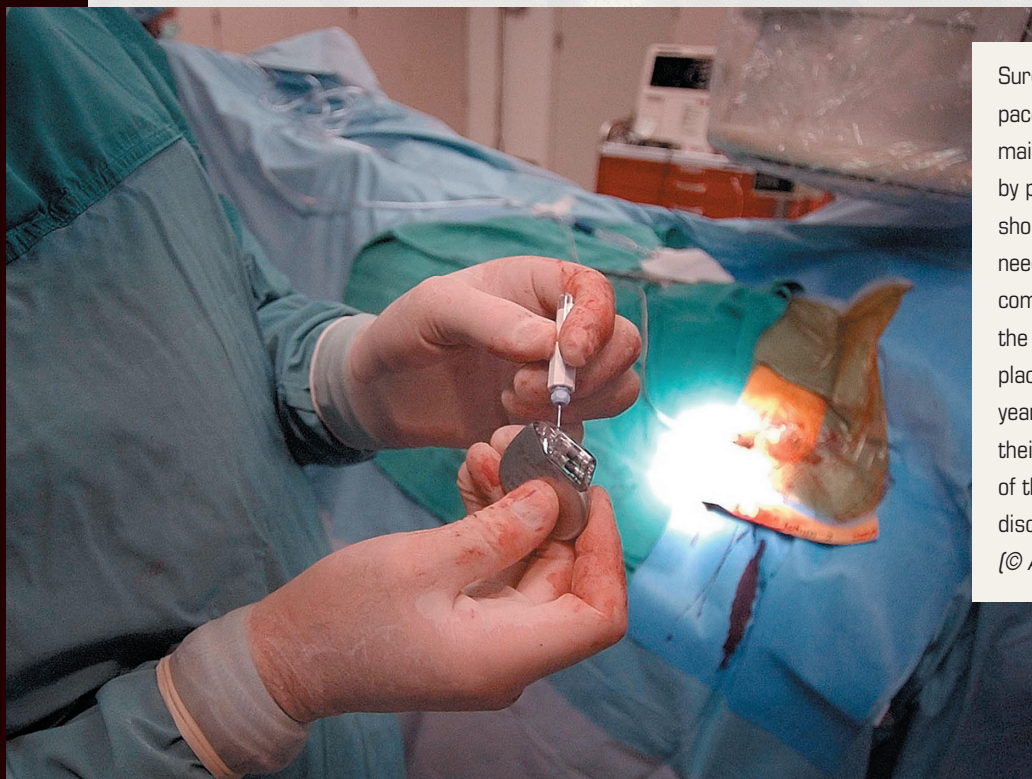# 19 ELECTROCHEMISTRY

Surgeons implant a heart pacemaker to help this patient maintain a reasonable heart rate by providing a gentle electrical shock to the heart muscle as needed. The most critical component of the pacemaker is the battery that must remain in place and active for up to seven years at a time. Batteries and their design are important parts of the electrochemistry discussed in this chapter. *(© AP/Wide World Photos)*

CHAPTER OUTLINE

19.1 Galvanic cells use redox reactions to generate electricity

19.2 Cell potentials can be related to reduction potentials

19.3 Standard reduction potentials can predict spontaneous reactions

19.4 Cell potentials are related to free energy changes

19.5 Concentrations in a galvanic cell affect the cell potential

19.6 Electrolysis uses electrical energy to cause chemical reactions

19.7 Stoichiometry of electrochemical reactions involves electric current and time

19.8 Practical applications of electrochemistry

THIS CHAPTER IN CONTEXT   Oxidation and reduction (redox) reactions occur in many chemical systems. Examples include our own respiratory system and the complementary photosynthetic system in plants. In addition there's the toasting of bread, the rusting of iron, the action of bleach on stains, and the production and combustion of petroleum that heats us, generates electricity, and moves our cars. In this chapter we will study how it is possible to separate the processes of oxidation (electron loss) and reduction (electron gain) and cause them to occur in different physical locations. When we are able to do this, we can use spontaneous redox reactions to produce electricity. And by reversing the process, we can use electricity to make nonspontaneous redox reactions happen to produce important products by a process called electrolysis.

Because electricity plays a role in these systems, the processes involved are described as **electrochemical changes.** The study of such changes is called **electrochemistry.** As you will learn, electrical measurements and

the principles of thermodynamics combine to give fundamental information about chemical reactions, such as free energy changes and equilibrium constants. In addition, you will learn some of the practical applications of electro-chemistry.

The last section of this chapter describes modern batteries. Development of new, highly efficient, light weight and relatively inexpensive batteries and fuel cells is an area of intensive research. These devices will be important contributors to efforts to conserve fossil fuels.

19.1 | GALVANIC CELLS USE REDOX REACTIONS TO GENERATE ELECTRICITY

Batteries have become common sources of portable power for a wide range of consumer products, from cell phones to iPods to laptops and hybrid cars. The energy from a battery comes from a spontaneous redox reaction in which the electron transfer is forced to take place through a wire. The apparatus that provides electricity in this way is called a **galvanic cell,** after Luigi Galvani (1737–1798), an Italian anatomist who discovered that electricity can cause the contraction of muscles. [It is also called a **voltaic cell,** after another Italian scientist, Alessandro Volta (1745–1827), whose inventions led ultimately to the development of modern batteries.]

Galvanic cells form a useful electrical circuit

If a shiny piece of metallic copper is placed into a solution of silver nitrate, a spontaneous reaction occurs. Gradually, a grayish white deposit forms on the copper and the solution itself becomes pale blue as hydrated Cu^{2+} ions enter the solution (see Figure 19.1). The equation is

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

Although the reaction is exothermic, no usable energy can be harnessed from it because all the energy is dispersed as heat.

To produce useful *electrical* energy, the two half-reactions involved in the net reaction must be made to occur in separate containers or compartments called **half-cells.** When this is done, electrons must flow through an external circuit to power devices
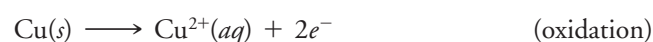

(a)   (b)   (c)
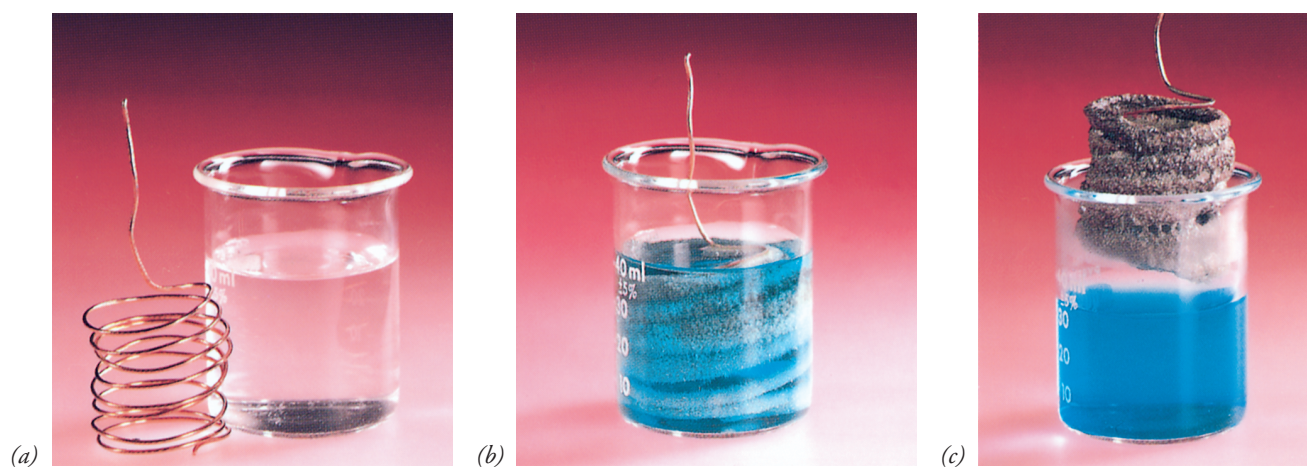
FIG. 19.1 **Reaction of copper with a solution of silver nitrate.** (*a*) A coil of copper wire stands next to a beaker containing a silver nitrate solution. (*b*) When the copper wire is placed in the solution, copper dissolves, giving the solution its blue color, and metallic silver deposits as glittering crystals on the wire. (*c*) After a while, much of the copper has dissolved and nearly all of the silver has deposited as the free metal. *(Michael Watson.)*

such as a laser pointer, a laptop computer, or your iPod. An apparatus to accomplish this—a **galvanic cell**—is made up of two half-cells, as illustrated in Figure 19.2. On the left, a silver electrode dips into a solution of $AgNO_3$, and, on the right, a copper electrode dips into a solution of $Cu(NO_3)_2$. The two electrodes are connected by an external electrical circuit and the two solutions are connected by a *salt bridge*, the function of which will be described shortly. When the circuit is completed by closing the switch, the reduction of Ag^+ to Ag occurs spontaneously in the half-cell on the left and oxidation of Cu to Cu^{2+} occurs spontaneously in the half-cell on the right. The reaction that takes place in each half-cell is a *half-reaction* of the type you learned to balance by the ion–electron method in Chapter 5. In the silver half-cell, the following half-reaction occurs.
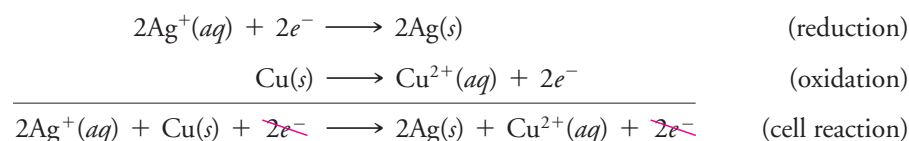
$$Ag^+(aq) + e^- \longrightarrow Ag(s) \qquad \text{(reduction)}$$

In the copper half-cell, the half-reaction is

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^- \qquad \text{(oxidation)}$$

When these reactions take place, electrons, left behind by oxidation of the copper, travel through the external circuit to the other electrode where they are transferred to the silver ions, as Ag^+ is reduced to the familiar shiny silver metal.

□ When electrons appear as a reactant, the process is reduction; when they appear as a product, it is oxidation.

The cell reaction is the net overall reaction in the cell

The overall reaction that takes place in the galvanic cell is called the **cell reaction.** To obtain it, we combine the individual electrode half-reactions, making sure that the number of electrons gained in one half-reaction equals the number lost in the other. Thus, to obtain the cell reaction we multiply the half-reaction for the reduction of silver by 2 and then add the two half-reactions to obtain the net reaction. (Notice that $2e^-$ appear on each side, and so they cancel.) This is exactly the same as the process we used to balance redox reactions by the ion–electron method described in Section 5.2.

$$2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s) \qquad \text{(reduction)}$$
$$\underline{Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^- \qquad \text{(oxidation)}}$$
$$2Ag^+(aq) + Cu(s) + \cancel{2e^-} \longrightarrow 2Ag(s) + Cu^{2+}(aq) + \cancel{2e^-} \qquad \text{(cell reaction)}$$

□ The two electrons canceled in this reaction are also the number of electrons transferred. These will be important later when we discuss the Nernst equation.
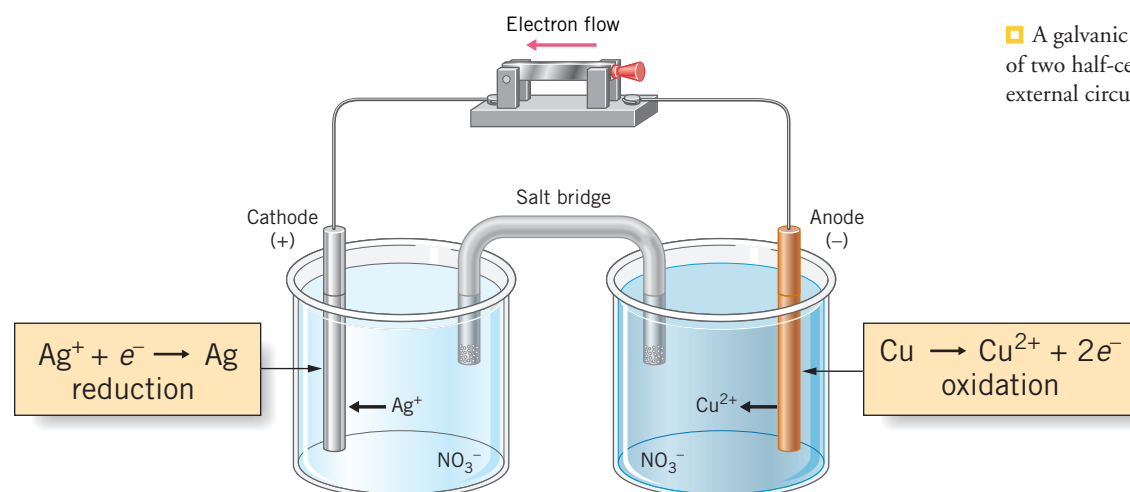
□ A galvanic cell is composed of two half-cells connected by an external circuit and a salt bridge.

