in the cell reaction is also a valuable product of the fuel cell.)

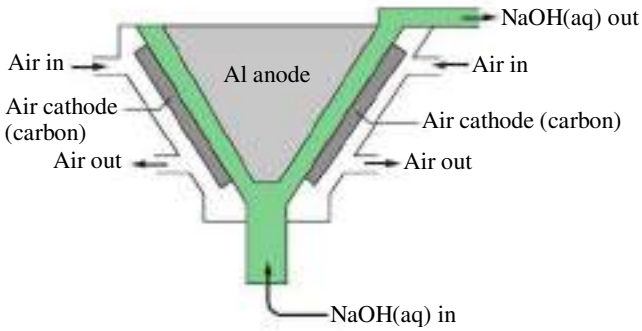
Air Batteries

In a fuel cell, $O_2(g)$ is the oxidizing agent that oxidizes a fuel such as $H_2(g)$ or $CH_4(g)$. Another kind of flow battery, because it uses $O_2(g)$ from air, is known as an *air battery*. The substance that is oxidized in an air battery is typically a metal.

One heavily studied battery system is the aluminum–air battery in which oxidation occurs at an aluminum anode and reduction at a carbon–air cathode. The electrolyte circulated through the battery is NaOH(aq). Because it is in the presence of a high concentration of OH^-, Al^{3+} produced at the anode forms the complex ion $[Al(OH)_4]^-$. The operation of the battery is suggested by Figure 20-19. The half-reactions and the overall cell reaction are

$$\begin{aligned}
&\textit{Reduction:} && 3\{O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)\}\\
&\textit{Oxidation:} && 4\{Al(s) + 4OH^-(aq) \longrightarrow [Al(OH)_4]^-(aq) + 3e^-\}\\
&\textit{Overall:} && 4Al(s) + 3O_2(g) + 6H_2O(l) + 4OH^-(aq) \longrightarrow 4[Al(OH)_4]^-(aq) \qquad \textbf{(20.28)}
\end{aligned}$$

The battery is kept charged by feeding chunks of Al and water into it. A typical air battery can power an automobile several hundred miles before refueling is necessary. The electrolyte is circulated outside the battery, where $Al(OH)_3(s)$ is precipitated from the $[Al(OH)_4]^-(aq)$. This $Al(OH)_3(s)$ is collected and can then be converted back to aluminum metal at an aluminum manufacturing facility.



◀ FIGURE 20-19
A simplified aluminum–air battery

20-9 CONCEPT ASSESSMENT

Why do dry cells and lead-acid cells "run down" during use? Do you think a fuel cell runs down? Explain.

20-6 Corrosion: Unwanted Voltaic Cells

The reactions occurring in voltaic cells (batteries) are important sources of electricity, but similar reactions also underlie corrosion processes. First, we will consider the electrochemical basis of corrosion, and then we will see how electrochemical principles can be applied to control corrosion.

Figure 20-20(a) demonstrates the basic processes in the corrosion of an iron nail. The nail is embedded in an agar gel in water. The gel contains the common acid–base indicator phenolphthalein and potassium ferricyanide, $K_3[Fe(CN)_6]$. Within hours of starting the experiment, a deep blue precipitate forms at the head and tip of the nail. Along the body of the nail, the agar gel turns pink. The blue precipitate, Turnbull's blue, establishes the presence of iron(II). The pink color is that of phenolphthalein in basic solution. From these observations, we write two simple half-equations.

▶ This and other tests for iron(II) are described more fully in Section 23-5.

$$\begin{aligned} &\textit{Reduction:} && O_2(g) + 2\,H_2O(l) + 4\,e^- \longrightarrow 4\,OH^-(aq) \\ &\textit{Oxidation:} && 2\,Fe(s) \longrightarrow 2\,Fe^{2+}(aq) + 4\,e^- \end{aligned}$$

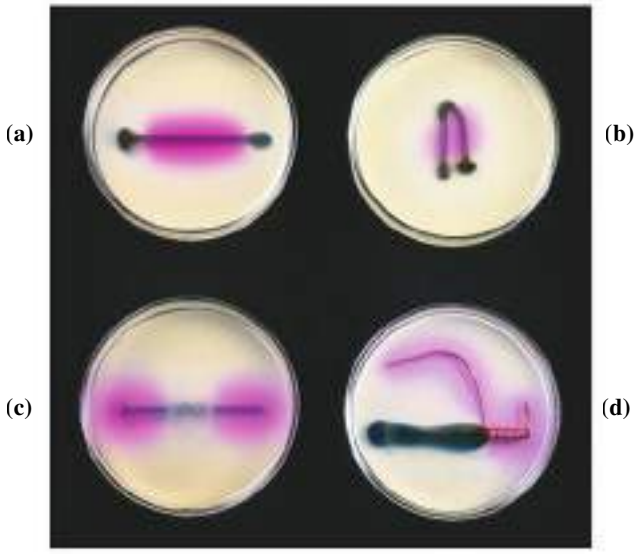
The potential difference for these two half-reactions is

$$E^\circ_{cell} = E^\circ_{O_2/OH^-} - E^\circ_{Fe^{2+}/Fe} = 0.401\ V - (-0.440\ V) = 0.841\ V$$

indicating that the corrosion process should be spontaneous when reactants and products are in their standard states. Typically, the corrosion medium has $[OH^-] \ll 1$ M, the reduction half-reaction is even more favorable, and E_{cell} is even greater than 0.841 V. Corrosion is especially significant in acidic solutions, in which the reduction half-reaction is

$$O_2(g) + 4\,H^+(aq) + 4\,e^- \longrightarrow 2\,H_2O(l) \qquad E^\circ_{O_2/H_2O} = 1.229\ V$$

In the corroding nail of Figure 20-20(a), oxidation occurs at the head and tip. Electrons given up in the oxidation move along the nail and are used to reduce dissolved O_2. The reduction product, OH^-, is detected by the phenolphthalein. In the bent nail in Figure 20-20(b), oxidation occurs at *three* points: the head and tip and also the bend. The nail is preferentially oxidized



▶ FIGURE 20-20
Demonstration of corrosion and methods of corrosion protection
The pink color results from the indicator phenolphthalein in the presence of base; the dark blue color results from the formation of Turnbull's blue $KFe[Fe(CN)_6]$. Corrosion (oxidation) of the nail occurs at strained regions: **(a)** the head and tip and **(b)** a bend in the nail. **(c)** Contact with zinc protects the nail from corrosion. Zinc is oxidized instead of the iron (forming the faint white precipitate of zinc ferricyanide). **(d)** Copper does not protect the nail from corrosion. Electrons lost in the oxidation half-reaction distribute themselves along the copper wire, as seen by the pink color that extends the full length of the wire.

at these points because the strained metal is more active (more anodic) than the unstrained metal. This situation is similar to the preferential rusting of a dented automobile fender.

Some metals, such as aluminum, form corrosion products that adhere tightly to the underlying metal and protect it from further corrosion. Iron oxide (rust), however, flakes off and constantly exposes fresh surface. This difference in corrosion behavior explains why cans made of iron deteriorate rapidly in the environment, whereas aluminum cans have an almost unlimited lifetime. The simplest method of protecting a metal from corrosion is to cover it with paint or some other protective coating impervious to water, an important reactant and solvent in corrosion processes.

Another method of protecting an iron surface is to plate it with a thin layer of a second metal. Iron can be plated with copper by electroplating or with tin by dipping the iron into molten tin. In either case, the underlying metal is protected as long as the coating remains intact. If the coating is cracked, as when a "tin" can is dented, the underlying iron is exposed and begins to corrode. Iron, being more active than copper and tin, undergoes oxidation; the reduction half-reaction occurs on the plating (Figs. 20-20d and 20-21).

When iron is coated with zinc (galvanized iron), the situation is different. Zinc is more active than iron. If a break occurs in the zinc plating, the iron is still protected because the zinc is oxidized instead of the iron, and corrosion products protect the zinc from further corrosion (Figs. 20-20c and 20-21).

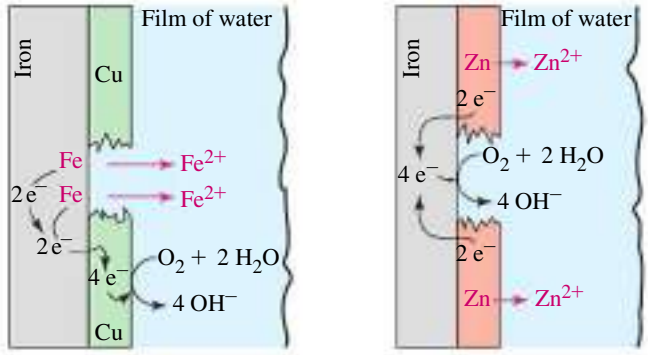
Still another method is used to protect large iron and steel objects in contact with water or moist soils—ships, storage tanks, pipelines, plumbing systems. This method involves connecting a chunk of magnesium or some other active metal to the object, either directly or through a wire. Oxidation occurs at the active metal, which slowly dissolves. The iron surface acquires electrons from the oxidation of the active metal; the iron acts as a cathode and supports a *reduction* half-reaction. As long as some of the active metal remains, the iron is protected. This type of protection is called **cathodic protection**, and the active metal is called, appropriately, a *sacrificial anode*. Millions of pounds of magnesium are used annually in the United States in sacrificial anodes.



▲ Galvanized nails



▲ **Magnesium sacrificial anodes** The small cylindrical bars of magnesium attached to the steel ship provide cathodic protection against corrosion.



(a) Copper-plated iron **(b)** Galvanized iron

▲ FIGURE 20-21
Protection of iron against electrolytic corrosion
In the *anodic* reaction, the metal that is more easily oxidized loses electrons to produce metal ions. In **(a)**, this is iron; in **(b)**, it is zinc. In the *cathodic* reaction, oxygen gas, which is dissolved in a thin film of water on the metal, is reduced to OH^-. Rusting of iron occurs in (a), but it does not in (b). When iron corrodes, Fe^{2+} and OH^- ions from the half-reactions initiate these further reactions.

$$Fe^{2+} + 2\,OH^- \longrightarrow Fe(OH)_2(s)$$

$$4\,Fe(OH)_2(s) + O_2 + 2\,H_2O \longrightarrow 4\,Fe(OH)_3(s)$$

$$2\,Fe(OH)_3(s) \longrightarrow \underset{\text{rust}}{Fe_2O_3 \cdot H_2O(s)} + H_2O(l)$$

20-10 CONCEPT ASSESSMENT

Of the metals Al, Cu, Ni, and Zn, which could act as a sacrificial anode for iron?

20-7 Electrolysis: Causing Nonspontaneous Reactions to Occur

KEEP IN MIND

that voltaic (galvanic) and electrolytic cells are the two categories subsumed under the more general term *electrochemical cell.*

Until now, the emphasis has been on voltaic (galvanic) cells, electrochemical cells in which chemical change is used to produce electricity. Another type of electrochemical cell—the **electrolytic cell**—uses electricity to produce a *nonspontaneous* reaction. The process in which a nonspontaneous reaction is driven by the application of electric energy is called **electrolysis**.

Let's explore the relationship between voltaic and electrolytic cells by returning briefly to the cell shown in Figure 20-4. When the cell functions spontaneously, electrons flow from the zinc to the copper and the overall chemical change in the voltaic cell is

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s) \qquad E^\circ_{cell} = 1.103\ V$$

Now suppose the same cell is connected to an external electric source of voltage greater than 1.103 V (Fig. 20-22). That is, the connection is made so that electrons are forced into the zinc electrode (now the cathode) and removed from the copper electrode (now the anode). The overall reaction in this case is the *reverse* of the voltaic cell reaction, and E°_{cell} is *negative.*

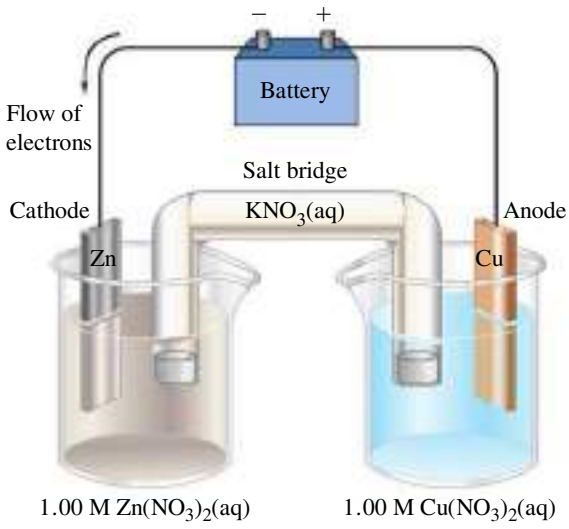
$$\begin{aligned} &\textit{Reduction:} && Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s) \\ &\textit{Oxidation:} && Cu(s) \longrightarrow Cu^{2+}(aq) + 2\,e^- \\ &\textit{Overall:} && Cu(s) + Zn^{2+}(aq) \longrightarrow Cu^{2+}(aq) + Zn(s) \end{aligned}$$

$$E^\circ_{cell} = E^\circ_{Zn^{2+}/Zn} - E^\circ_{Cu^{2+}/Cu} = -0.763\ V - 0.340\ V = -1.103\ V$$

Thus, reversing the direction of the electron flow changes the voltaic cell into an electrolytic cell.

Predicting Electrolysis Reactions

For the cell in Figure 20-22 to function as an electrolytic cell with reactants and products in their standard states, the external voltage has to exceed 1.103 V.



▶ FIGURE 20-22
An electrolytic cell
The direction of electron flow is the reverse of that in the voltaic cell of Figure 20-4, and so is the cell reaction. Now the zinc electrode is the *cathode* and the copper electrode, the *anode*. The battery must have a voltage in excess of 1.103 V in order to force electrons to flow in the reverse (nonspontaneous) direction.

20-2 ARE YOU WONDERING...

Why the anode is (+) in an electrolytic cell but (−) in a voltaic cell?