Electrodes are named according to the chemical processes that occur at them

The electrodes in electrochemical systems are identified by the names *cathode* and *anode*. The names are *always* assigned according to the nature of the chemical changes that occur at the electrodes. In any electrochemical system:

TOOLS
Electrode reactions

> The **cathode** is the electrode at which reduction (electron gain) occurs.
> The **anode** is the electrode at which oxidation (electron loss) occurs.

Thus, in the galvanic cell we've been discussing, the silver electrode is the cathode and the copper electrode is the anode.

Conduction of charge occurs in two ways

In the external circuit of a galvanic cell, electrical charge is transported from one electrode to the other by the movement of *electrons* through the wires. This is called **metallic conduction,** and is how metals in general conduct electricity. In this external circuit, electrons always travel from the anode, where they are left behind by the oxidation process, to the cathode, where they are picked up by the substance being reduced.

In electrochemical cells another kind of electrical conduction also takes place. In a solution that contains ions (or in a molten ionic compound), *electrical charge is carried through the liquid by the movement of ions, not electrons.* The transport of electrical charge by ions is called **electrolytic conduction.**

When the reactions take place in the copper–silver galvanic cell, positive copper ions *enter* the liquid that surrounds the anode while positive silver ions *leave* the liquid that surrounds the cathode (Figure 19.3). For the galvanic cell to work, the solutions in both half-cells must remain electrically neutral. This requires that ions be permitted to enter or leave the solutions. For example, when copper is oxidized, the solution surrounding the anode becomes filled with Cu^{2+} ions, so negative ions are needed to balance their charge. Similarly, when Ag^+ ions are reduced, NO_3^- ions are left behind in the solution and positive ions are needed to maintain neutrality. The **salt bridge** shown in Figure 19.2 allows the movement of ions required to keep the solutions electrically neutral. The salt bridge is also essential to complete the electrical circuit.

A salt bridge is a tube filled with a solution of a salt composed of ions not involved in the cell reaction. Often KNO_3 or KCl is used. The tube is fitted with porous plugs at each end that prevent the solution from pouring out but at the same time enable the solution in the salt bridge to exchange ions with the solutions in the half-cells.
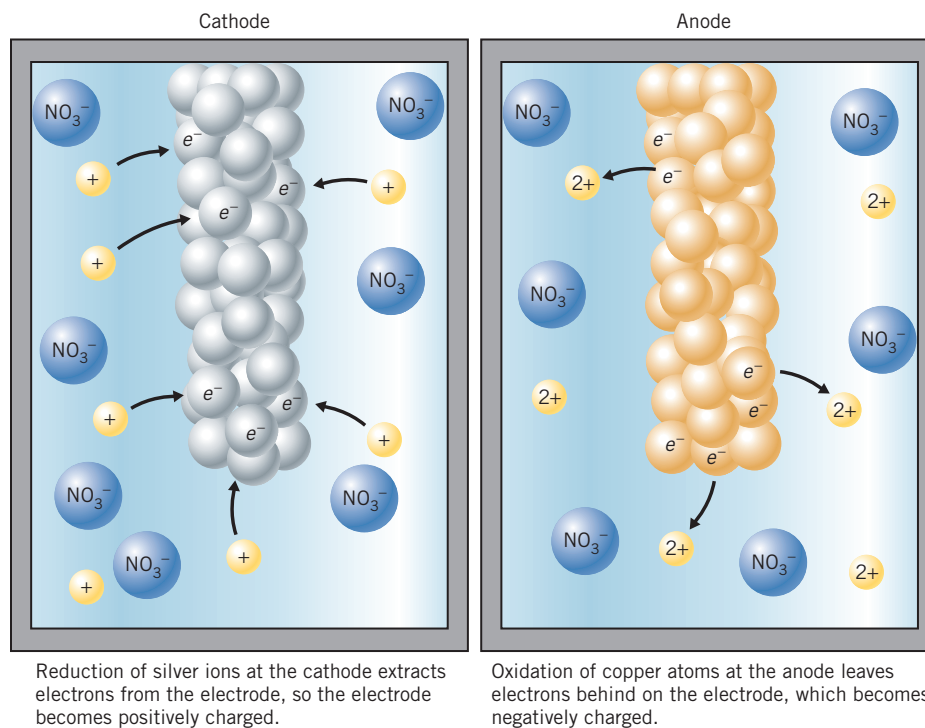
During operation of the cell, negative ions can diffuse from the salt bridge into the copper half-cell, or, to a much smaller extent, Cu^{2+} ions can leave the solution and enter the salt bridge. Both processes help keep the copper half-cell electrically neutral. At the silver half-cell, positive ions from the salt bridge can enter or negative NO_3^- ions can, once again to a much smaller extent, leave the half-cell by entering the salt bridge, to keep it electrically neutral.

Without the salt bridge, electrical neutrality could not be maintained and no electrical current could be produced by the cell. Therefore, *electrolytic contact*—contact by means of a solution containing ions—must be maintained for the cell to function.

If we look closely at the overall movement of ions during the operation of the galvanic cell, we find that negative ions (*anions*) move away from the cathode, where they are present in excess, and *toward the anode*, where they are needed to balance the charge of the positive ions being formed. Similarly, we find that positive ions (*cations*) move away from the anode, where they are in excess, and *toward the cathode*, where they can balance the charge of the anions left in excess. In fact, the reason positive ions are called cations and negative ions are called anions is because of the nature of the electrodes toward which they move.

□ Often the salt bridge is prepared by saturating a hot agar-agar solution with KNO_3 or KCl. After pouring into a U-shaped tube the agar-agar solidifies on cooling. The salt ions can move but the agar-agar does not flow out of the salt bridge.

Cathode   Anode

Reduction of silver ions at the cathode extracts electrons from the electrode, so the electrode becomes positively charged.

Oxidation of copper atoms at the anode leaves electrons behind on the electrode, which becomes negatively charged.

FIG. 19.3 Expanded view of Figure 19.2 to show changes that take place at the anode and cathode in the copper–silver galvanic cell. (Not drawn to scale.) At the anode, Cu^{2+} ions enter the solution when copper atoms are oxidized, leaving electrons behind on the electrode. Unless Cu^{2+} ions move away from the electrode or NO_3^- ions move toward it, the solution around the electrode will become positively charged. At the cathode, Ag^+ ions leave the solution and become silver atoms by acquiring electrons from the electrode surface. Unless more silver ions move toward the cathode or negative ions move away, the solution around the electrode will become negatively charged.

In summary,

> Cations move in the general direction of the cathode.
> Anions move in the general direction of the anode.

Charges on the electrodes come from electron loss and gain

At the anode of the galvanic cell described in Figures 19.2 and 19.3, copper atoms spontaneously leave the electrode and enter the solution as Cu^{2+} ions. The electrons that are left behind give the anode a slight negative charge. (We say the anode has a *negative polarity*.) At the cathode, electrons spontaneously join Ag^+ ions to produce neutral atoms, but the effect is the same as if Ag^+ ions become part of the electrode, so the cathode acquires a slight positive charge. (The cathode has a *positive polarity*.) During the operation of the cell, the amount of positive and negative charge on the electrodes is kept small by the flow of electrons (an electric current) through the external circuit from the anode to the cathode when the circuit is complete. In fact, unless electrons can flow out of the anode and into the cathode, the chemical reactions that occur at their surfaces will cease.

□ The small difference in charge between the electrodes is formed by the spontaneity of the overall reaction, that is, by the favorable free energy change. Nature's tendency toward electrical neutrality prevents a large buildup of charge on the electrodes and promotes the spontaneous flow of electricity through the external circuit.

Cell notation gives a shorthand description of a galvanic cell

As a matter of convenience, chemists have devised a shorthand way of describing the makeup of a galvanic cell. For example, the copper–silver cell that we have been using in our discussion is represented as follows.
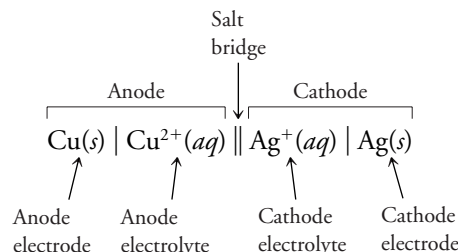
$$Cu(s)\,|\,Cu^{2+}(aq)\,||\,Ag^+(aq)\,|\,Ag(s)$$
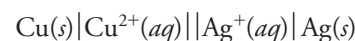
By convention, in **standard cell notation,** the anode half-cell is specified on the left, with the electrode material of the anode given first. In this case, the anode is copper metal. The single vertical bar represents a *phase boundary*—between the copper electrode and the solution that surrounds it. The double vertical bars represent the two phase boundaries, one at each

□ Also, notice that for each half-cell, the reactant in the redox half-reaction is given first. In the anode compartment, Cu is the reactant and is oxidized to Cu^{2+}, whereas in the cathode compartment, Ag^+ is the reactant and is reduced to Ag.

end of the salt bridge, which connects the solutions in the two half-cells. On the right, the cathode half-cell is described, with the material of the cathode given last. Thus, the electrodes themselves (copper and silver) are specified at opposite ends of the cell description.

$$Cu(s) \mid Cu^{2+}(aq) \parallel Ag^{+}(aq) \mid Ag(s)$$

Salt bridge

Anode — Cathode

Anode electrode — Anode electrolyte — Cathode electrolyte — Cathode electrode

Sometimes, both the oxidized and reduced forms of the reactants in a half-cell are soluble and cannot be used as an electrode. In these cases, an inert electrode composed of platinum or gold is used to provide a site for electron transfer. For example, a galvanic cell can be made using an anode composed of a zinc electrode dipping into a solution containing Zn^{2+}, and a cathode composed of a platinum electrode dipping into a solution containing both Fe^{2+} and Fe^{3+} ions. The cell reaction is

$$2Fe^{3+}(aq) + Zn(s) \longrightarrow 2Fe^{2+}(aq) + Zn^{2+}(aq)$$
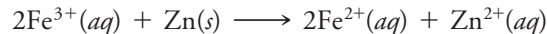
The cell notation for this galvanic cell is written as follows.

$$Zn(s) \mid Zn^{2+}(aq) \parallel Fe^{3+}(aq),\ Fe^{2+}(aq) \mid Pt(s)$$
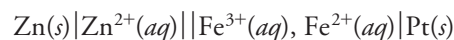
where we have separated the formulas for the two iron ions by a comma. In this cell, the reduction of the Fe^{3+} to Fe^{2+} takes place at the surface of the inert platinum electrode.

EXAMPLE 19.1
Describing Galvanic Cells

The following spontaneous reaction occurs when metallic zinc is dipped into a solution of copper sulfate.

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

Describe a galvanic cell that could take advantage of this reaction. What are the half-cell reactions? What is the standard cell notation? Make a sketch of the cell and label the cathode and anode, the charges on each electrode, the direction of ion flow, and the direction of electron flow.