Assigning the terms *anode* and *cathode* is not based on the electrode charges; it is based on the half-reactions at the electrode surfaces. Specifically,

- *Oxidation* always occurs at the *anode* of an electrochemical cell. Because of the buildup of electrons freed in the oxidation half-reaction, the anode of a *voltaic* cell is (−). Because electrons are withdrawn from it, the anode in an *electrolytic* cell is (+). For both cell types, the anode is the electrode from which electrons *exit* the cell.
- *Reduction* always occurs at the cathode of an electrochemical cell. Because of the *removal* of electrons by the reduction half-reaction, the cathode of a *voltaic* cell is (+). Because of the electrons forced onto it, the cathode of an *electrolytic* cell is (−). For both cell types, the cathode is the electrode at which electrons *enter* the cell.

The following table summarizes the relationship between a voltaic cell and an electrolytic cell.

	Voltaic Cell		Electrolytic Cell	
Oxidation:	$A \longrightarrow A^+ + e^-$	Anode (negative)	*Oxidation:* $B \longrightarrow B^+ + e^-$	Anode (positive)
Reduction:	$B^+ + e^- \longrightarrow B$	Cathode (positive)	*Reduction:* $A^+ + e^- \longrightarrow A$	Cathode (negative)
Overall:	$A + B^+ \longrightarrow A^+ + B$ $\Delta G < 0$ Spontaneous redox reaction releases energy		*Overall:* $A^+ + B \longrightarrow A + B^+$ $\Delta G > 0$ Nonspontaneous redox reaction absorbs energy to drive it	
	The system (the cell) does work on the surroundings		The surroundings (the source of energy) do work on the system	

Note that the sign of each electrode in an electrolytic cell is the same as the sign of the battery electrode to which it is attached.

We can make similar calculations for other electrolyses. What actually happens, however, does not always correspond to these calculations. Four complicating factors must be considered:

1. A voltage significantly in excess of the calculated value, an **overpotential**, may be necessary to cause a particular electrode reaction to occur. Overpotentials are needed to overcome interactions at the electrode surface and are particularly common when gases are involved. For example, the overpotential for the discharge of $H_2(g)$ at a mercury cathode is approximately 1.5 V; the overpotential on a platinum cathode is practically zero.
2. Competing electrode reactions may occur. In the electrolysis of *molten* sodium chloride with inert electrodes, only one oxidation and one reduction are possible.

$$\textit{Reduction:}\quad 2\,Na^+ + 2\,e^- \longrightarrow 2\,Na(l)$$
$$\textit{Oxidation:}\quad 2\,Cl^- \longrightarrow Cl_2(g) + 2\,e^-$$

In the electrolysis of *aqueous* sodium chloride with inert electrodes, there are *two* possible reduction half-reactions and *two* possible oxidation half-reactions.

Reduction: $2\,Na^+(aq) + 2\,e^- \longrightarrow Na(s)$ $\quad E^\circ_{Na^+/Na} = -2.71\ V$ **(20.29)**

$2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$ $\quad E^\circ_{H_2O/H_2} = (-0.83\ V)$ **(20.30)**

Oxidation: $2\,Cl^-(aq) \longrightarrow Cl_2(g) + 2\,e^-$ $\quad -E^\circ_{Cl_2/Cl^-} = -(1.36\ V)$ **(20.31)**

$2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^-$ $\quad -E^\circ_{O_2/H_2O} = -(1.23\ V)$ **(20.32)**

▶ We have written a *minus* sign in front of the electrode potentials in (20.31) and (20.32) as a way of emphasizing the *oxidation* rather than the reduction tendency.

Reaction (20.29) can be eliminated as a possible reduction half-reaction: Unless the overpotential for $H_2(g)$ is unusually high, the reduction of Na^+ is far more difficult to accomplish than that of H_2O. This leaves two possibilities for the cell reaction.

Half-reaction (20.30) + half-reaction (20.31):

Reduction: $2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)$

Oxidation: $2\,Cl^-(aq) \longrightarrow Cl_2(g) + 2\,e^-$

Overall: $2\,Cl^-(aq) + 2\,H_2O(l) \longrightarrow Cl_2(g) + H_2(g) + 2\,OH^-(aq)$ **(20.33)**

$$E^\circ_{cell} = E^\circ_{H_2O/H_2} - E^\circ_{Cl_2/Cl^-} = -0.83\ V - (1.36\ V) = -2.19\ V$$

Half-reaction (20.30) + half-reaction (20.32):

Reduction: $2\{2\,H_2O(l) + 2\,e^- \longrightarrow H_2(g) + 2\,OH^-(aq)\}$

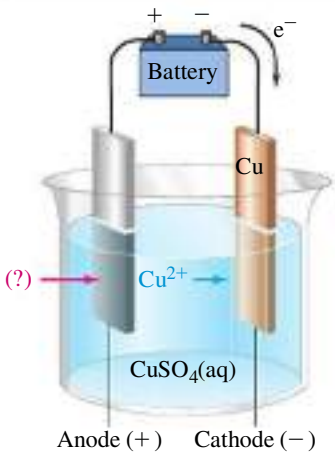
Oxidation: $2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^-$

Overall: $2\,H_2O(l) \longrightarrow 2\,H_2(g) + O_2(g)$ **(20.34)**

$$E^\circ_{cell} = E^\circ_{H_2O/H_2} - E^\circ_{O_2/H_2O} = -0.83\ V - (1.23\ V) = -2.06\ V$$



▲ The electrolysis of water into $H_2(g)$ and $O_2(g)$, shown by bubbles at the electrodes and the gases collecting in the test tubes—twice the volume of $H_2(g)$ as $O_2(g)$.



▲ FIGURE 20-23
Predicting electrode reactions in electrolysis—Example 20-11 illustrated
Electrons are forced onto the copper cathode by the external source (battery). Cu^{2+} ions are attracted to the cathode and are reduced to Cu(s). The oxidation half-reaction depends on the metal used for the anode.

In the electrolysis of NaCl(aq), $H_2(g)$ is the product expected at the *cathode*. Because cell reactions (20.33) and (20.34) have E°_{cell} values that are so similar, a mixture of $Cl_2(g)$ and $O_2(g)$ would be the expected product at the *anode*. Actually, because of the high overpotential of $O_2(g)$ compared to $Cl_2(g)$, cell reaction (20.33) predominates; $Cl_2(g)$ is essentially the only product at the anode.

3. The reactants very often are in *nonstandard* states. In the industrial electrolysis of NaCl(aq), $[Cl^-] \approx 5.5$ M, not the unit activity ($[Cl^-] \approx 1$ M) implied in half-reaction (20.31); therefore $E_{Cl_2/Cl^-} = 1.31$ V (*not* 1.36 V). Also, the pH in the anode half-cell is adjusted to 4, not the unit activity ($[H_3O^+] \approx 1$ M) implied in half-reaction (20.32); hence $E_{O_2/H_2O} = 0.99$ V (*not* 1.23 V). The net effect of these nonstandard conditions is to favor the production of O_2 at the anode. In practice, however, the $Cl_2(g)$ obtained contains less than 1% $O_2(g)$, indicating the overpowering effect of the high overpotential of $O_2(g)$. Not surprisingly, the proportion of $O_2(g)$ increases significantly in the electrolysis of very dilute NaCl(aq).
4. The nature of the electrodes matters. An *inert electrode*, such as platinum, provides a surface on which an electrolysis half-reaction occurs, but the reactants themselves must come from the electrolyte solution. An *active electrode* is one that can itself participate in the oxidation or reduction half-reaction. The distinction between inert and active electrodes is explored in Figure 20-23 and Example 20-12.

Quantitative Aspects of Electrolysis

We have seen how to calculate the theoretical voltage required for electrolysis. Equally important are calculations of the quantities of reactants consumed and products formed in an electrolysis. For these calculations, we will continue to use stoichiometric factors from the chemical equation, but another

EXAMPLE 20-12 Predicting Electrode Half-Reactions and Overall Reactions in Electrolysis

Refer to Figure 20-23. Predict the electrode reactions and the overall reaction when the anode is made of **(a)** copper and **(b)** platinum.

Analyze

In both cases we have to decide on the likely oxidation and reduction processes. The low reduction potential of $Cu^{2+}(aq)$ makes this the likely reduction process in both cases. What about oxidation processes? The possibilities are in **(a)** oxidation of the copper electrode (anode) ($E^\circ = 0.340$ V), oxidation of sulfate anion (2.01 V), and oxidation of water (1.23 V). Thus, the most easily oxidized is the copper at the anode. In **(b)**, the platinum electrode is inert and is not easily oxidized. Of the other two candidates, sulfate anion and water, water has the lower oxidation potential.

Solve

$$\textit{Reduction:} \quad Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s) \qquad E^\circ_{Cu^{2+}/Cu} = 0.340\ V$$

(a) At the cathode we have the reduction of $Cu^{2+}(aq)$. At the anode, Cu(s) can be oxidized to $Cu^{2+}(aq)$, as represented by

$$\textit{Oxidation:} \quad Cu(s) \longrightarrow Cu^{2+}(aq) + 2\,e^-$$

If the oxidation and reduction half-equations are added, $Cu^{2+}(aq)$ cancels out. The electrolysis reaction is simply

$$Cu(s)[\text{anode}] \longrightarrow Cu(s)[\text{cathode}] \qquad \textbf{(20.35)}$$

$$E^\circ_{cell} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Cu^{2+}/Cu} = 0.340\ V - 0.340\ V = 0$$

(b) The oxidation that occurs most readily is that of H_2O, shown in reaction (20.32).

$$\textit{Oxidation:} \quad 2\,H_2O(l) \longrightarrow O_2(g) + 4\,H^+(aq) + 4\,e^-$$
$$-E^\circ_{O_2/H_2O} = -1.23\ V$$

The electrolysis reaction and its E°_{cell} are

$$2\,Cu^{2+}(aq) + 2\,H_2O(l) \longrightarrow 2\,Cu(s) + 4\,H^+(aq) + O_2(g) \qquad \textbf{(20.36)}$$

$$E^\circ_{cell} = E^\circ(\text{reduction half-cell}) - E^\circ(\text{oxidation half-cell})$$
$$= E^\circ_{Cu^{2+}/Cu} - E^\circ_{O_2/H_2O}$$
$$= 0.340\ V - 1.23\ V = -0.89\ V$$

Assess

(a) Only a very small voltage is needed to overcome the resistance in the electric circuit for this electrolysis. For every Cu atom that enters the solution at the anode, an active electrode, one Cu^{2+} ion, deposits as a Cu atom at the cathode. Copper is transferred from the anode to the cathode through the solution as Cu^{2+} and the concentration of $CuSO_4(aq)$ remains unchanged.

(b) A potential greater than 0.89 V is required to electrolyze water and deposit copper. Keep in mind that when calculating E°_{cell} as a *difference* between two E° values, the E° values are reduction potentials. Because $-E^\circ$ corresponds to the half-cell potential for the oxidation process, the *difference* between two reduction potentials is equivalent to the *sum* of a reduction potential and an oxidation potential.

PRACTICE EXAMPLE A: Use data from Table 20.1 to predict the probable products when Pt electrodes are used in the electrolysis of KI(aq).

PRACTICE EXAMPLE B: In the electrolysis of $AgNO_3(aq)$, what are the expected electrolysis products if the anode is silver metal and the cathode is platinum?

factor enters in as well: the quantity of electric charge associated with one mole of electrons. This factor is provided by the Faraday constant, which we can write as

$$1\ \text{mol}\ e^- = 96{,}485\ C$$

Generally, electric charge is not measured directly; instead, it is the electric current that is measured. One *ampere* (A) of electric current represents the passage of 1 coulomb of charge per second (C/s). The product of current and time yields the total quantity of charge transferred.

$$\text{charge (C)} = \text{current (C/s)} \times \text{time (s)}$$

To determine the number of moles of electrons involved in an electrolysis reaction, we can write

$$\text{number of mol } e^- = \text{current}\left(\frac{\text{C}}{\text{s}}\right) \times \text{time (s)} \times \frac{1 \text{ mol } e^-}{96{,}485 \text{ C}}$$

As illustrated in Example 20-13, to determine the mass of a product in an electrolysis reaction, follow this conversion pathway.

$$\text{C/s} \longrightarrow \text{C} \longrightarrow \text{mol } e^- \longrightarrow \text{mol product} \longrightarrow \text{g product}$$

EXAMPLE 20-13 Calculating Quantities Associated with Electrolysis Reactions

The electrodeposition of copper can be used to determine the copper content of a sample. The sample is dissolved to produce $Cu^{2+}(aq)$, which is electrolyzed. At the cathode, the reduction half-reaction is $Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$. What mass of copper can be deposited in 1.00 hour by a current of 1.62 A?

Analyze

To find the mass of copper deposited, we first need to determine the number of moles of electrons generated in the given time. Because we know that for each copper(II) ion we need two electrons, we can calculate the mass by using the number of moles of electrons.

Solve

First, we determine the number of moles of electrons involved in the electrolysis in the manner outlined above:

$$1.00 \text{ h} \times \frac{60 \text{ min}}{1 \text{ h}} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{1.62 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ mol } e^-}{96{,}485 \text{ C}} = 0.0604 \text{ mol } e^-$$

The mass of Cu(s) produced at the cathode by this number of moles of electrons is calculated as follows:

$$\text{mass of Cu} = 0.0604 \text{ mol } e^- \times \frac{1 \text{ mol Cu}}{2 \text{ mol } e^-} \times \frac{63.5 \text{ g Cu}}{1 \text{ mol Cu}} = 1.92 \text{ g Cu}$$

Assess

The key factor in this calculation, relating moles of copper to moles of electrons, is printed in blue. This type of conversion is very similar to the one you learned when doing stoichiometric problems.

PRACTICE EXAMPLE A: If 12.3 g of Cu is deposited at the cathode of an electrolytic cell after 5.50 h, what was the current used?

PRACTICE EXAMPLE B: For how long would the electrolysis in Example 20-13 have to be carried out, using Pt electrodes and a current of 2.13 A, to produce 2.62 L $O_2(g)$ at 26.2 °C and 738 mmHg pressure at the anode?

20-8 Industrial Electrolysis Processes

Modern industry could not function in its present form without electrolysis reactions. A number of elements are produced almost exclusively by electrolysis—for example, aluminum, magnesium, chlorine, and fluorine. Among chemical compounds produced industrially by electrolysis are NaOH, $K_2Cr_2O_7$, $KMnO_4$, $Na_2S_2O_8$, and a number of organic compounds.



◀ The refining of copper by electrolysis.

Electrorefining

The *electrorefining* of metals involves the deposition of pure metal at a cathode, from a solution containing the metal ion. Copper produced by the smelting of copper ores is of sufficient purity for some uses, such as plumbing, but it is not pure enough for applications in which high electrical conductivity is required. For these applications, the copper must be more than 99.5% pure. The electrolysis reaction (20.35) on page 899 is used to obtain such high-purity copper. A chunk of impure copper is the anode and a thin sheet of pure copper is the cathode. During the electrolysis, Cu^{2+} produced at the anode migrates through an aqueous sulfuric acid–copper(II) sulfate solution to the cathode, where it is reduced to Cu(s). The pure copper cathode increases in size as the impure chunk of copper is consumed. As noted in Example 20-12a, the electrolysis is carried out at a low voltage—from 0.15 to 0.30 V. Under these conditions, Ag, Au, and Pt impurities are not oxidized at the anode, and they drop to the bottom of the tank as a sludge called *anode mud.* Sn, Bi, and Sb are oxidized, but they precipitate as oxides or hydroxides; Pb is oxidized but precipitates as $PbSO_4(s)$. As, Fe, Ni, Co, and Zn are oxidized but form water-soluble species. Recovery of Ag, Au, and Pt from the anode mud helps offset the cost of the electrolysis.

Electroplating

In *electroplating*, one metal is plated onto another, often less expensive, metal by electrolysis. This procedure is done for decorative purposes or to protect the underlying metal from corrosion. Silver-plated flatware, for example, consists of a thin coating of metallic silver on an underlying base of iron. In electroplating, the item to be plated is the cathode in an electrolytic cell. The electrolyte contains ions of the metal to be plated, which are attracted to the cathode, where they are reduced to metal atoms.

In copper plating, the electrolyte is usually copper sulfate. In silver plating, it is commonly $K[Ag(CN)_2](aq)$. The concentration of free silver ion in a solution of the complex ion $[Ag(CN)_2]^-(aq)$ is very low, and electroplating under these conditions promotes a strongly adherent microcrystalline deposit of the metal. Chromium plating is useful for its resistance to corrosion as well as its appearance. Steel can be chromium-plated from an aqueous solution of CrO_3 and H_2SO_4. The plating obtained, however, is thin and porous and tends to develop cracks. In practice, the steel is first plated with a thin coat of copper or nickel, and then the chromium plating is applied. Chromium plating or cadmium plating is used to weatherproof machine parts. Metal plating can even be applied to some plastics. The plastic must first be made electrically conductive—for example, by coating it with graphite powder. Copper plating of plastics has been used to improve the quality of some microelectronic circuit boards. Electroplating is even used, quite literally, to make money. The U.S. penny is no longer copper throughout. A zinc plug is electroplated with a thin coat of copper, and the copper-plated plug is stamped to create a penny.



▲ A rack of metal parts being lifted from the electrolyte solution after electroplating.

Electrosynthesis

Electrosynthesis is a method of producing substances through electrolysis reactions. It is useful for certain syntheses in which reaction conditions must be carefully controlled. Manganese dioxide occurs naturally as the mineral *pyrolusite*, but small crystal size and lattice imperfections make this material inadequate for certain modern applications, such as alkaline batteries. The electrosynthesis of MnO_2 is carried out in a solution of $MnSO_4$ in $H_2SO_4(aq)$ Pure $MnO_2(s)$ is formed by the oxidation of Mn^{2+} at an inert anode, such as graphite.

$$\textit{Oxidation:} \quad Mn^{2+}(aq) + 2\,H_2O(l) \longrightarrow MnO_2(s) + 4\,H^+(aq) + 2\,e^-$$

The reaction at the cathode is the reduction of H^+ to $H_2(g)$, and the overall electrolysis reaction is

$$Mn^{2+}(aq) + 2\,H_2O(l) \longrightarrow MnO_2(s) + 2\,H^+(aq) + H_2(g)$$

An example of electrosynthesis in organic chemistry is the reduction of acrylonitrile, $CH_2{=}CH{-}C{\equiv}N$, to adiponitrile, $N{\equiv}C(CH_2)_4C{\equiv}N$, at a lead cathode (chosen because of the high overpotential of H_2 on lead). Oxygen is released at the anode.

$$\textit{Reduction:} \quad 2\,CH_2{=}CH{-}C{\equiv}N + 2\,H_2O + 2\,e^- \longrightarrow N{\equiv}C(CH_2)_4C{\equiv}N + 2\,OH^-$$

The commercial importance of this electrolysis is that adiponitrile can be readily converted to two other compounds: hexamethylenediamine, $H_2NCH_2(CH_2)_4CH_2NH_2$, and adipic acid, $HOOCCH_2(CH_2)_2CH_2COOH$. These two compounds are the monomers used to make the polymer *Nylon-66* (page 1253).

The Chlor–Alkali Process

On page 898 we described the electrolysis of NaCl(aq) through the reduction half-reaction (20.30) and the oxidation half-reaction (20.31).

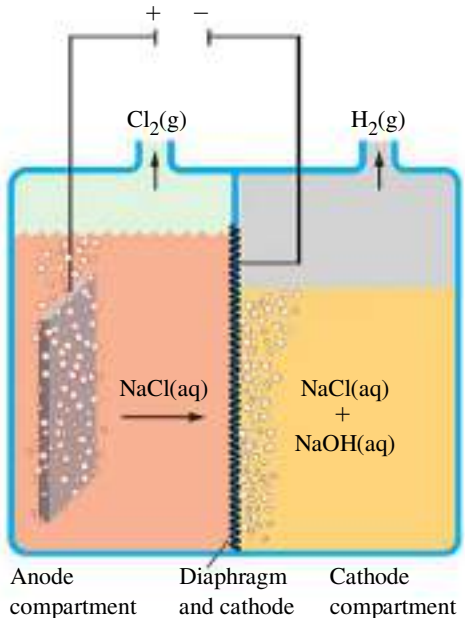
$$2\,Cl^-(aq) + 2\,H_2O(l) \longrightarrow 2\,OH^-(aq) + H_2(g) + Cl_2(g) \qquad E^\circ_{cell} = -2.19\ V$$

When conducted on an industrial scale, this electrolysis is called the *chlor–alkali process*, named after the two principal products: *chlorine* and the *alkali* NaOH(aq). The chlor–alkali process is one of the most important of all electrolytic processes because of the high value of these products.

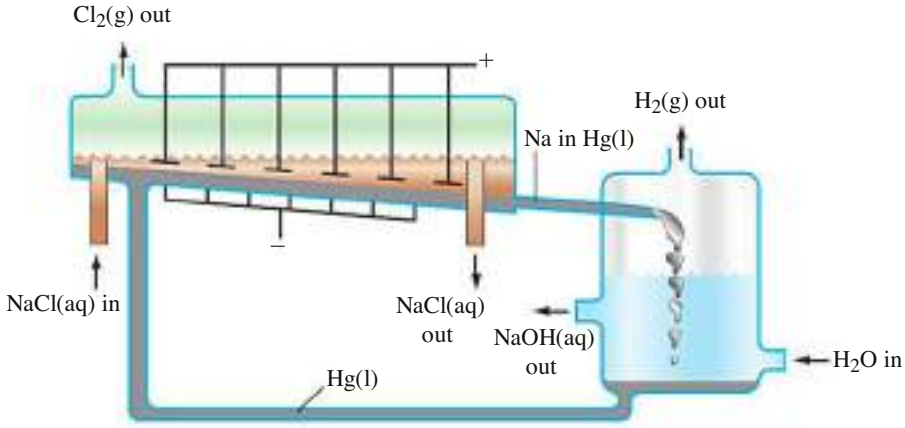
In the *diaphragm cell* depicted in Figure 20-24, $Cl_2(g)$ is produced in the anode compartment, and $H_2(g)$ and NaOH(aq) in the cathode compartment. If $Cl_2(g)$ comes in contact with NaOH(aq), the Cl_2 disproportionates into $ClO^-(aq)$, $ClO_3^-(aq)$, and $Cl^-(aq)$. The purpose of the diaphragm is to prevent this contact. The NaCl(aq) in the anode compartment is kept at a slightly higher level than that in the cathode compartment. This disparity creates a gradual flow of NaCl(aq) between the compartments and reduces the backflow of NaOH(aq) into the anode compartment. The solution in the cathode compartment, about 10%–12% NaOH(aq) and 14%–16% NaCl(aq), is concentrated and purified by evaporating some water and crystallizing the NaCl(s). The final product is 50% NaOH(aq), with up to 1% NaCl(aq).

The theoretical voltage required for this electrolysis is 2.19 V. However, as a result of the internal resistance of the cell and overpotentials at the electrodes, a voltage of about 3.5 V is used. The current is kept very high, typically about 1×10^5 A.

The NaOH(aq) produced in a diaphragm cell is not pure enough for certain uses, such as rayon manufacture. A higher purity is achieved if electrolysis is carried out in a mercury cell, illustrated in Figure 20-25. This cell takes advantage of the high overpotential for the reduction of $H_2O(l)$ to $H_2(g)$ and $OH^-(aq)$ at a



◀ FIGURE 20-24
A diaphragm chlor–alkali cell
The anode may be made of graphite or, in more modern technology, specially treated titanium metal. The diaphragm and cathode are generally fabricated as a composite unit consisting of asbestos or an asbestos–polymer mixture deposited on a steel wire mesh. To avoid the use of asbestos, a more modern development substitutes a fluorocarbon mesh for the asbestos.



▲ FIGURE 20-25
The mercury-cell chlor–alkali process
The cathode is a layer of Hg(l) that flows along the bottom of the tank. Anodes, at which $Cl_2(g)$ forms, are situated in the NaCl(aq) just above the Hg(l). Sodium formed at the cathode dissolves in the Hg(l), and the sodium amalgam is decomposed with water to produce NaOH(aq) and $H_2(g)$. The regenerated Hg(l) is recycled.

mercury cathode. The reduction that occurs instead is that of $Na^+(aq)$ to Na, which dissolves in Hg(l) to form an amalgam (Na–Hg alloy) with about 0.5% Na by mass.

$$2\,Na^+(aq) + 2\,Cl^-(aq) \longrightarrow 2\,Na(\text{in Hg}) + Cl_2(g) \qquad E^\circ_{cell} = -3.20\ V$$

When the Na amalgam is removed from the cell and treated with water, NaOH(aq) forms,

$$2\,Na(\text{in Hg}) + 2\,H_2O(l) \longrightarrow 2\,Na^+(aq) + 2\,OH^-(aq) + H_2(g) + Hg(l)$$

and the liquid mercury is recycled back to the electrolytic cell.

Although the mercury cell has the advantage of producing concentrated high-purity NaOH(aq), it has some disadvantages. The mercury cell requires a higher voltage (about 4.5 V) than does the diaphragm cell (3.5 V) and consumes more electrical energy, about 3400 kWh/ton Cl_2 in a mercury cell, compared with 2500 kWh/ton Cl_2 in a diaphragm cell. Another serious drawback is the

need to control mercury effluents to the environment. Mercury losses, which at one time were as high as 200 g Hg per ton Cl_2, have been reduced to about 0.25 g Hg per ton of Cl_2 in older plants and half this amount in new plants.

The ideal chlor–alkali process is one that is energy-efficient and does not use mercury. A type of cell offering these advantages is the *membrane cell*, in which the porous diaphragm of Figure 20-24 is replaced by a cation-exchange membrane, normally made of a fluorocarbon polymer. The membrane permits hydrated cations (Na^+ and H_3O^+) to pass between the anode and cathode compartments but severely restricts the backflow of Cl^- and OH^- ions. As a result, the sodium hydroxide solution produced contains less than 50 ppm chloride ion contaminant.

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The concepts presented in this chapter can be used to explain the roles played by ions in the generation of biological electric currents. Electric currents in biological systems are generated in muscle contraction and neuron activity, for example. For a discussion of the source of biological electric currents, go to the Focus On feature for Chapter 20, Membrane Potentials, on the MasteringChemistry site.

Summary

20-1 Electrode Potentials and Their Measurement—In an **electrochemical cell** electrons in an oxidation–reduction reaction are transferred at metal strips called **electrodes** and conducted through an external circuit. The oxidation and reduction half-reactions occur in separate regions called **half-cells**. In a half-cell, an electrode is immersed in a solution. The electrodes of the two half-cells are joined by a wire, and an electrical connection between the solutions is also made, as through a **salt bridge** (Fig. 20-3). The cell reaction involves oxidation at one electrode called the **anode** and reduction at the other electrode called the **cathode**. A **voltaic (galvanic) cell** produces electricity from a spontaneous oxidation–reduction reaction. The difference in electric potential between the two electrodes is the **cell voltage**; the unit of cell voltage is the **volt (V)**. The cell voltage is also called the **cell potential** or **electromotive force (emf)** and designated as E_{cell}. A **cell diagram** displays the components of a cell in a symbolic way (expression 20-4).