ANALYSIS: Answering all these questions relies on identifying the anode and cathode in the equation for the cell reaction; this is often the key to solving problems of this type. By definition, the anode is the electrode at which oxidation happens, and the cathode is where reduction occurs. The first step, therefore, is to determine which reactant is oxidized and which is reduced. One way to do this is to divide the cell reaction into half-reactions and balance them by adding electrons. Then, if electrons appear as a product, the half-reaction is oxidation; if the electrons appear as a reactant, the half-reaction is reduction.

**SOLUTION:** The balanced half-reactions are as follows.

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^{-}$$
$$Cu^{2+}(aq) + 2e^{-} \longrightarrow Cu(s)$$
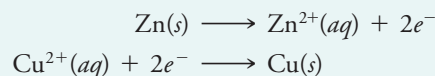
Zinc loses electrons and is oxidized, so it is the anode. The anode half-cell is therefore a zinc electrode dipping into a solution that contains Zn^{2+} [e.g., from dissolved $Zn(NO_3)_2$ or $ZnSO_4$]. Symbolically, the anode half-cell is written with the electrode material at the left of the vertical bar and the oxidation product at the right.

$$Zn(s) \mid Zn^{2+}(aq)$$
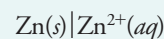
Copper ions gain electrons and are reduced to metallic copper, so the cathode half-cell consists of a copper electrode dipping into a solution containing Cu^{2+} [e.g., from dissolved

$Cu(NO_3)_2$ or $CuSO_4$]. The copper half-cell can be represented as follows, with the electrode material to the right of the vertical bar and the substance reduced on the left.
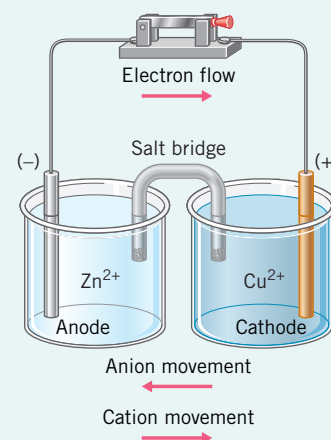
$$Cu^{2+}(aq)|Cu(s)$$
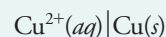
The standard cell notation places the zinc anode half-cell on the left and the copper cathode half-cell on the right separated by double bars that represent the salt bridge.

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

anode   cathode
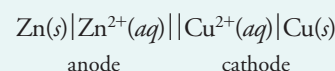
A sketch of the cell is shown in the margin. The anode always carries a negative charge in a galvanic cell, so the zinc electrode is negative and the copper electrode is positive. Electrons in the external circuit travel from the negative electrode to the positive electrode (i.e., from the Zn anode to the Cu cathode). Anions move toward the anode and cations move toward the cathode as shown.

Electron flow

Salt bridge

(−)   (+)

Zn^{2+} Cu^{2+}

Anode   Cathode

Anion movement

Cation movement

The zinc–copper cell. In the cell notation described in this example, we indicate the anode on the left and the cathode on the right. In this drawing of the apparatus, the anode half-cell is also shown on the left, but it could just as easily be shown on the right, as in Figure 19.2. Be sure you understand that where we place the apparatus on the lab bench doesn't affect which half-cell is the anode and which is the cathode.

ARE THE ANSWERS REASONABLE? All of the answers depend on determining which substance is oxidized and which is reduced, so we check that first. Oxidation is electron loss, and Zn must lose electrons to become Zn^{2+}, so zinc is oxidized and must be the anode. If zinc is the anode, then copper must be the cathode. We can then reason that the oxidation of zinc produces electrons that flow from the anode to the cathode.

Practice Exercise 1: Sketch and label a galvanic cell that makes use of the following spontaneous redox reaction.

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

Write the half-reactions for the anode and cathode. Give the standard cell notation. (Hint: Determine which reactant is being oxidized and which is being reduced.)

Practice Exercise 2: Write the anode and cathode half-reactions for the following galvanic cell. Write the equation for the overall cell reaction.

$$Al(s)|Al^{3+}(aq)||Ni^{2+}(aq)|Ni(s)$$
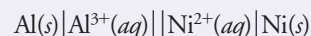
19.2 CELL POTENTIALS CAN BE RELATED TO REDUCTION POTENTIALS

A galvanic cell has an ability to push electrons through the external circuit. The magnitude of this ability is expressed as a **potential.** Potential is expressed in an electrical unit called the **volt (V),** which is a measure of the amount of energy, in joules, that can be delivered per **coulomb, C,** (the SI unit of charge) as the charges move through the circuit. Thus, a charge flowing under a potential of 1 volt can deliver 1 joule of energy per coulomb.

$$1 \text{ V} = 1 \text{ J/C} \tag{19.1}$$

The cell potential is the maximum potential produced by a galvanic cell

The voltage or potential of a galvanic cell varies with the amount of charge flowing through the circuit. The *maximum* potential that a given cell can generate is called its **cell potential,** E_{cell}, and it depends on the composition of the electrodes, the concentrations of the ions in the half-cells, and the temperature. The standard state for electrochemistry is defined as a system where the temperature is 25 °C, all concentrations are 1.00 M, and any gases are at 1.00 atm pressure. When the system is at standard state, the potential of a galvanic cell is the **standard cell potential,** symbolized by $E°_{cell}$.

☐ The potential generated by a galvanic cell has also been called the *electromotive force (emf)*. Modern electrochemistry uses the preferred abbreviations E_{cell} or $E°_{cell}$ to note cell potentials and standard cell potentials, respectively.

☐ If charge flows from a cell, some of the cell's voltage is lost overcoming its own internal resistance, and the measured voltage is less than the original E_{cell}.
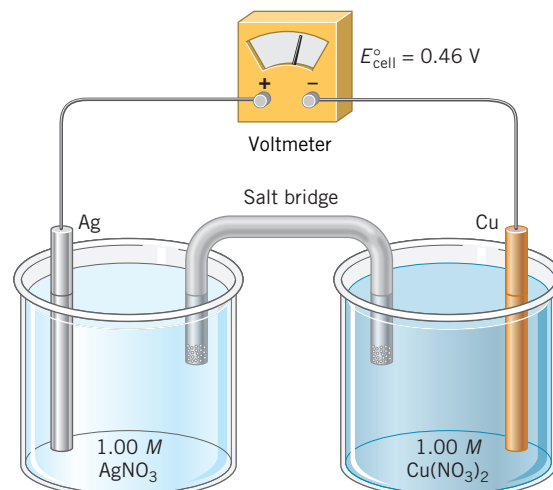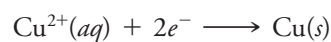
FIG. 19.4 **A cell designed to generate the standard cell potential.** The concentrations of the Cu^{2+} and Ag^+ ions in the half-cells are 1.00 M. It is very important to always connect the negative terminal of the voltmeter to the anode for correct readings.

Cell potentials are rarely larger than a few volts. For example, the standard cell potential for the galvanic cell constructed from silver and copper electrodes shown in Figure 19.4 is only 0.46 V, and one cell in an automobile battery produces only about 2 V. Batteries that generate higher voltages, such as an automobile battery, contain a number of cells arranged in series so that their potentials are additive.

Reduction potentials are a measure of the tendency of reduction half-reactions to occur

It is useful to think of each half-cell as having a certain natural tendency to acquire electrons and proceed as a *reduction*. The magnitude of this tendency is expressed by the half-reaction's **reduction potential.** When measured under standard conditions, namely, 25 °C, concentrations of 1.00 M for all solutes, and a pressure of 1 atm, the reduction potential is called the **standard reduction potential.** To represent a standard reduction potential, we will add a subscript to the symbol $E°$ that identifies the substance undergoing reduction. Thus, the standard reduction potential for the half-reaction

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

is specified as $E°_{Cu^{2+}}$.

> □ Standard reduction potentials are also called *standard electrode potentials*.

When two half-cells are connected to make a galvanic cell, the one with the larger standard reduction potential (the one with the greater tendency to undergo reduction) acquires electrons from the half-cell with the lower standard reduction potential, which is therefore forced to undergo oxidation. The standard cell potential, which is always taken to be a positive number, represents the *difference* between the standard reduction potential of one half-cell and the standard reduction potential of the other. In general, therefore,

TOOLS

Standard reduction potentials are used to calculate $E°_{cell}$

$$E°_{cell} = \left(\begin{array}{c}\text{standard reduction potential}\\\text{of the substance reduced}\end{array}\right) - \left(\begin{array}{c}\text{standard reduction potential}\\\text{of the substance oxidized}\end{array}\right) \quad (19.2)$$
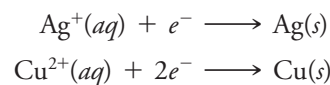
As an example, let's look at the copper–silver cell. From the cell reaction,

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

we can see that silver ions are reduced and copper is oxidized. If we compare the two possible reduction half-reactions,

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

the one for Ag^+ must have a greater tendency to proceed than the one for Cu^{2+}, because it is the silver ion that is actually reduced. This means that the standard reduction potential of Ag^+ must be algebraically larger than the standard reduction potential of Cu^{2+}. In other words, if we knew the values of $E^\circ_{Ag^+}$ and $E^\circ_{Cu^{2+}}$, we could calculate E°_{cell} with Equation 19.2 by subtracting the smaller standard reduction potential (copper) from the larger one (silver).
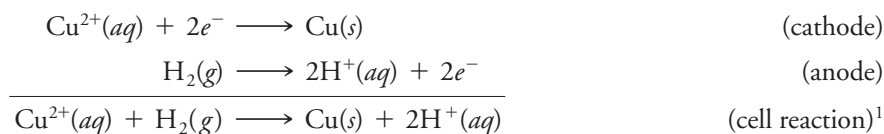
$$E^\circ_{cell} = E^\circ_{Ag^+} - E^\circ_{Cu^{2+}}$$

Assigning standard reduction potentials requires a reference electrode

Unfortunately there is no way to measure the standard reduction potential of an isolated half-cell. All we can measure is the difference in potential produced when two half-cells are connected. Therefore, to assign numerical values for standard reduction potentials, a reference electrode has been arbitrarily chosen and its standard reduction potential has been defined as *exactly* 0 V. This reference electrode is called the **standard hydrogen electrode** (see Figure 19.5). Gaseous hydrogen at a pressure of 1.00 atm is bubbled over a platinum electrode coated with very finely divided platinum, which provides a large catalytic surface area on which the electrode reaction can occur. This electrode is surrounded by a solution whose temperature is 25 °C and in which the hydrogen ion concentration is 1.00 M. The half-cell reaction at the platinum surface, written as a reduction, is

$$2H^+(aq, 1.00\ M) + 2e^- \rightleftharpoons H_2(g, 1.00\ \text{atm}) \qquad E^\circ_{H^+} = 0\ V\ (\text{exactly})$$
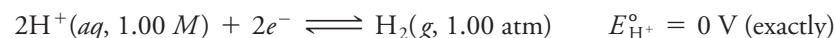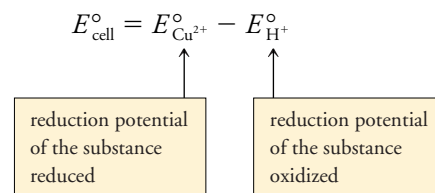
The double arrows indicate only that the reaction is reversible, not that there is true equilibrium. Whether the half-reaction occurs as reduction or oxidation depends on the standard reduction potential of the half-cell with which it is paired.
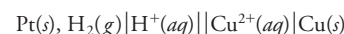
Figure 19.6 illustrates the hydrogen electrode connected to a copper half-cell to form a galvanic cell. When we use a voltmeter to measure the potential of the cell, we find that the copper electrode carries a positive charge and the hydrogen electrode a negative charge. Therefore, copper must be the cathode, and Cu^{2+} is reduced to Cu when the cell operates. Similarly, hydrogen must be the anode, and H_2 is oxidized to H^+. The half-reactions and cell reaction, therefore, are
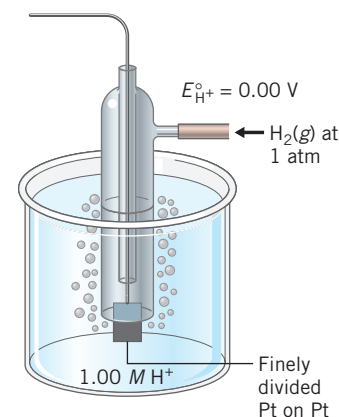
$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \qquad \qquad \text{(cathode)}$$
$$H_2(g) \longrightarrow 2H^+(aq) + 2e^- \qquad \qquad \text{(anode)}$$
$$\overline{Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)} \qquad \text{(cell reaction)[1]}$$

Using Equation 19.2, we can express E°_{cell} in terms of $E^\circ_{Cu^{2+}}$ and $E^\circ_{H^+}$.

$$E^\circ_{cell} = E^\circ_{Cu^{2+}} - E^\circ_{H^+}$$

| reduction potential of the substance reduced | reduction potential of the substance oxidized |

$E^\circ_{H^+} = 0.00$ V

$\longleftarrow H_2(g)$ at 1 atm

1.00 M H^+

Finely divided Pt on Pt

FIG. 19.5 **The hydrogen electrode.** The half-reaction is $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$.

[1]The cell notation for this cell is written as
$$Pt(s), H_2(g)|H^+(aq)||Cu^{2+}(aq)|Cu(s)$$
The notation for the hydrogen electrode (the anode in this case) is shown at the left of the double vertical bars. Although there is a phase boundary between H_2 and Pt, they are shown together to emphasize their simultaneous contact with the solution.

FIG. 19.6 **A galvanic cell composed of copper and hydrogen half-cells.** The cell reaction is
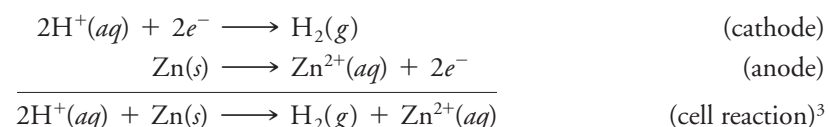$Cu^{2+}(aq) + H_2(g) \longrightarrow$
$\qquad Cu(s) + 2H^+(aq).$
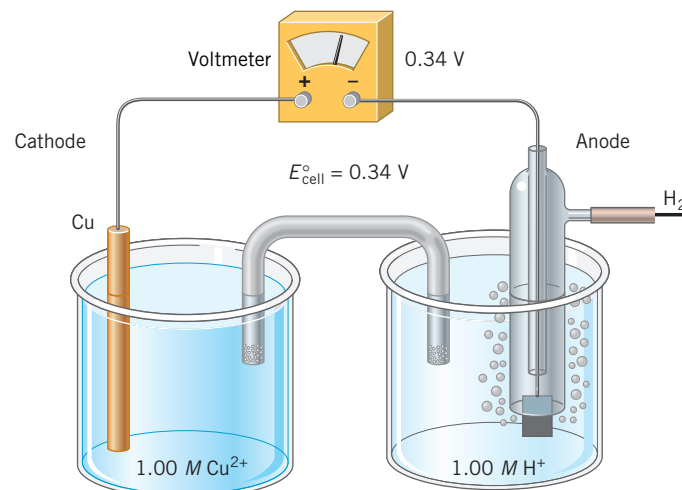
□ In a galvanic cell, the measured cell potential is ***always*** taken to be a positive value. This is important to remember.

The measured standard cell potential is 0.34 V and $E^\circ_{H^+}$ equals 0.00 V.[2] Therefore,

$$0.34 \text{ V} = E^\circ_{Cu^{2+}} - 0.00 \text{ V}$$

Relative to the hydrogen electrode, then, the standard reduction potential of Cu^{2+} is $+0.34$ V. (We have written the value with a plus sign because some standard reduction potentials are negative, as we will see.)

Now let's look at a galvanic cell set up between a zinc electrode and a hydrogen electrode (see Figure 19.7). This time we find that the hydrogen electrode is positive and the zinc electrode is negative, which tells us that the hydrogen electrode is the cathode and the zinc electrode is the anode. This means that hydrogen ion is being reduced and zinc is being oxidized. The half-reactions and cell reaction are therefore

$$2H^+(aq) + 2e^- \longrightarrow H_2(g) \qquad\qquad\qquad \text{(cathode)}$$
$$\underline{\qquad\qquad Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \qquad\qquad\qquad \text{(anode)}}$$
$$2H^+(aq) + Zn(s) \longrightarrow H_2(g) + Zn^{2+}(aq) \qquad\qquad \text{(cell reaction)}[3]$$

FIG. 19.7 **A galvanic cell composed of zinc and hydrogen half-cells.** The cell reaction is
$Zn(s) + 2H^+(aq) \longrightarrow$
$\qquad Zn^{2+}(aq) + H_2(g).$
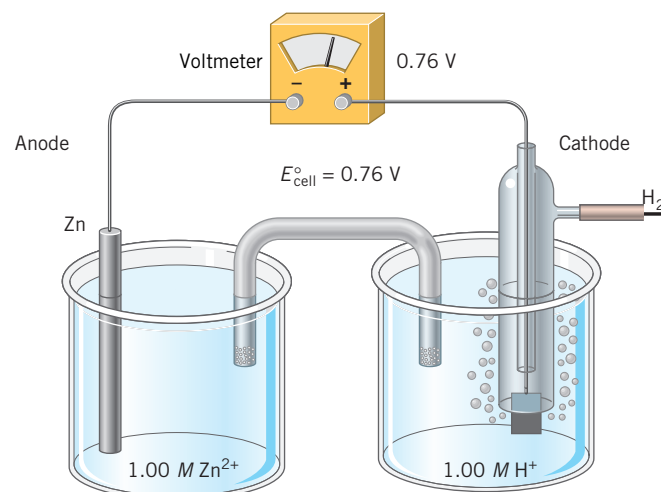
[2] The standard reduction potential for the reduction of hydrogen ions is exactly zero. We will be writing its value in mathematical problems with the number of decimal places required to maintain the precision of the opposing electrode potential. In this case we used two decimal places (0.00) to match the two decimal places of the 0.34 V standard cell potential.

[3] This cell is represented as
$$Zn(s)|Zn^{2+}(aq)||H^+(aq)|H_2(g), Pt(s)$$
This time the hydrogen electrode is the cathode and appears at the right of the double vertical bars.

From Equation 19.2, the standard cell potential is given by

$$E°_{cell} = E°_{H^+} - E°_{Zn^{2+}}$$

Substituting into this the measured standard cell potential of 0.76 V and $E°_{H^+} = 0.00$ V, we have

$$0.76 \text{ V} = 0.00 \text{ V} - E°_{Zn^{2+}}$$

which gives

$$E°_{Zn^{2+}} = -0.76 \text{ V}$$

Notice that the standard reduction potential of zinc is negative. A negative standard reduction potential simply means that the substance is not as easily reduced as H^+. In this case, it tells us that Zn is oxidized when it is paired with the hydrogen electrode.

The standard reduction potentials of many half-reactions can be compared to that for the standard hydrogen electrode in the manner described above. Table 19.1 lists values obtained for some typical half-reactions. They are arranged in decreasing order—the

TABLE 19.1 **Standard Reduction Potentials at 25 °C**

Half-Reaction	$E°$ (volts)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$	+2.01
$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O$	+1.69
$2HOCl(aq) + 2H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O$	+1.63
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O$	+1.51
$PbO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O$	+1.46
$BrO_3^-(aq) + 6H^+(aq) + 6e^- \rightleftharpoons Br^-(aq) + 3H_2O$	+1.44
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.42
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O$	+1.23
$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O$	+0.96
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$NiO_2(s) + 2H_2O + 2e^- \rightleftharpoons Ni(OH)_2(s) + 2OH^-(aq)$	+0.49
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O$	+0.17
$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-(aq)$	+0.07
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0
$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	−0.14
$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \rightleftharpoons Co(s)$	−0.28
$PbSO_4(s) + H^+(aq) + 2e^- \rightleftharpoons Pb(s) + HSO_4^-(aq)$	−0.36
$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	−0.40
$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	−0.44
$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	−0.74
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	−0.76
$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	−0.83
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	−1.66
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	−2.37
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	−2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	−2.76
$K^+(aq) + e^- \rightleftharpoons K(s)$	−2.92
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	−3.05

☐ Substances located to the left of the double arrows are *oxidizing agents*, because they become reduced when the reactions proceed in the forward direction. The best oxidizing agents are those most easily reduced, and they are located at the top of the table (e.g., F_2).

☐ Substances located to the right of the double arrows are *reducing agents*; they become oxidized when the reactions proceed from right to left. The best reducing agents are those found at the bottom of the table (e.g., Li).

half-reactions at the top have the greatest tendency to occur as reduction, while those at the bottom have the least tendency to occur as reduction.

EXAMPLE 19.2

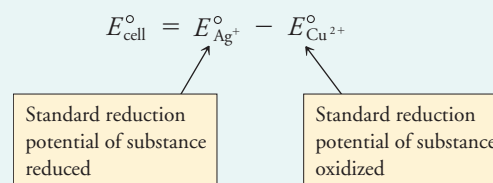**Calculating Standard Cell Potentials**

We mentioned earlier that the standard cell potential of the silver–copper galvanic cell has a value of $+0.46$ V. The cell reaction is

$$2Ag^+(aq) + Cu(s) \longrightarrow 2Ag(s) + Cu^{2+}(aq)$$
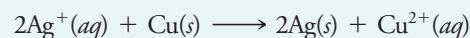
and we have seen that the standard reduction potential of Cu^{2+}, $E^\circ_{Cu^{2+}}$, is $+0.34$ V. What is the value of $E^\circ_{Ag^+}$, the standard reduction potential of Ag^+?

ANALYSIS: Since we know the standard potential of the cell and one of the two standard reduction potentials, Equation 19.2 will be our tool to calculate the unknown standard reduction potential. This requires that we identify the substance oxidized and the substance reduced. We can do this by dividing the cell reaction into half-reactions, or we can observe how the oxidation numbers of the reactants change. Recall that if the oxidation number increases algebraically, the substance undergoes oxidation, whereas if the oxidation number decreases, the substance is reduced.

SOLUTION: Silver changes from Ag^+ to Ag; its oxidation number decreases from $+1$ to 0, so Ag^+ is reduced. Similar reasoning tells us that copper is oxidized from Cu to Cu^{2+}. Therefore, according to Equation 19.2,

$$E^\circ_{cell} = E^\circ_{Ag^+} - E^\circ_{Cu^{2+}}$$

Standard reduction potential of substance reduced	Standard reduction potential of substance oxidized

Substituting values for E°_{cell} and $E^\circ_{Cu^{2+}}$,

$$0.46 \text{ V} = E^\circ_{Ag^+} - 0.34 \text{ V}$$

Then we solve for $E^\circ_{Ag^+}$.

$$E^\circ_{Ag^+} = 0.46 \text{ V} + 0.34 \text{ V}$$
$$= 0.80 \text{ V}$$

The standard reduction potential of silver ion is therefore $+0.80$ V.

IS THE ANSWER REASONABLE? We know the standard cell potential is the difference between the two standard reduction potentials. The difference between $+0.80$ V and $+0.34$ V (subtracting the smaller from the larger) is 0.46 V. Our calculated standard reduction potential for Ag^+ appears to be correct. You can also take a peek at Table 19.1 now for a final check.

Practice Exercise 3: Copper metal and zinc metal will both reduce Ag^+ ions under standard state conditions. Which metal, when used as an electrode in a galvanic cell, will have the larger E°_{cell} under these conditions? (Hint: Write the two possible chemical reactions.)