20-2 Standard Electrode Potentials—The reduction occurring at a **standard hydrogen electrode (SHE)**, $2\,H^+(a = 1) + 2\,e^- \xrightarrow{\text{on Pt}} H_2(g, 1\text{ bar})$, is arbitrarily assigned a potential of zero. A half-cell has a **standard electrode potential**, $E°$, in which all reactants and products are at unit activity. A half-cell reaction with a *positive* standard electrode potential ($E°$) occurs more readily than does reduction of H^+ ions at the SHE. A *negative* standard electrode potential signifies a lesser tendency to undergo reduction. The **standard cell potential** ($E°_{cell}$) of a voltaic cell is the *difference* between $E°$, of the cathode and $E°$, of the anode; that is, $E°_{cell} = E°(\text{cathode}) - E°(\text{anode})$.

20-3 E_{cell}, ΔG, and K—Cell voltages based on standard electrode potentials are $E°_{cell}$ values. The electrical work that can be obtained from a cell depends on the number of electrons involved in the cell reaction, the cell potential, and the **Faraday constant (*F*)**, which is the number of coulombs of charge per mole of electrons—96,485 C/mol e^-. An important relationship exists between $E°_{cell}$ and $\Delta G°$, namely, $\Delta G° = -zFE°_{cell}$. The equilibrium constant of the cell reaction K is related to $E°_{cell}$ through the expression $\Delta G° = -RT \ln K = -zFE°_{cell}$.

20-4 E_{cell} as a Function of Concentrations—In the **Nernst equation**, E_{cell} for nonstandard conditions is related to $E°_{cell}$ and the reaction quotient Q (equation 20.18). If $E_{cell} > 0$, the cell reaction is spontaneous in the forward direction for the stated conditions; if $E_{cell} < 0$, the forward reaction is *nonspontaneous* for those conditions. A **concentration cell** consists of two half-cells with identical electrodes but different solution concentrations.

20-5 Batteries: Producing Electricity Through Chemical Reactions—An important application of voltaic cells is found in various battery systems. A **battery** stores chemical energy so that it can be released as energy. Batteries consist of one or more voltaic cells and are divided into three major classes: **primary** (Leclanché), **secondary** (lead–acid, silver–zinc nicad, and lithium-ion), and **flow batteries** or **fuel cells** in which reactants, such as hydrogen and oxygen, are continuously fed into the battery and chemical energy is converted to electric energy.

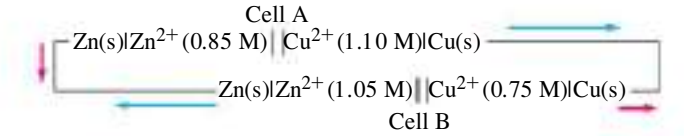
20-6 Corrosion: Unwanted Voltaic Cells—Electrochemistry plays a key role in corrosion and its control. Oxidation half-reactions produce anodic regions and reduction half-reactions, cathodic regions. **Cathodic protection** is achieved when a more active metal is attached to the metal being protected from corrosion. The more active metal, a "sacrificial" anode, is preferentially oxidized while the protected metal is a cathode at which a harmless reduction half-reaction occurs.

20-7 Electrolysis: Causing Nonspontaneous Reactions to Occur—In **electrolysis**, a nonspontaneous chemical reaction occurs as electrons from an external source are forced to flow in a direction opposite that in which they would flow spontaneously. The electrochemical cell in which electrolysis is conducted is called an **electrolytic cell**. $E°$, values are used to establish the theoretical voltage requirements for an electrolysis. Sometimes, particularly when a gas is liberated at an electrode, the voltage requirement for the electrode reaction exceeds the value of $E°$. The additional voltage requirement is called the **overpotential**. The amounts of reactants and products involved in an electrolysis can be calculated from the amount of electric charge passing through the electrolytic cell. The Faraday constant is featured in these calculations.

20-8 Industrial Electrolysis Processes—Electrolysis has many industrial applications, including electroplating, refining of metals, and production of substances such as NaOH(aq), $H_2(g)$, and $Cl_2(g)$.

Integrative Example

Two electrochemical cells are connected as shown.



(a) Do electrons flow in the direction of the red arrows or the blue arrows?

(b) What are the ion concentrations in the half-cells at the point at which current ceases to flow?

Analyze

The two cells differ only in their ion concentrations, which means that they have the same $E°_{cell}$ value but different E_{cell} values. In part **(a)**, use the Nernst equation (20.18) to determine which cell has the greater E_{cell} value when functioning as a voltaic cell. This will establish the direction that electrons flow. In part **(b),** write and solve an equation relating ion concentrations to the condition where the two cells have the same voltage but, being connected in opposition to each other, produce no net electric current.

Solve

(a) In each voltaic cell zinc is the anode, copper is the cathode, and the cell reaction is

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

The E_{cell} values are given by the Nernst equation.

$$E_{cell} = E°_{cell} - (0.0592/2)\log[Zn^{2+}]/[Cu^{2}] \qquad \textbf{(20.37)}$$

Note that for Cell A,

$$[Zn^{2+}]/[Cu^{2+}] = 0.85\ M/1.10\ M < 1$$
$$\log[Zn^{2+}]/[Cu^{2+}] < 0, \quad \text{and} \quad E_{cell} > E°_{cell}$$

For Cell B,

$$[Zn^{2+}]/[Cu^{2+}] = 1.05\ M/0.75\ M > 1$$
$$\log[Zn^{2+}]/[Cu^{2+}] > 0, \text{ and } E_{cell} < E°_{cell}$$

The voltage of Cell A is greater than that of Cell B.

In the connection of the two cells shown in the diagram, Cell A is a *voltaic cell* and Cell B is an *electrolytic cell*. There is an emf from Cell B that resists that of Cell A, but on balance, the electron flow is in the direction of the red arrows.

(b) As electrons flow between the two cells, the overall reaction in Cell A causes $[Zn^{2+}]$ to increase, $[Cu^{2+}]$ to decrease, and E_{cell} to decrease. The overall reaction in Cell B causes $[Zn^{2+}]$ to decrease, $[Cu^{2+}]$ to increase, and the back emf to increase. When the back emf from Cell B equals E_{cell} of Cell A, electrons cease to flow.

The cell diagrams when this condition is reached, with x representing *changes* in concentrations, are

Cell A: $Zn(s)|Zn^{2+}(0.85 + x)\ M||Cu^{2+}(1.10 - x)\ M|Cu(s)$
Cell B: $Zn(s)|Zn^{2+}(1.05 - x)\ M||Cu^{2+}(0.75 + x)\ M|Cu(s)$

Use equation (20.37) to obtain E_{cell} for each cell.

$$\textit{Cell A:}\quad E_{cell} = E^\circ_{cell} - \frac{0.0592\ \text{V}}{2}\log\frac{(0.85 + x)}{(1.10 - x)}$$

$$\textit{Cell B:}\quad E_{cell} = E^\circ_{cell} - \frac{0.0592\ \text{V}}{2}\log\frac{(1.05 - x)}{(0.75 + x)}$$

Set the two expressions equal to one another, cancel the terms E°_{cell} and $(0.0592\ \text{V})/2$, to obtain

$$\log\frac{(0.85 + x)}{(1.10 - x)} = \log\frac{(1.05 - x)}{(0.75 + x)}$$

Because the logarithms of the quantities on the two sides are equal, so too are the quantities themselves.

$$\frac{(0.85 + x)}{(1.10 - x)} = \frac{(1.05 - x)}{(0.75 + x)}$$

The expression to be solved is a quadratic equation

$$(0.85 + x)(0.75 + x) = (1.10 - x)(1.05 - x)$$

Cancel x^2 on each side

$$0.64 + 1.60x + x^2 = 1.16 - 2.15x + x^2$$
$$0.64 + 1.60x = 1.16 - 2.15x$$

Solve to obtain

$$3.75x = 0.52 \quad \text{and} \quad x = 0.14$$

When electrons no longer flow, the ion concentrations are as follows:

$$\textit{Cell A:}\quad [Zn^{2+}] = 0.99\ \text{M};\ [Cu^{2+}] = 0.96\ \text{M}.$$
$$\textit{Cell B:}\quad [Zn^{2+}] = 0.91\ \text{M};\ [Cu^{2+}] = 0.89\ \text{M}.$$

Assess

Once the direction of electron flow had been established, it was possible to decide in which cell $[Zn^{2+}]$ would increase and in which cell it would decrease. At equilibrium the two cell potentials became equal. That the calculated equilibrium concentrations are correct can be seen in $0.99/0.96 \approx 0.91/0.89$.

PRACTICE EXAMPLE A: Current fuel cells use the reaction of $H_2(g)$ and $O_2(g)$ to form $H_2O(l)$. Often, the $H_2(g)$ is obtained by the steam reforming of a hydrocarbon, such as $C_3H_8(g) + 3\,H_2O(g) \longrightarrow 3\,CO(g) + 7\,H_2(g)$. A future possibility is a fuel cell that converts a hydrocarbon, such as propane, directly to $CO_2(g)$ and $H_2O(l)$:

$$C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l)$$

Based on this reaction, use data from Table 20.1 and Appendix D to determine E° for the reduction of $CO_2(g)$ to $C_3H_8(g)$ in an acidic solution.

PRACTICE EXAMPLE B: A battery system that may be used to power automobiles in the future is the aluminum–air battery. This is a *flow battery* in which oxidation occurs at an aluminum anode and reduction at a carbon–air cathode. The electrolyte circulated through the battery is NaOH(aq); the ultimate reaction product is $Al(OH)_3(s)$, which is removed from the battery as it is formed. In operation the battery can be kept charged by feeding Al anode slugs and water into it; oxygen is drawn from the air (see Fig. 20-18). The battery can power an automobile several hundred miles between charges. The $Al(OH)_3(s)$ removed from the battery can be converted back to aluminum in an aluminum manufacturing facility.

(a) In actual practice Al^{3+} produced at the anode does not precipitate as $Al(OH)_3(s)$ but is obtained as the complex ion $[Al(OH)_4]^-$ in the presence of NaOH(aq). $Al(OH)_3$ is precipitated from the circulating NaOH(aq) electrolyte *outside* the battery. Write plausible equations for oxidation and reduction half-reactions, and for the net reaction that occurs in the battery.

(b) The theoretical voltage of the aluminum–air cell is +2.73 V. Use this information and data from Table 20.1 to obtain E° for the reduction

$$[Al(OH)_4]^- + 3\,e^- \longrightarrow Al(s) + 4\,OH^- \quad E^\circ = ?$$

(c) Given that E°_{cell} for the reaction is +2.73 V, that $\Delta G^\circ_f[OH^-(aq)] = -157\ \text{kJ mol}^{-1}$, and that $\Delta G^\circ_f[H_2O(l)] = -237.2\ \text{kJ mol}^{-1}$, determine the Gibbs energy of formation, ΔG°_f, of the aluminate ion, $[Al(OH)_4]^-$.

(d) What mass of aluminum is consumed if 10.0 A of electric current is drawn from the battery for 4.00 h?

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Exercises

(Use data from Table 20.1 and Appendix D as necessary.)

Standard Electrode Potentials

1. From the observations listed, estimate the value of $E°$ for the half-reaction $M^{2+}(aq) + 2\,e^- \longrightarrow M(s)$.
   (a) The metal M reacts with $HNO_3(aq)$, but not with HCl(aq); M displaces $Ag^+(aq)$, but not $Cu^{2+}(aq)$.
   (b) The metal M reacts with HCl(aq), producing $H_2(g)$, but displaces neither $Zn^{2+}(aq)$ nor $Fe^{2+}(aq)$.
2. You must estimate $E°$ for the half-reaction $In^{3+}(aq) + 3\,e^- \longrightarrow In(s)$. You have no electrical equipment, but you do have all of the metals listed in Table 20.1 and aqueous solutions of their ions, as well as In(s) and $In^{3+}(aq)$. Describe the experiments you would perform and the accuracy you would expect in your result.
3. $E°_{cell} = 0.201$ V for the reaction

$$3\,Pt(s) + 12\,Cl^-(aq) + 2\,NO_3^-(aq) + 8\,H^+(aq) \longrightarrow 3[PtCl_4]^{2-}(aq) + 2\,NO(g) + 4\,H_2O(l)$$

   What is $E°$ for the reduction of $[PtCl_4]^{2-}$ to Pt in acidic solution?
4. Given that $E°_{cell} = 3.20$ V for the reaction

$$2\,Na(\text{in Hg}) + Cl_2(g) \longrightarrow 2\,Na^+(aq) + 2\,Cl^-(aq)$$

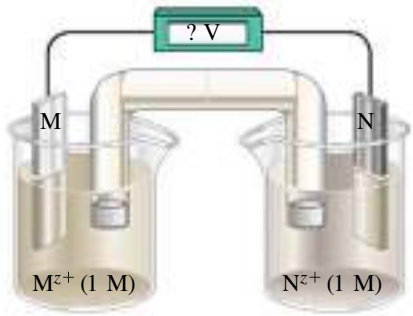
   What is $E°$ for the reduction $2\,Na^+(aq) + 2\,e^- \longrightarrow 2\,Na(\text{in Hg})$?
5. Given that $E°_{cell}$ for the aluminum-air battery is 2.71 V, what is $E°$ for the reduction half-reaction $[Al(OH)_4]^-(aq) + 3\,e^- \longrightarrow Al(s) + 4\,OH^-(aq)$? [*Hint:* Refer to cell reaction (20.28).]
6. The theoretical $E°_{cell}$ for the methane–oxygen fuel cell is 1.06 V. What is $E°$ for the reduction half-reaction $CO_2(g) + 8\,H^+(aq) + 8\,e^- \longrightarrow CH_4(g) + 2\,H_2O(l)$? [*Hint:* Refer to cell reaction (20.27).]
7. The following sketch is of a voltaic cell consisting of two standard electrodes for two metals, M and N:

$$M^{z+}(aq) + z\,e^- \longrightarrow M(s) \qquad E°_{M^{z+}/M}$$
$$N^{z+}(aq) + z\,e^- \longrightarrow N(s) \qquad E°_{N^{z+}/N}$$

   Use the standard reduction potentials of these half-reactions to answer the questions that follow:

$$Ag^+(aq) + e^- \longrightarrow Ag(s)$$
$$Zn^{2+}(aq) + 2\,e^- \longrightarrow Zn(s)$$
$$Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$$
$$Al^{3+}(aq) + 3\,e^- \longrightarrow Al(s)$$

   (a) Determine which pair of these half-cell reactions leads to a cell reaction with the largest positive cell potential, and calculate its value. Which couple is at the anode and which at the cathode?
   (b) Determine which pair of these half-cell reactions leads to the cell with the smallest positive cell potential, and calculate its value. Which couple is at the anode and which is at the cathode?