Practice Exercise 4: The galvanic cell described in Practice Exercise 1 has a standard cell potential of 1.93 V. The standard reduction potential of Mg^{2+} corresponding to the half-reaction $Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$ is -2.37 V. Calculate the standard reduction potential of iron(II). Check your answer by referring to Table 19.1.

FACETS OF CHEMISTRY

19.1

### Corrosion of Iron and Cathodic Protection

A problem that has plagued humanity ever since the discovery of methods for obtaining iron and other metals from their ores has been corrosion—the reaction of a metal with substances in the environment. The rusting of iron in particular is a serious problem because iron and steel have so many uses.

The rusting of iron is a complex chemical reaction that involves both oxygen and moisture (see Figure 1). Iron won't rust in pure water that's oxygen free, and it won't rust in pure oxygen in the absence of moisture. The corrosion process is apparently electrochemical in nature, as shown in the accompanying diagram. At one place on the surface, iron becomes oxidized in the presence of water and enters solution as Fe^{2+}.

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$$
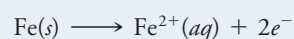
At this location the iron is acting as an anode.

The electrons that are released when the iron is oxidized travel through the metal to some other place where the iron is exposed to oxygen. This is where reduction takes place (it's a cathodic region on the metal surface), and oxygen is reduced to give hydroxide ion.

$$\tfrac{1}{2}O_2(aq) + H_2O + 2e^- \longrightarrow 2OH^-(aq)$$
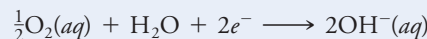
The iron(II) ions that are formed at the anodic regions gradually diffuse through the water and eventually contact the hydroxide ions. This causes a precipitate of $Fe(OH)_2$ to form, which is very easily oxidized by O_2 to give $Fe(OH)_3$. This hydroxide readily loses water. In fact, complete dehydration gives the oxide,

$$2Fe(OH)_3 \longrightarrow Fe_2O_3 + 3H_2O$$

When partial dehydration of the $Fe(OH)_3$ occurs, *rust* is formed. It has a composition that lies between that of the hydroxide and that of the oxide, Fe_2O_3, and is usually referred to as a *hydrated oxide*. Its formula is generally represented as $Fe_2O_3 \cdot xH_2O$.
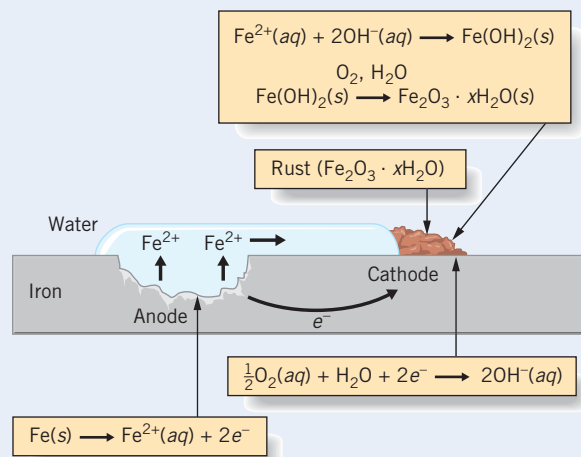
This mechanism for the rusting of iron explains one of the more interesting aspects of this damaging process. Perhaps you've noticed that when rusting occurs on the body of a car, the rust appears at and around a break (or a scratch) in the surface of the paint, but the damage extends under the painted surface for some distance. Apparently, the Fe^{2+} ions that are formed at the anode sites are able to diffuse rather long distances to the hole in the paint, where they finally react with air to form the rust.

Cathodic Protection

One way to prevent the rusting of iron is to coat it with another metal. This is done with "tin" cans, which are actually steel cans that have been coated with a thin layer of tin. However, if the layer of tin is scratched and the iron beneath is exposed, the corrosion is accelerated because iron has a lower reduction potential than tin; the iron becomes the anode in an electrochemical cell and is easily oxidized.

Another way to prevent corrosion is called *cathodic protection*. It involves placing the iron in contact with a metal that is *more easily* oxidized. This causes iron to be a cathode and the other metal to be the anode. If corrosion occurs, iron is protected from oxidation because it is cathodic and the other metal reacts instead.

Zinc is most often used to provide cathodic protection to other metals. For example, zinc sacrificial anodes can be attached to the rudder of a boat (see Figure 2). When the rudder is submerged, the zinc will gradually corrode but the metal of the rudder will not. Periodically, the anodes are replaced to provide continued protection.

Steel objects that must withstand the weather are often coated with a layer of zinc, a process called galvanizing. You've seen this on chain-link fences and metal garbage pails. Even if the steel is exposed through a scratch, it is prevented from being oxidized because it is in contact with a metal that is more easily oxidized.

FIG. 1 **Corrosion of iron.** Iron dissolves in anodic regions to give Fe^{2+}. Electrons travel through the metal to cathodic sites where oxygen is reduced, forming OH^-. The combination of the Fe^{2+} and OH^-, followed by air oxidation, gives rust.
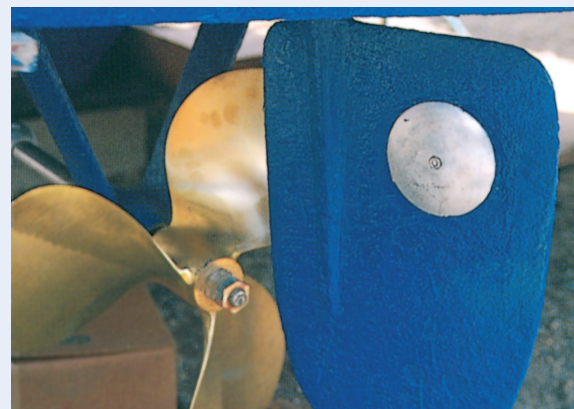
FIG. 2 **Cathodic protection.** Before launching, a shiny new zinc anode disk is attached to the bronze rudder of this boat to provide cathodic protection. Over time, the zinc will corrode instead of the less reactive bronze. (The rudder is painted with a special blue paint to inhibit the growth of barnacles.) *(Courtesy James Brady.)*

At this point you may have wondered why the term *cell potential* is used in some places, and *standard cell potential* is used in others. Based on our definitions, the term standard cell potential is used in places where the system is at standard state (i.e., 1.00 *M* concentrations, 1.00 atm pressures, and 25.0 °C). Cell potential is used for *any* set of concentrations, pressures, and temperatures, including the standard conditions. For convenience, our calculations in the next two sections will use standard cell potentials.

19.3 | STANDARD REDUCTION POTENTIALS CAN PREDICT SPONTANEOUS REACTIONS

Redox reactions can be predicted by comparing reduction potentials

It's easy to predict the spontaneous reaction between the substances in two half-reactions, at standard state, because we know that *the half-reaction with the more positive reduction potential always takes place as written (namely, as a reduction), while the other half-reaction is forced to run in reverse (as an oxidation).*

EXAMPLE 19.3
Predicting a Spontaneous Reaction

What spontaneous reaction occurs if Cl_2 and Br_2 are added to a solution that contains both Cl^- and Br^-? Assume that the cell is at standard state.

ANALYSIS: We know that in the spontaneous redox reaction, the more easily reduced substance will be the one that undergoes reduction. By assuming we are at standard state we can use the standard reduction potentials for Cl_2 and Br_2 to compare their $E°$ values and determine which is the more easily reduced, and then we will use that information to write the correct "cell reaction." This is the spontaneous reaction, *whether or not it occurs in a galvanic cell.*

SOLUTION: There are two possible reduction half-reactions.

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$$
$$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$$
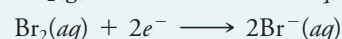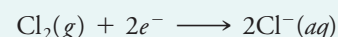
Referring to Table 19.1, we find that Cl_2 has a more positive standard reduction potential (+1.36 V) than does Br_2 (+1.07 V). This means Cl_2 will be reduced and the half-reaction for Br_2 will be reversed, changing to an oxidation. Therefore, the spontaneous reaction has the following half-reactions.

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq) \qquad \text{(a reduction)}$$
$$2Br^-(aq) \longrightarrow Br_2(aq) + 2e^- \qquad \text{(an oxidation)}$$
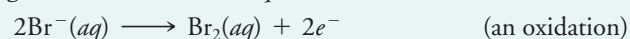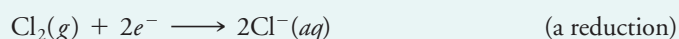
The net reaction is obtained by combining the half-reactions.

$$Cl_2(g) + 2Br^-(aq) \longrightarrow Br_2(aq) + 2Cl^-(aq)$$

□ Strictly speaking, the $E°$ values only tell us what to expect under standard conditions. However, only when $E°_{cell}$ is small can changes in the concentrations change the direction of the spontaneous reaction.
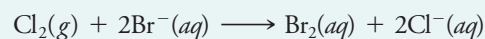
IS THE ANSWER REASONABLE? We can check to be sure we've read the correct values for $E°_{Cl_2}$ and $E°_{Br_2}$ from Table 19.1, and we can check the half-reactions we used to find the equation for the net reaction. (Experimentally, chlorine does indeed oxidize bromide ion to bromine, a fact used to recover bromine from seawater and natural brine solutions.)

When our cell is at standard state, reactants and products of *spontaneous* redox reactions are easy to spot when standard reduction potentials are listed in order of most positive to least positive (most negative), as in Table 19.1. For *any* pair of half-reactions, the one higher up in the table has the more positive standard reduction potential and occurs as a reduction. The other half-reaction is reversed and occurs as an oxidation. *Therefore, for a spontaneous reaction, the **reactants** are found on the left side of the higher half-reaction and on the right side of the lower half-reaction. (This is usually, but not always, true of systems that are not at standard state.)*

Predict the reaction that will occur, at 25 °C, when Ni and Fe are added to a solution that is 1.00 M in both Ni^{2+} and Fe^{2+}.

ANALYSIS: This system is at standard state and we can use the standard reduction potentials to predict the reaction. The first question we would ask is, "What *possible* reactions could occur?" We have a situation involving possible changes of ions to atoms or of atoms to ions. In other words, the system involves a possible redox reaction, and you've seen we can predict these using data in Table 19.1. One way to do this is to note the relative positions of the half-reactions when arranged as they are in Table 19.1.

$$\boxed{Ni^{2+}(aq)} + 2e^- \rightleftharpoons Ni(s) \qquad E^\circ_{Ni^{2+}} = -0.25$$

$$Fe^{2+}(aq) + 2e^- \rightleftharpoons \boxed{Fe(s)} \qquad E^\circ_{Fe^{2+}} = -0.44$$
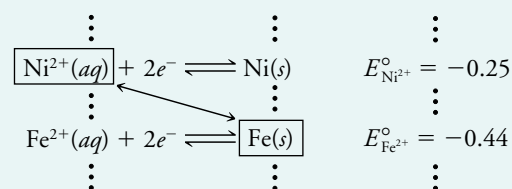
In the table, the half-reaction higher up has the more positive (in this case, less negative) standard reduction potential, and will occur as a reduction. As a result, the reactants in the spontaneous reaction are related by the diagonal line that slants from upper left to lower right, as illustrated above. In other words, Ni^{2+} will react with Fe. The products are the substances on the opposite sides of the half-reaction, Ni and Fe^{2+}.

SOLUTION: We've done nearly all the work in our analysis of the problem. All that's left is to write the equation. The reactants are Ni^{2+} and Fe; the products are Ni and Fe^{2+}.

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

The equation is balanced in terms of both atoms and charges, so this is the reaction that will occur in the system specified in the problem.

IS THE ANSWER REASONABLE? Notice that we've predicted the reaction very easily using just the *positions* of the half-reactions relative to each other in the table; we really didn't have to use the values of their standard reduction potentials. We could check ourselves by proceeding as in Example 19.3. In the table, we see that Ni^{2+} has a more positive (less negative) standard reduction potential than Fe^{2+}, so Ni^{2+} is reduced and its half-cell reaction is written just as in Table 19.1. The half-cell reaction for Fe^{2+} in Table 19.1, however, must be reversed; it is Fe that will be oxidized.

$$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s) \qquad \text{(reduction)}$$
$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^- \qquad \text{(oxidation)}$$
$$\overline{Ni^{2+}(aq) + Fe(s) \longrightarrow Ni(s) + Fe^{2+}(aq)} \qquad \text{(net reaction)}$$
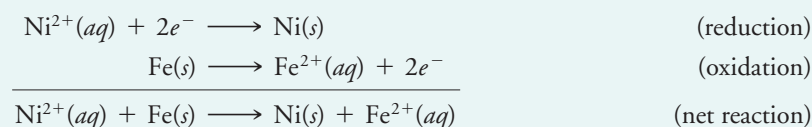
Practice Exercise 5: Based only on the half-reactions in Table 19.1, determine what reaction will occur in each of the following mixtures, at standard state. (a) I_2, I^- and Fe^{2+}, Fe^{3+}, (b) Mg, Mg^{2+} and Cr, Cr^{3+}, (c) Co, Co^{2+} and H_2SO_3, SO_4^{2-}. (Hint: Use Table 19.1 to write the possible half-reactions and, if necessary, determine E°_{cell}.)

Practice Exercise 6: Use the positions of the half-reactions in Table 19.1 to predict the spontaneous reaction when Br^-, SO_4^{2-}, H_2SO_3, and Br_2 are mixed in an acidic solution at standard state.

Practice Exercise 7: From the positions of the respective half-reactions in Table 19.1, predict whether the following reaction will occur if all the ions are 1.0 M at 25 °C. If it is not, write the equation for the spontaneous reaction.

$$Ni^{2+}(aq) + 2Fe^{2+}(aq) \longrightarrow Ni(s) + 2Fe^{3+}(aq)$$
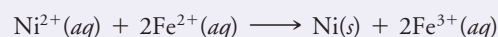
Standard reduction potentials predict the cell reaction and standard cell potential of a galvanic cell

We've just seen that we can use standard reduction potentials to predict spontaneous redox reactions. If we intend to use these reactions in a galvanic cell, we can also predict what the standard cell potential will be, as illustrated in the next example.

EXAMPLE 19.5

Predicting the Cell Reaction and Standard Cell Potential of a Galvanic Cell

A typical cell of a lead storage battery of the type used to start automobiles is constructed using electrodes made of lead and lead(IV) oxide (PbO_2) and with sulfuric acid as the electrolyte. The half-reactions and their standard reduction potentials in this system are

$$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O$$

$$E^\circ_{PbO_2} = 1.69 \text{ V}$$

$$PbSO_4(s) + H^+(aq) + 2e^- \rightleftharpoons Pb(s) + HSO_4^-(aq)$$

$$E^\circ_{PbSO_4} = -0.36 \text{ V}$$

What is the cell reaction and what is the standard potential of the cell?

ANALYSIS: Our method for predicting spontaneous reactions specifies that the system should be at standard state. Although a battery is not at standard state, we will assume standard state to make the calculations easier. In the spontaneous cell reaction, the half-reaction with th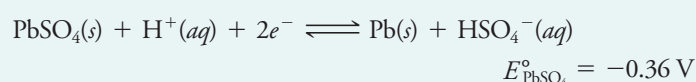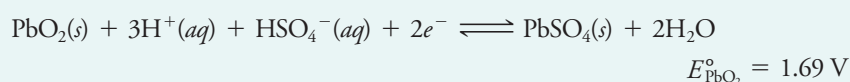e larger (more positive) standard reduction potential will take place as reduction while the other half-reaction will be reversed and occur as oxidation. The standard cell potential is simply the difference between the two standard reduction potentials, calculated using Equation 19.2.

□ Remember that half-reactions are combined following the same procedure used in the ion–electron method of balancing redox reactions (Section 5.2).

SOLUTION: PbO_2 has a larger, more positive standard reduction potential than $PbSO_4$, so the first half-reaction will occur in the direction written. The second must be reversed to occur as an oxidation. In the cell, therefore, the half-reactions are

$$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O$$
$$Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2e^-$$
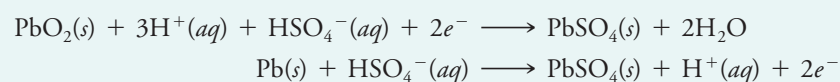
Adding the two half-reactions and canceling electrons gives the cell reaction,

$$PbO_2(s) + Pb(s) + 2H^+(aq) + 2HSO_4^-(aq) \longrightarrow 2PbSO_4(s) + 2H_2O$$

The cell standard potential is obtained by using Equation 19.2.

$$E^\circ_{cell} = (E^\circ \text{ of substance reduced}) - (E^\circ \text{ of substance oxidized})$$

Since the first half-reaction occurs as a reduction and the second as an oxidation,

$$E^\circ_{cell} = E^\circ_{PbO_2} - E^\circ_{PbSO_4}$$
$$= (1.69 \text{ V}) - (-0.36 \text{ V})$$
$$= 2.05 \text{ V}$$

ARE THE ANSWERS REASONABLE? The half-reactions involved in the problem are located in Table 19.1, and their relative positions tell us that PbO_2 will be reduced and that lead will be oxidized. Therefore, we've combined the half-reactions correctly and we can feel confident that we've also applied Equation 19.2 correctly. In addition, the standard cell potential of 2.05 volts tells us that small differences from standard state will still allow us to come to the same conclusion.

At standard state, what would be the cell reaction and the standard cell potential of a galvanic cell employing the following half-reactions?

$$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s) \qquad E^°_{Al^{3+}} = -1.66\ V$$
$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^°_{Cu^{2+}} = +0.34\ V$$

Which half-cell would be the anode?

ANALYSIS: This problem is very similar to the preceding one, so we expect to proceed in essentially the same way.

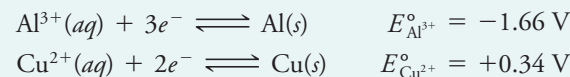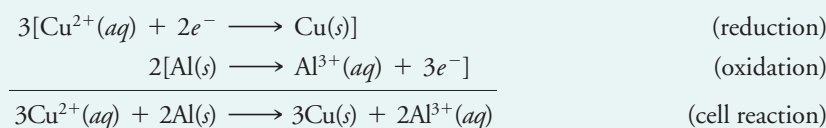**SOLUTION:** Our method for predicting spontaneous reactions indicates that the half-reaction with the more positive standard reduction potential will occur as a reduction; the other will occur as an oxidation. In this cell, then, Cu^{2+} is reduced and Al is oxidized. To obtain the cell reaction, we add the two half-reactions, remembering that the electrons must cancel. This means we must multiply the copper half-reaction by three and the aluminum half-reaction by two.

$$3[Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)] \qquad \text{(reduction)}$$
$$\underline{2[Al(s) \longrightarrow Al^{3+}(aq) + 3e^-]} \qquad \text{(oxidation)}$$
$$3Cu^{2+}(aq) + 2Al(s) \longrightarrow 3Cu(s) + 2Al^{3+}(aq) \qquad \text{(cell reaction)}$$

The anode in the cell is aluminum because that is where oxidation takes place (by definition). To obtain the standard cell potential, we substitute into Equation 19.2.

$$\begin{aligned} E^°_{cell} &= E^°_{Cu^{2+}} - E^°_{Al^{3+}} \\ &= (0.34\ V) - (-1.66\ V) \\ &= 2.00\ V \end{aligned}$$

An important point to notice here is that *although we multiply the half-reactions by factors to make the electrons cancel, **we do not multiply the standard reduction potentials by these factors.***[4] To obtain the standard cell potential, we simply subtract one standard reduction potential from the other.

ARE THE ANSWERS REASONABLE? If we locate the half-reactions in Table 19.1, their relative positions tell us we've written the correct equation for the spontaneous reaction. It also means we've identified correctly the substances reduced and oxidized, so we've correctly applied Equation 19.2.

Practice Exercise 8: What are the overall cell reaction and the standard cell potential of a galvanic cell employing the following half-reactions?

$$NiO_2(s) + 2H_2O + 2e^- \rightleftharpoons Ni(OH)_2(s) + 2OH^-(aq) \qquad E^°_{NiO_2} = 0.49\ V$$
$$Fe(OH)_2(s) + 2e^- \rightleftharpoons Fe(s) + 2OH^-(aq) \qquad E^°_{Fe(OH)_2} = -0.88\ V$$
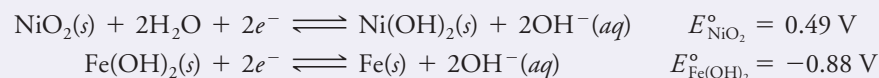
(Hint: Recall that standard cell potentials are based on a spontaneous reaction.)

☐ These are the reactions in an Edison cell, a type of rechargeable storage battery.

Practice Exercise 9: The four substances in the following two half-reactions are placed in the same beaker, at standard state. Write the balanced equation for the spontaneous reaction and determine the standard cell potential if the two reactions are used in a galvanic cell.

$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^°_{Cu^{2+}} = +0.34\ V$$
$$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s) \qquad E^°_{Cr^{3+}} = -0.74\ V$$

---

[4] Reduction potentials are intensive quantities; they have the units volts, which are joules *per coulomb*. The same number of joules are available for each coulomb of charge regardless of the total number of electrons shown in the equation. Therefore, reduction potentials are never multiplied by factors before they are subtracted to give the cell potential.

Practice Exercise 10: What are the overall cell reaction and the standard cell potential of a galvanic cell employing the following half-reactions at standard state?

$$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s) \qquad\qquad E°_{Cr^{3+}} = -0.74 \text{ V}$$
$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O \qquad E°_{MnO_4^-} = +1.51 \text{ V}$$
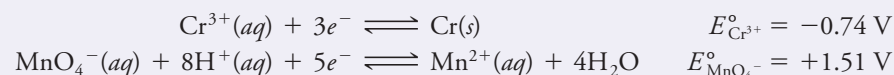
The calculated cell potential can tell us whether a reaction is spontaneous

Because we can predict the spontaneous redox reaction that will take place among a mixture of reactants, it also should be possible to predict whether or not a particular reaction, *as written*, can occur spontaneously. We can do this by calculating the standard cell potential that corresponds to the reaction in question and seeing if the standard potential is *positive*.

TOOLS

$E°_{cell}$ *and spontaneous reactions*
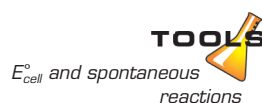
In a galvanic cell, the calculated standard cell potential for the spontaneous reaction is always positive. If the calculated standard cell potential is negative, the reaction is spontaneous in the reverse direction.

☐ These generalizations apply under standard conditions: 1 *M* concentrations of all ions, 1 atm pressure for gases, and 25 °C.

For example, to obtain the standard cell potential for a spontaneous reaction in our previous examples, we subtracted the standard reduction potentials in a way that gave a positive answer. Therefore, if we compute the standard cell potential for a particular reaction *based on the way the equation is written* and the standard potential comes out positive, we know the reaction is spontaneous. If the calculated standard cell potential comes out negative, however, the reaction is nonspontaneous. In fact, it is really spontaneous in the opposite direction.

E X A M P L E   1 9 . 7

Determining whether a Reaction Is Spontaneous by Using the Calculated Standard Cell Potential

Determine whether the following reactions, at standard state, are spontaneous as written. If a reaction is not spontaneous, write the equation for the reaction that is.

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

(2) $3Cu(s) + 2NO_3^-(aq) + 8H^+(aq) \longrightarrow 3Cu^{2+}(aq) + 2NO(g) + 4H_2O$
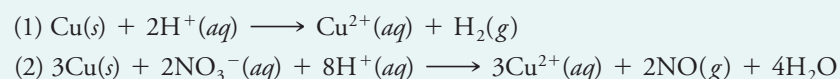
**ANALYSIS:** Our goal for each reaction will be to calculate the standard cell potential based on the reaction as written. Our tool for spontaneous reactions states that if $E°_{cell}$ is positive, then the reaction is spontaneous. However, if $E°_{cell}$ is negative, then the reaction is not spontaneous as written and reversing the equation will give the spontaneous reaction.