8. Given these half-reactions and associated standard reduction potentials, answer the questions that follow:

$$[Zn(NH_3)_4]^{2+}(aq) + 2\,e^- \longrightarrow Zn(s) + 4\,NH_3(aq) \qquad E° = -1.015\text{ V}$$
$$Ti^{3+}(aq) + e^- \longrightarrow Ti^{2+}(aq) \qquad E° = -0.37\text{ V}$$
$$VO^{2+}(aq) + 2\,H^+(aq) + e^- \longrightarrow V^{3+}(aq) + H_2O(l) \qquad E° = 0.340\text{ V}$$
$$Sn^{2+}(aq) + 2\,e^- \longrightarrow Sn(aq) \qquad E° = -0.14\text{ V}$$

   (a) Determine which pair of half-cell reactions leads to a cell reaction with the largest positive cell potential, and calculate its value. Which couple is at the anode and which is at the cathode?
   (b) Determine which pair of these half-cell reactions leads to the cell with the smallest positive cell potential, and calculate its value. Which couple is at the anode and which is at the cathode?

Predicting Oxidation–Reduction Reactions

9. Ni^{2+} has a more positive reduction potential than Cd^{2+}.
   (a) Which ion is more easily reduced to the metal?
   (b) Which metal, Ni or Cd, is more easily oxidized?
10. Refer to standard reduction potentials, and predict which metal in each of the following pairs is the stronger reducing agent:
    (a) sodium or potassium
    (b) magnesium or barium
11. Assume that all reactants and products are in their standard states, and use data from Table 20.1 to predict whether a spontaneous reaction will occur in the forward direction in each case.
    (a) $Sn(s) + Pb^{2+}(aq) \longrightarrow Sn^{2+}(aq) + Pb(s)$
    (b) $Cu^{2+}(aq) + 2\,I^-(aq) \longrightarrow Cu(s) + I_2(s)$
    (c) $4\,NO_3^-(aq) + 4\,H^+(aq) \longrightarrow 3\,O_2(g) + 4\,NO(g) + 2\,H_2O(l)$
    (d) $O_3(g) + Cl^-(aq) \longrightarrow OCl^-(aq) + O_2(g)$ (basic solution)
12. For the reduction half-reaction $Hg_2^{2+}(aq) + 2\,e^- \longrightarrow 2\,Hg(l)$, $E° = 0.797$ V. Will Hg(l) react with and dissolve in HCl(aq)? in $HNO_3(aq)$? Explain.
13. Use data from Table 20.1 to predict whether, to any significant extent,
    (a) Mg(s) will displace Pb^{2+} from aqueous solution;
    (b) Sn(s) will react with and dissolve in 1 M HCl;

(c) SO_4^{2-} will oxidize Sn^{2+} to Sn^{4+} in acidic solution;
(d) $MnO_4^-(aq)$ will oxidize $H_2O_2(aq)$ to $O_2(g)$ in acidic solution;
(e) $I_2(s)$ will displace $Br^-(aq)$ to produce $Br_2(l)$.

14. Consider the reaction $Co(s) + Ni^{2+}(aq) \longrightarrow Co^{2+}(aq) + Ni(s)$, with $E^\circ_{cell} = 0.02$ V. If Co(s) is added to a solution with $[Ni^{2+}] = 1$ M, should the reaction go to completion? Explain.

15. Dichromate ion ($Cr_2O_7^{2-}$) in acidic solution is a good oxidizing agent. Which of the following oxidations can be accomplished with dichromate ion in acidic solution? Explain.
(a) $Sn^{2+}(aq)$ to $Sn^{4+}(aq)$
(b) $I_2(s)$ to $IO_3^-(aq)$
(c) $Mn^{2+}(aq)$ to $MnO_4^-(aq)$

16. The standard electrode potential for the reduction of $Eu^{3+}(aq)$ to $Eu^{2+}(aq)$ is −0.43 V. Use the data in Appendix D to determine which of the following is capable of reducing $Eu^{3+}(aq)$ to $Eu^{2+}(aq)$ under standard-state conditions: Al(s), Co(s), $H_2O_2(aq)$, Ag(s), $H_2C_2O_4(aq)$.

17. Predict whether the following metals will react with the acid indicated. If a reaction does occur, write the net ionic equation for the reaction. Assume that reactants and products are in their standard states. **(a)** Ag in $HNO_3(aq)$; **(b)** Zn in HI(aq); **(c)** Au in HNO_3 (for the couple Au^{3+}/Au, $E^\circ = 1.52$ V).

18. Predict whether, to any significant extent,
(a) Fe(s) will displace $Zn^{2+}(aq)$;
(b) $MnO_4^-(aq)$ will oxidize $Cl^-(aq)$ to $Cl_2(g)$ in acidic solution;
(c) Ag(s) will react with 1 M HCl(aq);
(d) $O_2(g)$ will oxidize $Cl^-(aq)$ to $Cl_2(g)$ in acidic solution.

Galvanic Cells

19. Write cell reactions for the electrochemical cells diagrammed here, and use data from Table 20.1 to calculate E°_{cell} for each reaction.
(a) $Al(s)\,|Al^{3+}(aq)\,||Sn^{2+}(aq)\,|Sn(s)$
(b) $Pt(s)\,|Fe^{2+}(aq), Fe^{3+}(aq)\,||Ag^+(aq)\,|Ag(s)$
(c) $Cr(s)\,|Cr^{2+}(aq)\,||Au^{3+}(aq)\,|Au(s)$
(d) $Pt(s)\,|O_2(g)\,|H^+(aq)\,||OH^-(aq)\,|O_2(g)\,|Pt(s)$

20. Write the half-reactions and the balanced chemical equation for the electrochemical cells diagrammed here. Use data from Table 20.1 and Appendix D to calculate E°_{cell} for each reaction.
(a) $Cu(s)\,|Cu^{2+}(aq)\,||Cu^+(aq)\,|Cu(s)$
(b) $Ag(s)\,|AgI(s)\,|I^-(aq)\,||Cl^-(aq)\,|AgCl(s)\,|Ag(s)$
(c) $Pt|Ce^{4+}(aq), Ce^{3+}(aq)\,||I^-(aq), I_2(s)\,|C(s)$
(d) $U(s)\,|U^{3+}(aq)\,||V^{2+}(aq)\,|V(s)$

21. Use the data in Appendix D to calculate the standard cell potential for each of the following reactions. Which reactions will occur spontaneously?
(a) $H_2(g) + F_2(g) \longrightarrow 2\,H^+(aq) + 2\,F^-(aq)$
(b) $Cu(s) + Ba^{2+}(aq) \longrightarrow Cu^{2+}(aq) + Ba(s)$
(c) $3\,Fe^{2+}(aq) \longrightarrow Fe(s) + 2\,Fe^{3+}(aq)$
(d) $Hg(l) + HgCl_2(aq) \longrightarrow Hg_2Cl_2(s)$

22. In each of the following examples, sketch a voltaic cell that uses the given reaction. Label the anode and cathode; indicate the direction of electron flow; write a balanced equation for the cell reaction; and calculate E°_{cell}.
(a) $Cu(s) + Fe^{3+}(aq) \longrightarrow Cu^{2+}(aq) + Fe^{2+}(aq)$
(b) $Pb^{2+}(aq)$ is displaced from solution by Al(s)
(c) $Cl_2(g) + H_2O(l) \longrightarrow Cl^-(aq) + O_2(g) + H^+(aq)$
(d) $Zn(s) + H^+ + NO_3^- \longrightarrow Zn^{2+} + H_2O(l) + NO(g)$

23. Use the data in Appendix D to calculate the standard cell potential for each of the following reactions. Which reactions will occur spontaneously?
(a) $Fe^{3+}(aq) + Ag(s) \longrightarrow Fe^{2+}(aq) + Ag^+(aq)$
(b) $Sn(s) + Sn^{4+}(aq) \longrightarrow 2\,Sn^{2+}(aq)$
(c) $2\,Hg^{2+}(aq) + 2\,Br^-(aq) \longrightarrow Hg_2^{2+}(aq) + Br_2(l)$
(d) $2\,NO_3^-(aq) + 4\,H^+(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,NO_2(g) + 2\,H_2O(l)$

24. Write a cell diagram and calculate the value of E°_{cell} for a voltaic cell in which
(a) $Cl_2(g)$ is reduced to $Cl^-(aq)$ and Fe(s) is oxidized to $Fe^{2+}(aq)$;
(b) $Ag^+(aq)$ is displaced from solution by Zn(s);
(c) The cell reaction is $2\,Cu^+(aq) \longrightarrow Cu^{2+}(aq) + Cu(s)$;
(d) $MgBr_2(aq)$ is produced from Mg(s) and $Br_2(l)$.

ΔG°, E°_{cell}, and K

25. Determine the values of ΔG° for the following reactions carried out in voltaic cells.
(a) $2\,Al(s) + 3\,Cu^{2+}(aq) \longrightarrow 2\,Al^{3+}(aq) + 3\,Cu(s)$
(b) $O_2(g) + 4\,I^-(aq) + 4\,H^+(aq) \longrightarrow 2\,H_2O(l) + 2\,I_2(s)$
(c) $Cr_2O_7^{2-}(aq) + 14\,H^+(aq) + 6\,Ag(s) \longrightarrow 2\,Cr^{3+}(aq) + 6\,Ag^+(aq) + 7\,H_2O(l)$

26. Write the equilibrium constant expression for each of the following reactions, and determine the value of K at 25 °C. Use data from Table 20.1.
(a) $2\,V^{3+}(aq) + Ni(s) \longrightarrow 2\,V^{2+}(aq) + Ni^{2+}(aq)$
(b) $MnO_2(s) + 4\,H^+(aq) + 2\,Cl^-(aq) \longrightarrow Mn^{2+}(aq) + 2\,H_2O(l) + Cl_2(g)$
(c) $2\,OCl^-(aq) \longrightarrow 2\,Cl^-(aq) + O_2(g)$ (basic solution)

27. For the reaction

$$MnO_4^-(aq) + 8\,H^+(aq) + 5\,Ce^{3+}(aq) \longrightarrow 5\,Ce^{4+}(aq) + Mn^{2+}(aq) + 4\,H_2O(l)$$

use data from Table 20.1 to determine **(a)** E°_{cell}; **(b)** ΔG°; **(c)** K; **(d)** whether the reaction goes substantially to completion when the reactants and products are initially in their standard states.

28. For the reaction that occurs in the voltaic cell

$$Pt|Pb^{4+}(aq), Pb^{2+}(aq)||Sn^{4+}(aq), Sn^{2+}(aq)|C(s)$$

use data from Appendix D to determine **(a)** the equation for the cell reaction; **(b)** E°_{cell}; **(c)** ΔG°; **(d)** K; **(e)** whether the reaction goes substantially to completion when the reactants and products are initially in their standard states.

29. For the reaction $2\,Cu^+(aq) + Sn^{4+}(aq) \longrightarrow 2\,Cu^{2+}(aq) + Sn^{2+}(aq)$, $E^\circ_{cell} = -0.0050$ V,
(a) can a solution be prepared at 298 K that is 0.500 M in each of the four ions?
(b) If not, in which direction will a reaction occur?

30. For the reaction $2\,H^+(aq) + BrO_4^-(aq) + 2\,Ce^{3+}(aq) \longrightarrow BrO_3^-(aq) + 2\,Ce^{4+}(aq) + H_2O(l)$, $E^\circ_{cell} = -0.017$ V, answer the following questions:
(a) Can a solution be prepared at 298 K that has $[BrO_4^-] = [Ce^{4+}] = 0.675$ M, $[BrO_3^-] = [Ce^{3+}] = 0.600$ M and pH = 1?
(b) If not, in which direction will a reaction occur?

31. Use thermodynamic data from Appendix D to calculate a theoretical voltage of the silver–zinc button cell described on page 890.

32. The theoretical voltage of the aluminum–air battery is $E^\circ_{cell} = 2.71$ V. Use data from Appendix D and equation (20.28) to determine ΔG°_f for $Al[(OH)_4]^-$.

33. By the method of combining reduction half-equations illustrated on page 875, determine $E^\circ_{IrO_2/Ir}$, given that $E^\circ_{Ir^{3+}/Ir} = 1.156$ V and $E^\circ_{IrO_2/Ir^{3+}} = 0.223$ V.

34. Determine $E^\circ_{MoO_2/Mo^{3+}}$, given that $E^\circ_{H_2MoO_4/MoO_2} = 0.646$ V and $E^\circ_{H_2MoO_4/Mo^{3+}} = 0.428$ V. (See page 875).

Concentration Dependence of E_{cell}—The Nernst Equation

35. A voltaic cell represented by the following cell diagram has $E_{cell} = 1.250$ V. What must be $[Ag^+]$ in the cell?

$$Zn(s)|Zn^{2+}(1.00\ M)||Ag^+(x\ M)|Ag(s)$$

36. For the cell pictured in Figure 20-11, what is E_{cell} if the unknown solution in the half-cell on the left **(a)** has pH = 5.25; **(b)** is 0.0103 M HCl; **(c)** is 0.158 M $HC_2H_3O_2$ ($K_a = 1.8 \times 10^{-5}$)?