To calculate $E°_{cell}$, we need to divide the equation into its half-reactions, find the necessary standard reduction potentials in Table 19.1, and then use Equation 19.2 to calculate $E°_{cell}$. The signs of $E°_{cell}$ will then tell us whether the reactions are spontaneous under standard conditions.

SOLUTION: (1) The half-reactions involved in this reaction are

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^- \qquad\qquad \text{(oxidation)}$$
$$2H^+(aq) + 2e^- \longrightarrow H_2(g) \qquad\qquad \text{(reduction)}$$
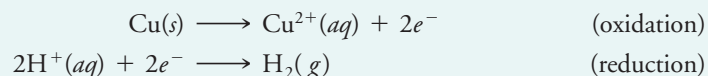
The H^+ is reduced and Cu is oxidized, so Equation 19.2 will take the form

$$E°_{cell} = E°_{H^+} - E°_{Cu^{2+}}$$

Standard reduction potential of substance reduced

Standard reduction potential of substance oxidized

Substituting values from Table 19.1 gives

$$E_{cell}^{\circ} = (0.00 \text{ V}) - (0.34 \text{ V})$$
$$= -0.34 \text{ V}$$

The calculated standard cell potential is negative, so reaction (1) is not spontaneous in the forward direction. The spontaneous reaction is actually the reverse of (1).

$$Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$$
Reaction (1) reversed
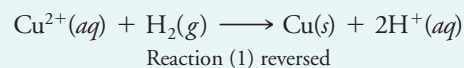
(2) The half-reactions involved in this equation are

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$$
$$NO_3^-(aq) + 4H^+(aq) + 3e^- \longrightarrow NO(g) + 2H_2O$$
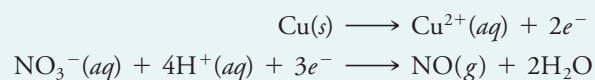
The Cu is oxidized while the NO_3^- is reduced. According to Equation 19.2,

$$E_{cell}^{\circ} = E_{NO_3^-}^{\circ} - E_{Cu^{2+}}^{\circ}$$

Substituting values from Table 19.1 gives

$$E_{cell}^{\circ} = (0.96 \text{ V}) - (0.34 \text{ V})$$
$$= +0.62 \text{ V}$$

Because the calculated standard cell potential is positive, reaction 2 is spontaneous in the forward direction, as written.

□ Copper dissolves in HNO_3 because it contains the oxidizing agent NO_3^-.

ARE THE ANSWERS REASONABLE? By noting the relative positions of the half-reactions in Table 19.1, you can confirm that we've answered the questions correctly.

Practice Exercise 11: Determine if each of the following reactions, under standard state conditions, is spontaneous.

(a) $Br_2(aq) + 2I^-(aq) \longrightarrow 2Br^-(aq) + I_2(s)$
(b) $MnO_4^-(aq) + 5Ag(aq) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 5Ag^+(s) + 4H_2O$

(Hint: Determine the sign of the calculated standard cell potential.)

Practice Exercise 12: Under standard state conditions, which of the following reactions occur spontaneously?

(a) $Br_2(aq) + Cl_2(g) + 2H_2O \longrightarrow 2Br^-(aq) + 2HOCl(aq) + 2H^+(aq)$
(b) $3Zn(s) + 2Cr^{3+}(aq) \longrightarrow 3Zn^{2+}(aq) + 2Cr(s)$

In the previous examples and exercises we have been rigorous in specifying that standard reduction potentials are used when the system is at standard state. If the cell is not at standard state, the cell potential will not be the same as the standard cell potential, but in the majority of cases, the algebraic sign of the calculated cell potential will be the same and we can reach the same conclusions.

19.4 CELL POTENTIALS ARE RELATED TO FREE ENERGY CHANGES

The fact that cell potentials allow us to predict the spontaneity of redox reactions is no coincidence. There is a relationship between the cell potential and the free energy change for a reaction. In Chapter 18 we saw that ΔG for a reaction is a measure of the maximum useful work that can be obtained from a chemical reaction. Specifically, the relationship is

$$-\Delta G = \text{maximum work} \qquad (19.3)$$

In an electrical system, work is supplied by the flow of electric charge created by the potential of the cell. It can be calculated from the equation

$$\text{Maximum work} = n\mathscr{F}E_{\text{cell}} \qquad (19.4)$$

TOOLS
Faraday constant

where n is the number of moles of electrons transferred, $\mathscr{F}$ is a constant called the **Faraday constant** which is equal to the number of coulombs of charge equivalent to 1 mol of electrons (9.65×10^4 coulombs per mole of electrons), and E_{cell} is the potential of the cell in volts. To see that Equation 19.4 gives work (which has the units of energy) we can analyze the units. In Equation 19.1 you saw that 1 volt = 1 joule/coulomb. Therefore,

☐ More precisely, one **Faraday** ($\mathscr{F}$) = 96,485 C.

$$\text{Maximum work} = \overline{\text{mole } e^-} \times \left(\frac{\cancel{\text{coulombs}}}{\cancel{\text{mole } e^-}}\right) \times \left(\frac{\text{joule}}{\cancel{\text{coulombs}}}\right) = \text{joule}$$

$$\begin{matrix} \updownarrow & & \updownarrow & & \updownarrow \\ n & & \mathscr{F} & & E_{\text{cell}} \end{matrix}$$

Combining Equations 19.3 and 19.4 gives us

$$\Delta G = -n\mathscr{F}E_{\text{cell}} \qquad (19.5)$$

At standard state we are dealing with the *standard* cell potential, so we can calculate the *standard* free energy change.

TOOLS
Standard free energy change is related to the standard cell potential
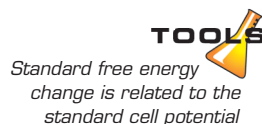
$$\Delta G° = -n\mathscr{F}E°_{\text{cell}} \qquad (19.6)$$

Referring back to Chapter 18, if ΔG has a negative value, a reaction will be spontaneous and this corresponds to a positive value of E_{cell}. Up to now we have been careful to predict spontaneity for standard state systems where $E°_{\text{cell}}$ is equal to E_{cell}. In Example 19.11 below we will see how to calculate E_{cell} and precisely predict if a reaction is spontaneous.

EXAMPLE 19.8
Calculating the Standard Free Energy Change

Calculate $\Delta G°$ for the following reaction, given that its standard cell potential is 0.320 V at 25 °C.

$$\text{NiO}_2(s) + 2\text{Cl}^-(aq) + 4\text{H}^+(aq) \longrightarrow \text{Cl}_2(g) + \text{Ni}^{2+}(aq) + 2\text{H}_2\text{O}$$
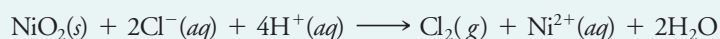
ANALYSIS: Our tool for solving this problem is Equation 19.6. Taking the coefficients in the equation to stand for *moles*, two moles of Cl^- are oxidized to Cl_2 and two moles of electrons are transferred to the NiO_2 ($n = 2 \text{ mol } e^-$). We will also use the faraday constant, $1 \mathscr{F} = 96,500 \text{ C/mol } e^-$ (recall that the SI abbreviation for coulomb is C).

$$1 \mathscr{F} = \frac{96,500 \text{ C}}{1 \text{ mol } e^-}$$

SOLUTION: Using Equation 19.6, we have

$$\Delta G° = -(2 \text{ } \cancel{\text{mol } e^-}) \times \left(\frac{9.65 \times 10^4 \text{ } \cancel{\text{C}}}{1 \text{ } \cancel{\text{mol } e^-}}\right) \times \left(\frac{0.320 \text{ J}}{\cancel{\text{C}}}\right)$$

$$= -6.18 \times 10^4 \text{ J}$$

$$= -61.8 \text{ kJ}$$

IS THE ANSWER REASONABLE? Let's do some approximate arithmetic. The faraday constant equals approximately 100,000, or 10^5. The product $2 \times 0.32 = 0.64$, so $\Delta G°$ should be about 0.64×10^5 or 6.4×10^4 J. The answer seems to be okay.

Practice Exercise 13: A certain reaction has an $E°_{cell}$ of 0.107 volts and has a $\Delta G°$ of -30.9 kJ. How many electrons are transferred in the reaction? (Hint: See Equation 19.6.)

Practice Exercise 14: Calculate $\Delta G°$ for the reactions that take place in the galvanic cells described in Practice Exercises 11 and 12.

Equilibrium constants can be calculated from $E°_{cell}$

One useful application of electrochemistry is the determination of equilibrium constants. In Chapter 18 you saw that $\Delta G°$ is related to the equilibrium constant by the expression

$$\Delta G° = -RT \ln K_c$$

where we have used K_c for the equilibrium constant because electrochemical reactions occur in solution. We've seen in this chapter that $\Delta G°$ is also related to $E°_{cell}$

$$\Delta G° = -n\mathcal{F}E°_{cell}$$

Therefore, $E°_{cell}$ and the equilibrium constant are also related. Equating the right sides of the two equations, we have

$$-n\mathcal{F}E°_{cell} = -RT \ln K_c$$

Solving for $E°_{cell}$ gives[5]

$$E°_{cell} = \frac{RT}{n\mathcal{F}} \ln K_c \qquad (19.7)$$

TOOLS

Equilibrium constants are related to standard cell potentials

For the units to work out correctly, the value of R must be 8.314 J mol^{-1} K^{-1}, T must be the temperature in kelvins, $\mathcal{F}$ equals 9.65×10^4 C per mole of e^-, and n equals the number of moles of electrons transferred in the reaction.

EXAMPLE 19.9
Calculating Equilibrium Constants from $E°_{cell}$

Calculate K_c for the reaction in Example 19.8.

ANALYSIS: Equation 19.7 is our tool for solving this problem. We need to collect the terms to insert in this equation to solve it. We need to find $E°_{cell}$, n, R, T, and $\mathcal{F}$. Remember that T is in kelvins and R must have the appropriate units of J mol^{-1} K^{-1}.

SOLUTION: The reaction in Example 19.8 has $E°_{cell} = 0.320$ V and $n = 2$. The temperature is 25 °C or 298 K. Let's solve Equation 19.7 for $\ln K_c$ and then substitute values.

$$\ln K_c = \frac{E°_{cell}\, n\mathcal{F}}{RT}$$

Substituting values and using the relationship that $1\ \text{V} = 1\ \text{J C}^{-1}$,

$$\ln K_c = \frac{0.320\ \cancel{J}\ \cancel{C^{-1}} \times 2 \times 9.65 \times 10^4\ \cancel{C}\ \cancel{mol^{-1}}}{8.314\ \cancel{J}\ \cancel{mol^{-1}}\ \cancel{K^{-1}} \times 298\ \cancel{K}}$$

$$= 24.9$$

Taking the antilogarithm,

$$K_c = e^{24.9} = 7 \times 10^{10}$$

---

[5] For historical reasons, Equation 19.7 is sometimes expressed in terms of common logs (base 10 logarithms). Natural and common logarithms are related by the equation

$$\ln x = 2.303 \log x$$

For reactions at 25 °C (298 K), all of the constants (R, T, and $\mathcal{F}$) can be combined with the factor 2.303 to give 0.0592 joules/coulomb. Because joules/coulomb equals volts, Equation 19.7 reduces to

$$E°_{cell} = \frac{0.0592\ \text{V}}{n} \log K_c$$

where n is the number of moles of electrons transferred in the cell reaction as it is written.

IS THE ANSWER REASONABLE? As a rough check, we can look at the magnitude of E_{cell}° and apply some simple reasoning. When E_{cell}° is positive, ΔG° is negative, and in Chapter 18 you learned that when ΔG° is negative, the reaction proceeds far toward completion when equilibrium is reached. Therefore, we expect that K_c will be large, and that agrees with our answer.