37. Use the Nernst equation and Table 20.1 to calculate E_{cell} for each of the following cells.
(a) $Al(s)|Al^{3+}(0.18\ M)||Fe^{2+}(0.85\ M)|Fe(s)$
(b) $Ag(s)|Ag^+(0.34\ M)||Cl^-(0.098\ M), Cl_2(g, 0.55\ atm)|Pt(s)$

38. Use the Nernst equation and data from Appendix D to calculate E_{cell} for each of the following cells.
(a) $Mn(s)|Mn^{2+}(0.40\ M)||Cr^{3+}(0.35\ M), Cr^{2+}(0.25\ M)|Pt(s)$
(b) $Mg(s)|Mg^{2+}(0.016\ M)||[Al(OH)_4]^-(0.25\ M), OH^-(0.042\ M)|Al(s)$

39. Consider the reduction half-reactions listed in Appendix D, and give plausible explanations for the following observations:
(a) For some half-reactions, E depends on pH; for others, it does not.
(b) Whenever H^+ appears in a half-equation, it is on the *left* side.
(c) Whenever OH^- appears in a half-equation, it is on the *right* side.

40. Write an equation to represent the oxidation of $Cl^-(aq)$ to $Cl_2(g)$ by $PbO_2(s)$ in an acidic solution. Will this reaction occur spontaneously in the forward direction if all other reactants and products are in their standard states and **(a)** $[H^+] = 6.0$ M; **(b)** $[H^+] = 1.2$ M; **(c)** pH = 4.25? Explain.

41. If $[Zn^{2+}]$ is maintained at 1.0 M,
(a) what is the minimum $[Cu^{2+}]$ for which reaction (20.3) is spontaneous in the forward direction?
(b) Should the displacement of $Cu^{2+}(aq)$ by Zn(s) go to completion? Explain.

42. Can the displacement of Pb(s) from 1.0 M $Pb(NO_3)_2$ be carried to completion by tin metal? Explain.

43. A concentration cell is constructed of two hydrogen electrodes: one immersed in a solution with $[H^+] = 1.0$ M and the other in 0.65 M KOH.
(a) Determine E_{cell} for the reaction that occurs.
(b) Compare this value of E_{cell} with E° for the reduction of H_2O to $H_2(g)$ in basic solution, and explain the relationship between them.

44. If the 0.65 M KOH of Exercise 43 is replaced by 0.65 M NH_3,
(a) will E_{cell} be higher or lower than in the cell with 0.65 M KOH?
(b) What will be the value of E_{cell}?

45. A voltaic cell is constructed as follows:

$$Ag(s)|Ag^+(satd\ Ag_2CrO_4)||Ag^+(0.125\ M)|Ag(s)$$

What is the value of E_{cell}? For Ag_2CrO_4, $K_{sp} = 1.1 \times 10^{-12}$.

46. A voltaic cell, with $E_{cell} = 0.180$ V, is constructed as follows:

$$Ag(s)|Ag^+(satd\ Ag_3PO_4)||Ag^+(0.140\ M)|Ag(s)$$

What is the K_{sp} of Ag_3PO_4?

47. For the voltaic cell,

$$Sn(s)|Sn^{2+}(0.075\ M)||Pb^{2+}(0.600\ M)|Pb(s)$$

(a) what is E_{cell} initially?
(b) If the cell is allowed to operate spontaneously, will E_{cell} increase, decrease, or remain constant with time? Explain.
(c) What will be E_{cell} when $[Pb^{2+}]$ has fallen to 0.500 M?
(d) What will be $[Sn^{2+}]$ at the point at which $E_{cell} = 0.020$ V?
(e) What are the ion concentrations when $E_{cell} = 0$?

48. For the voltaic cell,

$$Ag(s)\,|Ag^+(0.015\ M)\,||Fe^{3+}(0.055\ M),\ Fe^{2+}(0.045\ M)\,|Pt(s)$$

(a) what is E_{cell} initially?
(b) As the cell operates, will E_{cell} increase, decrease, or remain constant with time? Explain.
(c) What will be E_{cell} when $[Ag^+]$ has increased to 0.020 M?
(d) What will be $[Ag^+]$ when $E_{cell} = 0.010$ V?
(e) What are the ion concentrations when $E_{cell} = 0$?

49. Show that the oxidation of $Cl^-(aq)$ to $Cl_2(g)$ by $Cr_2O_7^{2-}(aq)$ in acidic solution, with reactants and products in their standard states, does not occur spontaneously. Explain why it is still possible to use this method to produce $Cl_2(g)$ in the laboratory. What experimental conditions would you use?

50. Derive a balanced equation for the reaction occurring in the cell:

$$Fe(s)\,|Fe^{2+}(aq)\,||Fe^{3+}(aq),\ Fe^{2+}(aq)\,|Pt(s)$$

(a) If $E^\circ_{cell} = 1.21$ V, calculate ΔG° and the equilibrium constant for the reaction.
(b) Use the Nernst equation to determine the potential for the cell:

$$Fe(s)\,|Fe^{2+}(aq, 1.0 \times 10^{-3}\ M)\,||Fe^{3+}(aq, 1.0 \times 10^{-3}\ M),\ Fe^{2+}(aq, 0.10\ M)\,|Pt(s)$$

(c) In light of **(a)** and **(b)**, what is the likelihood of being able to observe the disproportionation of Fe^{2+} into Fe^{3+} and Fe under standard conditions?

Batteries and Fuel Cells

51. The iron–chromium redox battery makes use of the reaction

$$Cr^{2+}(aq) + Fe^{3+}(aq) \longrightarrow Cr^{3+}(aq) + Fe^{2+}(aq)$$

occurring at a chromium anode and an iron cathode.
(a) Write a cell diagram for this battery.
(b) Calculate the theoretical voltage of the battery.

52. Refer to the discussion of the Leclanché cell (page 888).
(a) Combine the several equations written for the operation of the Leclanché cell into a single overall equation.
(b) Given that the voltage of the Leclanché cell is 1.55 V, estimate the electrode potentials, E, for each of the half-reactions. Why are your values only estimates?

53. What is the theoretical standard cell voltage, E°_{cell}, of each of the following voltaic cells: **(a)** the hydrogen–oxygen fuel cell described by equation (20.26); **(b)** the zinc–air battery; **(c)** a magnesium–iodine battery?

54. For the alkaline Leclanché cell (page 888)
(a) write the overall cell reaction.
(b) Determine E°_{cell} for that cell reaction.

55. One of the advantages of the aluminum-air battery over the iron–air and zinc–air batteries is the greater quantity of charge transferred per unit mass of metal consumed. Show that this is indeed the case. Assume that zinc and iron are oxidized to oxidation state +2 in air batteries.

56. Describe how you might construct batteries with each of the following voltages: **(a)** 0.10 V; **(b)** 2.5 V; **(c)** 10.0 V. Be as specific as you can about the electrodes and solution concentrations you would use, and indicate whether the battery would consist of a single cell or two or more cells connected in series.

57. A lithium battery, which is different from a lithium-ion battery, uses lithium metal as one electrode and carbon in contact with MnO_2 in a paste of KOH as the other electrode. The electrolyte is lithium perchlorate in a nonaqueous solvent, and the construction is similar to the silver battery. The half-cell reactions involve the oxidation of lithium and the reaction

$$MnO_2(s) + 2\,H_2O(l) + e^- \longrightarrow Mn(OH)_3(s) + OH^-(aq) \qquad E^\circ = -0.20\ V$$

Draw a cell diagram for the lithium battery, identify the negative and positive electrodes, and estimate the cell potential under standard conditions.

58. For each of the following potential battery systems, describe the electrode reactions and the net cell reaction you would expect. Determine the theoretical voltage of the battery.
(a) $Zn-Br_2$
(b) $Li-F_2$

Electrochemical Mechanism of Corrosion

59. Refer to Figure 20-20, and describe in words or with a sketch what you would expect to happen in each of the following cases.
(a) Several turns of copper wire are wrapped around the head and tip of an iron nail.
(b) A deep scratch is filed at the center of an iron nail.
(c) A galvanized nail is substituted for the iron nail.

60. When an iron pipe is partly submerged in water, the iron dissolves more readily below the waterline than at the waterline. Explain this observation by relating it to the description of corrosion given in Figure 20-21.

61. Natural gas transmission pipes are sometimes protected against corrosion by the maintenance of a small potential difference between the pipe and an inert electrode buried in the ground. Describe how the method works.

62. In the construction of the Statue of Liberty, a framework of iron ribs was covered with thin sheets of

copper less than 2.5 mm thick. A layer of asbestos separated the copper skin and iron framework. Over time, the asbestos wore away and the iron ribs corroded. Some of the ribs lost more than half their mass in the 100 years before the statue was restored. At the same time, the copper skin lost only about 4% of its thickness. Use electrochemical principles to explain these observations.

Electrolysis Reactions

63. How many grams of metal are deposited at the cathode by the passage of 2.15 A of current for 75 min in the electrolysis of an aqueous solution containing **(a)** Zn^{2+}; **(b)** Al^{3+}; **(c)** Ag^{+}; **(d)** Ni^{2+}?

64. A quantity of electric charge brings about the deposition of 3.28 g Cu at a cathode during the electrolysis of a solution containing $Cu^{2+}(aq)$. What volume of $H_2(g)$, measured at 28.2 °C and 763 mmHg, would be produced by this same quantity of electric charge in the reduction of $H^{+}(aq)$ at a cathode?

65. Which of the following reactions occur spontaneously, and which can be brought about only through electrolysis, assuming that all reactants and products are in their standard states? For those requiring electrolysis, what is the *minimum* voltage required?

(a) $2\,H_2O(l) \longrightarrow 2\,H_2(g) + O_2(g)$ [in 1 M $H^{+}(aq)$]

(b) $Zn(s) + Fe^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Fe(s)$

(c) $2\,Fe^{2+}(aq) + I_2(s) \longrightarrow 2\,Fe^{3+}(aq) + 2\,I^{-}(aq)$

(d) $Cu(s) + Sn^{4+}(aq) \longrightarrow Cu^{2+}(aq) + Sn^{2+}(aq)$

66. An aqueous solution of K_2SO_4 is electrolyzed by means of Pt electrodes.

(a) Which of the following gases should form at the *anode:* O_2, H_2, SO_2, SO_3? Explain.

(b) What product should form at the *cathode*? Explain.

(c) What is the *minimum* voltage required? Why is the actual voltage needed likely to be higher than this value?

67. If a lead storage battery is charged at too high a voltage, gases are produced at each electrode. (It is possible to recharge a lead-storage battery only because of the high overpotential for gas formation on the electrodes.)

(a) What are these gases?

(b) Write a cell reaction to describe their formation.

68. A dilute aqueous solution of Na_2SO_4 is electrolyzed between Pt electrodes for 3.75 h with a current of 2.83 A. What volume of gas, saturated with water vapor at 25 °C and at a total pressure of 742 mmHg, would be collected at the *anode*? Use data from Table 12.4, as required.

69. Calculate the quantity indicated for each of the following electrolyses.

(a) the mass of Zn deposited at the cathode in 42.5 min when 1.87 A of current is passed through an aqueous solution of Zn^{2+}

(b) the time required to produce 2.79 g I_2 at the anode if a current of 1.75 A is passed through KI(aq)

70. Calculate the quantity indicated for each of the following electrolyses.

(a) $[Cu^{2+}]$ *remaining* in 425 mL of a solution that was originally 0.366 M $CuSO_4$, after passage of 2.68 A for 282 s and the deposition of Cu at the cathode

(b) the time required to reduce $[Ag^{+}]$ in 255 mL of $AgNO_3(aq)$ from 0.196 to 0.175 M by electrolyzing the solution between Pt electrodes with a current of 1.84 A

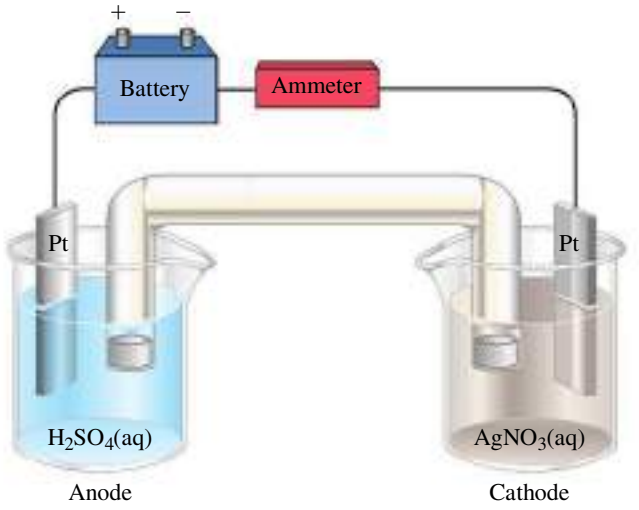
71. A *coulometer* is a device for measuring a quantity of electric charge. In a silver coulometer, $Ag^{+}(aq)$ is reduced to Ag(s) at a Pt cathode. If 1.206 g Ag is deposited in 1412 s by a certain quantity of electricity, **(a)** how much electric charge (in C) must have passed, and **(b)** what was the magnitude (in A) of the electric current?

72. Electrolysis is carried out for 2.00 h in the following cell. The platinum *cathode*, which has a mass of 25.0782 g, weighs 25.8639 g after the electrolysis. The platinum *anode* weighs the same before and after the electrolysis.

(a) Write plausible equations for the half-reactions that occur at the two electrodes.

(b) What must have been the magnitude of the current used in the electrolysis (assuming a constant current throughout)?

(c) A gas is collected at the anode. What is this gas, and what volume should it occupy if (when dry) it is measured at 23 °C and 755 mmHg pressure?



73. A solution containing both Ag^{+} and Cu^{2+} ions is subjected to electrolysis. **(a)** Which metal should plate out first? **(b)** Plating out is finished after a current of 0.75 A is passed through the solution for 2.50 hours. If the total mass of metal is 3.50 g, what is the mass percent of silver in the product?

74. A solution containing a mixture of a platinum(II) salt contaminated by approximately 10 mole % of another oxidation state is electrolyzed at 1.20 A for 32.0 minutes, at which point no more platinum is deposited.

(a) What is the oxidation state of the contaminant?

(b) What is the composition of the mixture?

Integrative and Advanced Exercises

75. Two voltaic cells are assembled in which the following reactions occur.

$$V^{2+}(aq) + VO^{2+}(aq) + 2\,H^{+}(aq) \longrightarrow 2\,V^{3+}(aq) + H_2O(l) \quad E^{\circ}_{cell} = 0.616\ V$$

$$V^{3+}(aq) + Ag^{+}(aq) + H_2O(l) \longrightarrow VO^{2+}(aq) + 2\,H^{+}(aq) + Ag(s) \quad E^{\circ}_{cell} = 0.439\ V$$

Use these data and other values from Table 20.1 to calculate E° for the half-reaction $V^{3+} + e^{-} \longrightarrow V^{2+}$.

76. Suppose that a fully charged lead–acid battery contains 1.50 L of 5.00 M H_2SO_4. What will be the concentration of H_2SO_4 in the battery after 2.50 A of current is drawn from the battery for 6.0 h?

77. The energy consumption in electrolysis depends on the product of the charge and the voltage [volt × coulomb = V · C = J(joules)]. Determine the theoretical energy consumption per 1000 kg Cl_2 produced in a diaphragm chlor–alkali cell (page 902) that operates at 3.45 V. Express this energy in **(a)** kJ; **(b)** kilowatt-hours, kWh.

78. For the half-reaction $Cr^{3+} + e^{-} \longrightarrow Cr^{2+}$, $E^{\circ} = -0.424$ V. If excess Fe(s) is added to a solution in which $[Cr^{3+}] = 1.00$ M, what will be $[Fe^{2+}]$ when equilibrium is reached at 298 K?

$$Fe(s) + 2\,Cr^{3+} \rightleftharpoons Fe^{2+} + 2\,Cr^{2+}$$

79. A voltaic cell is constructed based on the following reaction and initial concentrations:

$$Fe^{2+}(0.0050\ M) + Ag^{+}(2.0\ M) \rightleftharpoons Fe^{3+}(0.0050\ M) + Ag(s)$$

Calculate $[Fe^{2+}]$ when the cell reaction reaches equilibrium.

80. To construct a voltaic cell with $E_{cell} = 0.0860$ V, what $[Cl^{-}]$ must be present in the cathode half-cell to achieve this result?

$$Ag(s)\,|\,Ag^{+}(\text{satd AgI})\,||\,Ag^{+}(\text{satd AgCl, } x\ M\ Cl^{-})\,|\,Ag(s)$$

81. Describe a laboratory experiment that you could perform to evaluate the Faraday constant, *F*, and then show how you could use this value to determine the Avogadro constant.

82. The hydrazine fuel cell is based on the reaction

$$N_2H_4(aq) + O_2(g) \longrightarrow N_2(g) + 2\,H_2O(l)$$

The theoretical E°_{cell} of this fuel cell is 1.559 V. Use this information and data from Appendix D to calculate a value of ΔG°_f for $[N_2H_4(aq)]$.

83. It is sometimes possible to separate two metal ions through electrolysis. One ion is reduced to the free metal at the cathode, and the other remains in solution. In which of these cases would you expect complete or nearly complete separation: **(a)** Cu^{2+} and K^{+}; **(b)** Cu^{2+} and Ag^{+}; **(c)** Pb^{2+} and Sn^{2+}? Explain.

84. Show that for some fuel cells the efficiency value, $\varepsilon = \Delta G^{\circ}/\Delta H^{\circ}$, can have a value greater than 1.00. Can you identify one such reaction? [*Hint:* Use data from Appendix D.]

85. In one type of Breathalyzer (alcohol meter), the quantity of ethanol in a sample is related to the amount of electric current produced by an ethanol–oxygen fuel cell. Use data from Table 20.1 and Appendix D to determine **(a)** E°_{cell} and **(b)** E° for the reduction of $CO_2(g)$ to $CH_3CH_2OH(g)$.

86. You prepare 1.00 L of a buffer solution that is 1.00 M NaH_2PO_4 and 1.00 M Na_2HPO_4. The solution is divided in half between the two compartments of an electrolytic cell. Both electrodes used are Pt. Assume that the only electrolysis is that of water. If 1.25 A of current is passed for 212 min, what will be the pH in each cell compartment at the end of the electrolysis?

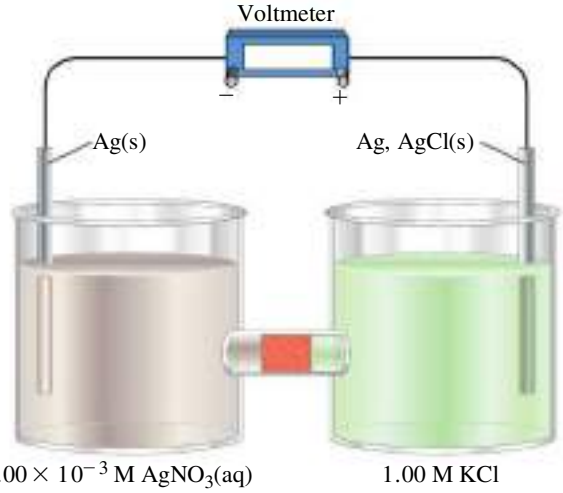
87. Assume that the volume of each solution in Figure 20-22 is 100.0 mL. The cell is operated as an electrolytic cell, using a current of 0.500 A. Electrolysis is stopped after 10.00 h, and the cell is allowed to function as a voltaic cell. What is E_{cell} at this point?

88. A common reference electrode consists of a silver wire coated with AgCl(s) and immersed in 1 M KCl.

$$AgCl(s) + e^{-} \longrightarrow Ag(s) + Cl^{-}(1\ M) \quad E^{\circ} = 0.2223\ V$$

(a) What is E°_{cell} when this electrode is a cathode in combination with a standard zinc electrode as an anode?
(b) Cite several reasons why this electrode should be easier to use than a standard hydrogen electrode.
(c) By comparing the potential of this silver–silver chloride electrode with that of the silver–silver ion electrode, determine K_{sp} for AgCl.

89. The electrodes in the following electrochemical cell are connected to a voltmeter as shown. The half-cell on the right contains a standard silver–silver chloride electrode (see Exercise 88). The half-cell on the left contains a silver electrode immersed in 100.0 mL of 1.00×10^{-3} M $AgNO_3(aq)$. A porous plug through which ions can migrate separates the half-cells.
(a) What is the initial reading on the voltmeter?
(b) What is the voltmeter reading after 10.00 mL of 0.0100 M K_2CrO_4 has been added to the half-cell on the left and the mixture has been thoroughly stirred?
(c) What is the voltmeter reading after 10.00 mL of 10.0 M NH_3 has been added to the half-cell described in part (b) and the mixture has been thoroughly stirred?



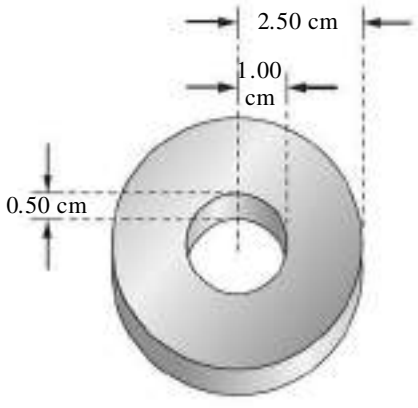
90. An important source of Ag is recovery as a by-product in the metallurgy of lead. The percentage of Ag in lead was determined as follows. A 1.050-g sample was dissolved in nitric acid to produce $Pb^{2+}(aq)$ and $Ag^{+}(aq)$. The solution was then diluted to 500.0 mL with water, a Ag electrode was immersed in the solution, and the potential difference between this electrode and a SHE was found to be 0.503 V. What was the percent Ag by mass in the lead metal?

91. A test for completeness of electrodeposition of Cu from a solution of $Cu^{2+}(aq)$ is to add $NH_3(aq)$. A blue color signifies the formation of the complex ion $[Cu(NH_3)_4]^{2+}$ ($K_f = 1.1 \times 10^{13}$). Let 250.0 mL of 0.1000 M $CuSO_4(aq)$ be electrolyzed with a 3.512 A current for 1368 s. At this time, add a sufficient quantity of $NH_3(aq)$ to complex any remaining Cu^{2+} and to maintain a free $[NH_3] = 0.10$ M. If $[Cu(NH_3)_4]^{2+}$ is detectable at concentrations as low as 1×10^{-5} M, should the blue color appear?

92. A solution is prepared by saturating 100.0 mL of 1.00 M $NH_3(aq)$ with AgBr. A silver electrode is immersed in this solution, which is joined by a salt bridge to a standard hydrogen electrode. What will be the measured E_{cell}? Is the standard hydrogen electrode the anode or the cathode?

93. The electrolysis of $Na_2SO_4(aq)$ is conducted in two separate half-cells joined by a salt bridge, as suggested by the cell diagram $Pt|Na_2SO_4(aq)||Na_2SO_4(aq)|Pt$.
(a) In one experiment, the solution in the anode compartment becomes more acidic and that in the cathode compartment, more basic during the electrolysis. When the electrolysis is discontinued and the two solutions are mixed, the resulting solution has pH = 7. Write half-equations and the overall electrolysis equation.
(b) In a second experiment, a 10.00-mL sample of an unknown concentration of $H_2SO_4(aq)$ and a few drops of phenolphthalein indicator are added to the $Na_2SO_4(aq)$ in the cathode compartment. Electrolysis is carried out with a current of 21.5 mA (milliamperes) for 683 s, at which point, the solution in the cathode compartment acquires a lasting pink color. What is the molarity of the unknown $H_2SO_4(aq)$?

94. A Ni anode and an Fe cathode are placed in a solution with $[Ni^{2+}] = 1.0$ M and then connected to a battery. The Fe cathode has the shape shown. How long must electrolysis be continued with a current of 1.50 A to build a 0.050-mm-thick deposit of nickel on the iron? (Density of nickel = 8.90 g/cm^3.)



95. Initially, each of the half-cells in Figure 20-21 contained a 100.0-mL sample of solution with an ion concentration of 1.000 M. The cell was operated as an electrolytic cell, with copper as the anode and zinc as the cathode. A current of 0.500 A was used. Assume that the only electrode reactions occurring were those involving Cu/Cu^{2+} and Zn/Zn^{2+}. Electrolysis was stopped after 10.00 h, and the cell was allowed to function as a voltaic cell. What was E_{cell} at that point?

96. Silver tarnish is mainly Ag_2S:

$$Ag_2S(s) + 2\,e^- \longrightarrow 2\,Ag(s) + S^{2-}(aq) \qquad E^\circ = -0.691\ V$$

A tarnished silver spoon is placed in contact with a commercially available metallic product in a glass baking dish. Boiling water, to which some $NaHCO_3$ has been added, is poured into the dish, and the product and spoon are completely covered. Within a short time, the removal of tarnish from the spoon begins.
(a) What metal or metals are in the product?
(b) What is the probable reaction that occurs?
(c) What do you suppose is the function of the $NaHCO_3$?
(d) An advertisement for the product appears to make two claims: (1) No chemicals are involved, and (2) the product will never need to be replaced. How valid are these claims? Explain.



97. Your task is to determine E° for the reduction of $CO_2(g)$ to $C_3H_8(g)$ in two different ways and to explain why each gives the same result. **(a)** Consider a fuel cell in which the cell reaction corresponds to the complete combustion of propane gas. Write the half-cell reactions and the overall reaction. Determine ΔG° and E°_{cell} for the reaction, then obtain $E^\circ_{CO_2/C_3H_8}$. **(b)** Without considering the oxidation that occurs simultaneously, obtain $E^\circ_{CO_2/C_3H_8}$ directly from tabulated thermodynamic data for the reduction half-reaction.

98. Equation (20.15) gives the relationship between the standard Gibbs energy of a reaction and the standard cell potential. We know how the Gibbs energy varies with temperature.
(a) Making the assumption that ΔH° and ΔS° do not vary significantly over a small temperature range, derive an equation for the temperature variation of E°_{cell}.
(b) Calculate the cell potential of a Daniell cell at 50 °C under standard conditions. The overall cell reaction for a Daniell cell is $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$.

99. Show that for nonstandard conditions the temperature variation of a cell potential is

$$E(T_1) - E(T_2) = (T_1 - T_2)\frac{(\Delta S^\circ - R \ln Q)}{zF}$$

where $E(T_1)$ and $E(T_2)$ are the cell potentials at T_1 and T_2, respectively. We have assumed that the value of Q is maintained at a constant value. For the nonstandard cell below, the potential drops from 0.394 V at 50.0 °C to 0.370 V at 25.0 °C. Calculate Q, $\Delta H°$, and $\Delta S°$ for the reaction, and calculate K for the two temperatures.

$$Cu(s)\,|Cu^{2+}(aq)\,||Fe^{3+}(aq),\,Fe^{2+}(aq)\,|Pt(s)$$

Choose concentrations of the species involved in the cell reaction that give the value of Q that you have calculated, and then determine the equilibrium concentrations of the species at 50.0 °C.

100. Show that for a combination of half-cell reactions that produce a standard reduction potential for a half-cell that is not directly observable, the standard reduction potential is

$$E° = \frac{\sum n_i E_i°}{\sum n_i}$$

where n_i is the number of electrons in each half-reaction of potential $E_i°$. Use the following half-reactions:

$$H_5IO_6(aq) + H^+(aq) + 2\,e^- \longrightarrow IO_3^-(aq) + 3H_2O(l) \qquad E° = 1.60\ V$$

$$IO_3^-(aq) + 6\,H^+(aq) + 5\,e^- \longrightarrow \frac{1}{2}I_2(s) + 3\,H_2O(l) \qquad E° = 1.19\ V$$

$$2\,HIO(aq) + 2\,H^+(aq) + 2\,e^- \longrightarrow I_2(s) + 2\,H_2O(l) \qquad E° = 1.45\ V$$

$$I_2(s) + 2\,e^- \longrightarrow 2\,I^-(aq) \qquad E° = 0.535\ V$$

Calculate the standard reduction potential for

$$H_6IO_6 + 5\,H^+ + 2\,I^- + 3\,e^- \longrightarrow \frac{1}{2}I_2 + 4\,H_2O + 2\,HIO$$

Feature Problems

101. Consider the following electrochemical cell:

$$Pt(s)\,|H_2(g, 1\ atm)\,|H^+(1\ M)\,||Ag^+(x\ M)\,|Ag(s)$$

(a) What is $E°_{cell}$—that is, the cell potential when $[Ag^+] = 1$ M?
(b) Use the Nernst equation to write an equation for E_{cell} when $[Ag^+] = x$.
(c) Now imagine titrating 50.0 mL of 0.0100 M $AgNO_3$ in the cathode half-cell compartment with 0.0100 M KI. The titration reaction is

$$Ag^+(aq) + I^-(aq) \longrightarrow AgI(s)$$

Calculate $[Ag^+]$ and then E_{cell} after addition of the following volumes of 0.0100 M KI: (i) 0.0 mL; (ii) 20.0 mL; (iii) 49.0 mL; (iv) 50.0 mL; (v) 51.0 mL; (vi) 60.0 mL.
(d) Use the results of part (c) to sketch the titration curve of E_{cell} versus volume of titrant.

102. Ultimately, $\Delta G_f°$ values must be based on experimental results; in many cases, these experimental results are themselves obtained from $E°$ values. Early in the twentieth century, G. N. Lewis conceived of an experimental approach for obtaining standard potentials of the alkali metals. This approach involved using a solvent with which the alkali metals do not react. Ethylamine was the solvent chosen. In the following cell diagram, Na(amalg, 0.206%) represents a solution of 0.206% Na in liquid mercury.

1. $Na(s)\,|Na^+(\text{in ethylamine})\,|Na(\text{amalg}, 0.206\%) \qquad E_{cell} = 0.8453\ V$

Although Na(s) reacts violently with water to produce $H_2(g)$, at least for a short time, a sodium amalgam electrode does not react with water. This makes it possible to determine E_{cell} for the following voltaic cell.

2. $Na(\text{amalg}, 0.206\%)\,|Na^+(1\ M)\,||H^+(1\ M)\,|H_2(g, 1\ atm) \qquad E_{cell} = 1.8673\ V$

(a) Write equations for the cell reactions that occur in the voltaic cells (1) and (2).
(b) Use equation (20.14) to establish ΔG for the cell reactions written in part (a).
(c) Write the overall equation obtained by combining the equations of part (a), and establish $\Delta G°$ for this overall reaction.
(d) Use the $\Delta G°$ value from part (c) to obtain $E°_{cell}$ for the overall reaction. From this result, obtain $E°_{Na^+/Na}$. Compare your result with the value listed in Appendix D.

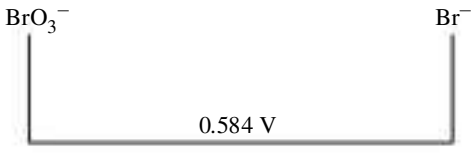
103. The following sketch is called an electrode potential diagram. Such diagrams summarize electrode potential data more efficiently than do listings such as that in Appendix D. In this diagram for bromine and its ions in basic solution,

$$BrO_4^- \xrightarrow{1.025\ V} BrO_3^-$$

signifies

$$BrO_4^-(aq) + H_2O(l) + 2\,e^- \longrightarrow BrO_3^-(aq) + 2\,OH^-(aq),\ E°_{BrO_4^-/BrO_3^-} = 1.025\ V$$

Similarly,

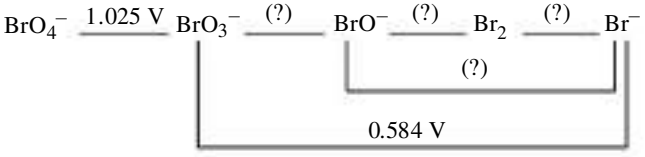


signifies

$$BrO_3^-(aq) + 3\,H_2O(l) + 6\,e^- \longrightarrow Br^-(aq) + 6\,OH^-(aq),\ E°_{BrO_3^-/Br^-} = 0.584\ V$$

With reference to Appendix D and to the method of determining $E°$ values outlined on page 875, supply the missing data in the following diagram.

Basic solution ($[OH^-] = 1$ M):



104. Only a tiny fraction of the diffusible ions move across a cell membrane in establishing a Nernst potential (see Focus On 20: Membrane Potentials), so there is no detectable concentration change. Consider a typical cell with a volume of 10^{-8} cm^3, a surface area (A) of 10^{-6} cm^2, and a membrane thickness (l) of 10^{-6} cm. Suppose that $[K^+] = 155$ mM inside the cell and $[K^+] = 4$ mM outside the cell and that the observed Nernst potential across the cell wall is 0.085 V. The membrane acts as a charge-storing device called a *capacitor*, with a *capacitance*, C, given by

$$C = \frac{\varepsilon_0 \varepsilon A}{l}$$

where ε_0 is the *dielectric constant* of a vacuum and the product $\varepsilon_0\varepsilon$ is the dielectric constant of the membrane, having a typical value of $3 \times 8.854 \times 10^{-12}$ C^2 N^{-1}m^{-2} for a biological membrane. The SI unit of capacitance is the *farad*, 1 F = 1 coulomb per volt = 1 C V^{-1} = 1 × C^2 N^{-1} m^{-1}.

(a) Determine the capacitance of the membrane for the typical cell described.
(b) What is the net charge required to maintain the observed membrane potential?
(c) How many K^+ ions must flow through the cell membrane to produce the membrane potential?
(d) How many K^+ ions are in the typical cell?
(e) Show that the fraction of the intracellular K^+ ions transferred through the cell membrane to produce the membrane potential is so small that it does not change $[K^+]$ within the cell.

105. When deciding whether a particular reaction corresponds to a cell with a positive standard cell potential, which of the following thermodynamic properties would you use to get your answer without performing any calculations? Which would you not use? Explain. **(a)** $\Delta G°$; **(b)** $\Delta S°$; **(c)** $\Delta H°$; **(d)** $\Delta U°$; **(e)** K.

106. Consider two cells involving two metals X and Y

$$X(s)\,|X^+(aq)\,||H^+(aq), H_2(g, 1\text{ bar})\,|Pt(s)$$
$$X(s)\,|X^+(aq)\,||Y^{2+}(aq)\,|Y(s)$$

In the first cell electrons flow from the metal X to the standard hydrogen electrode. In the second cell electrons flow from metal X to metal Y. Is $E°_{X^+/X}$ greater or less than zero? Is $E°_{X^+/X} > E_{Y^{2+}/Y}$? Explain.

107. Describe in words how you would calculate the standard potential of the $Fe^{2+}/Fe(s)$ couple from those of Fe^{3+}/Fe^{2+} and $Fe^{3+}/Fe(s)$.

Self-Assessment Exercises

108. In your own words, define the following symbols or terms: **(a)** $E°$; **(b)** F; **(c)** anode; **(d)** cathode.

109. Briefly describe each of the following ideas, methods, or devices: **(a)** salt bridge; **(b)** standard hydrogen electrode (SHE); **(c)** cathodic protection; **(d)** fuel cell.

110. Explain the important distinctions between each pair of terms: **(a)** half-reaction and overall cell reaction; **(b)** voltaic cell and electrolytic cell; **(c)** primary battery and secondary battery; **(d)** E_{cell} and $E°_{cell}$.

111. Of the following statements concerning electrochemical cells, the correct ones are: **(a)** The cathode is the negative electrode in both voltaic and electrolytic cells. **(b)** The function of a salt bridge is to permit the migration of electrons between the half-cell compartments of an electrochemical cell. **(c)** The anode is the negative electrode in a voltaic cell. **(d)** Electrons leave the cell from either the cathode or the anode, depending on what electrodes are used. **(e)** Reduction occurs at the cathode in both voltaic and electrolytic cells. **(f)** If electric current is drawn from a voltaic cell long enough, the cell becomes an electrolytic cell. **(g)** The cell reaction is an oxidation-reduction reaction.

112. For the half-reaction $Hg^{2+}(aq) + 2\,e^- \longrightarrow Hg(l)$, $E° = 0.854$ V. This means that **(a)** Hg(1) is more readily oxidized than $H_2(g)$; **(b)** $Hg^{2+}(aq)$ is more readily reduced than $H^+(aq)$; **(c)** Hg(l) will dissolve in 1 M HCl; **(d)** Hg(l) will displace Zn(s) from an aqueous solution of Zn^{2+} ion.

113. The value of $E°_{cell}$ for the reaction $Zn(s) + Pb^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Pb(s)$ is 0.66 V. This means that for the reaction $Zn(s) + Pb^{2+}(0.01\text{ M}) \longrightarrow Zn^{2+}(0.10\text{ M}) + Pb(s)$, E_{cell} equals **(a)** 0.72 V; **(b)** 0.69 V; **(c)** 0.66 V; **(d)** 0.63 V.

114. For the reaction $Co(s) + Ni^{2+}(aq) \longrightarrow Co^{2+}(aq) + Ni(s)$, $E°_{cell} = 0.03$ V. If cobalt metal is added to an aqueous solution in which $[Ni^{2+}] = 1.0$ M, **(a)** the reaction will not proceed in the forward direction at all; **(b)** the displacement of Ni(s) from the $Ni^{2+}(aq)$ will go to completion; **(c)** the displacement of Ni(s) from the solution will proceed to a considerable extent, but the reaction will not go to completion; **(d)** there is no way to predict how far the reaction will proceed.

115. The gas evolved at the *anode* when $K_2SO_4(aq)$ is electrolyzed between Pt electrodes is most likely to be **(a)** O_2; **(b)** H_2; **(c)** SO_2; **(d)** SO_3; **(e)** a mixture of sulfur oxides.

116. The quantity of electric charge that will deposit 4.5 g Al at a cathode will also produce the following volume at STP of $H_2(g)$ from $H^+(aq)$ at a cathode: **(a)** 44.8 L; **(b)** 22.4 L; **(c)** 11.2 L; **(d)** 5.6 L.

117. If a chemical reaction is carried out in a fuel cell, the maximum amount of useful work that can be obtained is **(a)** ΔG; **(b)** ΔH; **(c)** $\Delta G/\Delta H$; **(d)** $T\,\Delta S$.

118. For the reaction $Zn(s) + H^+(aq) + NO_3^-(aq) \longrightarrow Zn^{2+}(aq) + H_2O(l) + NO(g)$, describe the voltaic cell in which it occurs, label the anode and cathode,

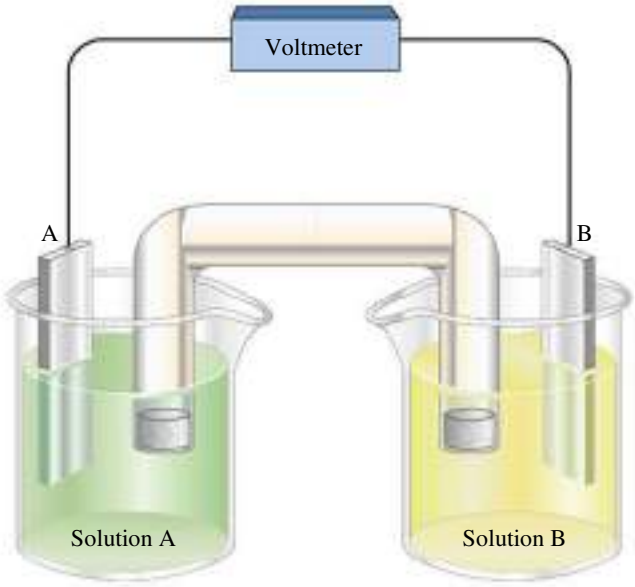
use a table of standard electrode potentials to evaluate E°_{cell}, and balance the equation for the cell reaction.

119. The following voltaic cell registers an $E_{cell} = 0.108$ V. What is the pH of the unknown solution?

$$Pt|H_2(g, 1\ atm)|H^+(x\ M)||H^+(1.00\ M)|H_2(g, 1\ atm)|Pt$$

120. $E^\circ_{cell} = -0.0050$ V for the reaction, $2\ Cu^+(aq) + Sn^{4+}(aq) \longrightarrow 2\ Cu^{2+}(aq) + Sn^{2+}(aq)$.
(a) Can a solution be prepared that is 0.500 M in each of the four ions at 298 K?
(b) If not, in what direction must a net reaction occur?

121. For each of the following combinations of electrodes (A and B) and solutions, indicate
- the overall cell reaction
- the direction in which electrons flow spontaneously (from A to B, or from B to A)
- the magnitude of the voltage read on the voltmeter, V



	A	Solution A	B	Solution B
(a)	Cu	1.0 M Cu^{2+}	Fe	1.0 M Fe^{2+}
(b)	Pt	1.0 M Sn^{2+}/1.0 M Sn^{4+}	Ag	1.0 M Ag^+
(c)	Zn	0.10 M Zn^{2+}	Fe	1.0×10^{-3} M Fe^{2+}

122. Use data from Table 20.1, as necessary, to predict the probable products when Pt electrodes are used in the electrolysis of **(a)** $CuCl_2(aq)$; **(b)** $Na_2SO_4(aq)$; **(c)** $BaCl_2(l)$; **(d)** KOH(aq).

123. Using the method presented in Appendix E, construct a concept map showing the relationship between electrochemical cells and thermodynamic properties.

124. Construct a concept map illustrating the relationship between batteries and electrochemical ideas.

125. Construct a concept map illustrating the principles of electrolysis and its industrial applications.