A more complete check would require evaluating the fraction used to compute $\ln K_c$. First, we should check to be sure we've substituted correctly into the equation for $\ln K_c$. Next, we could do some approximate arithmetic to check the value of $\ln K_c$. Rounding all numbers to one significant figure we get

$$\ln K_c = \frac{0.3 \text{ J C}^{-1} \times 2 \times 10 \times 10^4 \text{ C mol}^{-1}}{10 \text{ J mol}^{-1}\text{K}^{-1} \times 300 \text{ K}} = \frac{6 \times 10^4}{3000} = 2 \times 10^1 = 20$$

This is close to the 24.9 we calculated above and we are confident the calculation was done correctly.

Practice Exercise 15: The calculated standard cell potential for the reaction

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

is $E_{cell}^{\circ} = -0.46$ V. Calculate K_c for the reaction as written. Is the reaction spontaneous? If not, what is K_c for the spontaneous reaction? (Hint: The tool described by Equation 19.7 is important here.)

Practice Exercise 16: Use the following half-reactions and the data in Table 19.1 to write the equation for the spontaneous reaction. Write the equilibrium law for the reaction and use the standard cell potential to determine the value of the equilibrium constant. How is this related to the K_{sp} for AgBr?

$$Ag^{+}(aq) + e^{-} \longrightarrow Ag(s)$$
$$AgBr(s) + e^{-} \longrightarrow Ag(s) + Br^{-}(aq)$$
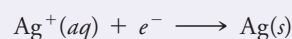
19.5 CONCENTRATIONS IN A GALVANIC CELL AFFECT THE CELL POTENTIAL

At 25 °C when all of the ion concentrations in a cell are 1.00 M and when the partial pressures of any gases involved in the cell reaction are 1.00 atm, the cell potential is equal to the standard potential. When the concentrations or pressures change, however, so does the potential. For example, in an operating cell or battery, the potential gradually drops as the reactants are used up and as the cell reaction approaches its natural equilibrium status. When it reaches equilibrium, the potential has dropped to zero—the battery is dead.

The Nernst equation defines the relationship of cell potential to ion concentrations

The effect of concentration on the cell potential can be obtained from thermodynamics. In Chapter 18, you learned that the free energy change is related to the reaction quotient Q by the equation

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

Substituting for ΔG and ΔG° from Equations 19.5 and 19.6 gives

$$-n\mathscr{F}E_{cell} = -n\mathscr{F}E_{cell}^{\circ} + RT \ln Q$$

Dividing both sides by $-n\mathscr{F}$ gives

TOOLS

Nernst equation

$$E_{cell} = E_{cell}^{\circ} - \frac{RT}{n\mathscr{F}} \ln Q \qquad (19.8)$$

This equation is commonly known as the **Nernst equation,**[6] named after Walther Nernst, a German chemist and physicist. Notice, if $Q = 1$ then $\ln Q = 0$ and $E_{cell} = E°_{cell}$.

In writing the Nernst equation for a galvanic cell, we will construct the mass action expression (from which we calculate Q) using molar concentrations for ions and partial pressures in atmospheres for gases.[7] Thus, for the following cell using a hydrogen electrode (with the partial pressure of H_2 not necessarily equal to 1 atm) and having the reaction

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

the Nernst equation would be written

$$E_{cell} = E°_{cell} - \frac{RT}{n\mathcal{F}} \ln \frac{[H^+]^2}{[Cu^{2+}]P_{H_2}}$$

◻ This is a heterogeneous reaction, so we have not included the concentration of the solid, Cu(s), in the mass action expression.

EXAMPLE 19.10
Calculating the Effect of Concentration on E_{cell}

Suppose a galvanic cell employs the following half-reactions.

$$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \qquad E°_{Ni^{2+}} = -0.25V$$
$$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s) \qquad E°_{Cr^{3+}} = -0.74 V$$
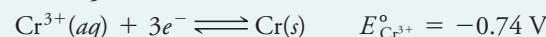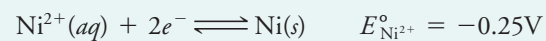
Calculate the cell potential when $[Ni^{2+}] = 1.0 \times 10^{-4} M$ and $[Cr^{3+}] = 2.0 \times 10^{-3} M$.

ANALYSIS: Because the concentrations are not $1.00 M$, we must use the Nernst equation (Equation 19.8) as our tool, but first we need the cell reaction. We need it to determine the number of electrons transferred, n, and we need it to determine the correct form of the mass action expression from which we calculate the numerical value of Q. We must also note that the reacting system is heterogeneous; both solid metals and a liquid solution of their dissolved ions are involved. We have to remember that a mass action expression does not contain concentration terms for solids, such as Ni and Cr.

SOLUTION: Nickel has the more positive (less negative) standard reduction potential, so its half-reaction will occur as a reduction. This means that chromium will be oxidized. Making electron gain equal to electron loss, the cell reaction is found as follows.

$$3[Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)] \qquad \qquad \text{(reduction)}$$
$$\underline{2[Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-]} \qquad \qquad \text{(oxidation)}$$
$$3Ni^{2+}(aq) + 2Cr(s) \longrightarrow 3Ni(s) + 2Cr^{3+}(aq) \qquad \text{(cell reaction)}$$
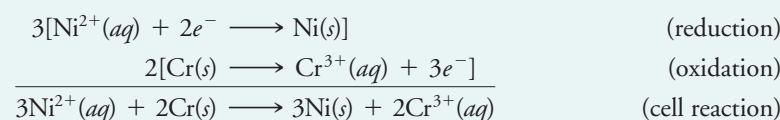
The total number of electrons transferred is six, which means $n = 6$. Now we can write the Nernst equation for the system.

$$E_{cell} = E°_{cell} - \frac{RT}{n\mathcal{F}} \ln \frac{[Cr^{3+}]^2}{[Ni^{2+}]^3}$$

Notice that we've constructed the mass action expression, from which we will calculate the reaction quotient, using the concentrations of the ions raised to powers equal to their coefficients in the net cell reaction, and that we have not included concentration terms for the two solids. This is the procedure we followed for heterogeneous equilibria in Chapter 14.

[6] Using common logarithms instead of natural logarithms and calculating the constants for 25 °C gives another form of the Nernst equation that is sometimes used:

$$E_{cell} = E°_{cell} - \frac{0.0592 \text{ V}}{n} \log Q$$

[7] Because of interionic attractions, ions do not always behave as though their concentrations are equal to their molarities. Strictly speaking, therefore, we should use effective concentrations (called activities) in the mass action expression. Effective concentrations are difficult to calculate, so for simplicity we will use molarities and accept the fact that our calculations are not entirely accurate.

Next we need E_{cell}°. Since Ni^{2+} is reduced,

$$E_{cell}^\circ = E_{Ni^{2+}}^\circ - E_{Cr^{3+}}^\circ$$
$$= (-0.25 \text{ V}) - (-0.74 \text{ V})$$
$$= 0.49 \text{ V}$$

Now we can substitute this value for E_{cell}° along with $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, $T = 298 \text{ K}$, $n = 6$, $\mathcal{F} = 9.65 \times 10^4 \text{ C mol}^{-1}$, $[Ni^{2+}] = 1.0 \times 10^{-4} \text{ } M$, and $[Cr^{3+}] = 2.0 \times 10^{-3} \text{ } M$ into the Nernst equation. This gives

$$E_{cell} = 0.49 \text{ V} - \frac{8.314 \text{ J } \cancel{mol^{-1}} \cancel{K^{-1}} \times 298 \cancel{K}}{6 \times 9.65 \times 10^4 \text{ C } \cancel{mol^{-1}}} \ln \frac{(2.0 \times 10^{-3})^2}{(1.0 \times 10^{-4})^3}$$

$$= 0.49 \text{ V} - (0.00428 \text{ V}) \ln (4.0 \times 10^6)$$
$$= 0.49 \text{ V} - (0.00428 \text{ V})(15.20)$$
$$= 0.49 \text{ V} - 0.0651 \text{ V}$$
$$= 0.42 \text{ V}$$

The potential of the cell is expected to be 0.42 V.

IS THE ANSWER REASONABLE? There's no simple way to check the answer. However, there are certain important points to consider. First, check that you've combined the half-reactions correctly to calculate E_{cell}° and given the balanced cell reaction, because we need the coefficients of the equation to obtain the correct superscripts in the Nernst equation. Then, be sure you've used the Kelvin temperature, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, and made the other substitutions correctly.

EXAMPLE 19.11

The Spontaneous Reaction May Be Concentration Dependent

The reaction of tin metal with acid can be written as

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

Calculate the cell potential (a) when the system is at standard state, (b) when the pH is 2.00, and (c) when the pH is 5.00. Assume that $[Sn^{2+}] = 1.00 \text{ } M$ and the partial pressure of H_2 is also 1.00 atm.

ANALYSIS: In this reaction the tin metal is the substance that is oxidized and hydrogen ions are reduced. Part (a) is at standard state, and we have used our tool for combining standard reduction potentials to solve problems like that in Examples 19.6 and 19.7. For parts (b) and (c) we must use the Nernst equation as our tool. We determine the number of electrons transferred by noting that tin loses two electrons and each hydrogen gains an electron. Therefore two electrons are transferred from tin to the hydrogen ions. We can also set up Q for the Nernst equation by substituting 1.00 for both $[Sn^{2+}]$ and P_{H_2}:

$$Q = \frac{[Sn^{2+}]P_{H_2}}{[H^+]^2} = \frac{1.00}{[H^+]^2}$$

We can also calculate the hydrogen ion concentrations for the pH 2.00 and pH 5.00 solutions as $1.0 \times 10^{-2} \text{ } M$ and $1.0 \times 10^{-5} \text{ } M$ respectively.

SOLUTION: For part (a) we find the difference between standard reduction potentials as

$$E_{cell}^\circ = 0.00 \text{ V} - (-0.14) \text{ V} = +0.14 \text{ V}$$

For parts (b) and (c) we substitute into the Nernst equation

$$E_{cell} = E°_{cell} - \frac{RT}{n\mathscr{F}} \ln \frac{1.00}{[H^+]^2}$$

(b) $E_{cell} = 0.14 \text{ V} - \dfrac{8.314 \text{ J } mol^{-1} K^{-1} \times 298 \text{ K}}{2 \times 9.65 \times 10^4 \text{ C } mol^{-1}} \ln \dfrac{1.00}{(1.0 \times 10^{-2})^2}$

$E_{cell} = 0.14 \text{ V} - 0.12 \text{ V} = +0.02 \text{ V}$

(c) $E_{cell} = 0.14 \text{ V} - \dfrac{8.314 \text{ J } mol^{-1} K^{-1} \times 298 \text{ K}}{2 \times 9.65 \times 10^4 \text{ C } mol^{-1}} \ln \dfrac{1.00}{(1.0 \times 10^{-5})^2}$

$E_{cell} = 0.14 \text{ V} - 0.30 \text{ V} = -0.16 \text{ V}$

At standard state the reaction is spontaneous. At pH 2.00 it is spontaneous but the potential is a small positive value. At pH 5.00 the reaction is not spontaneous.

ARE THE ANSWERS REASONABLE? The first question to answer is, "Does this make sense?" and indeed it does. Looking at the natural logarithm part of the equation we see that as the $[H^+]$ decreases, the ln term increases and makes a more negative adjustment to the $E°_{cell}$. Since a decrease in $[H^+]$ is an increase in pH, we expect E_{cell} will decrease as pH increases. We cannot easily estimate natural logarithms so a check of calculations may be easiest if the values are entered into your calculator in the reverse order from the first calculation.

Practice Exercise 17: A galvanic cell is constructed with a copper electrode dipping into a 0.015 M solution of Cu^{2+} ions and an electrode made of magnesium immersed in a 2.2×10^{-6} M solution of magnesium ions. Write the balanced chemical reaction. What is the cell potential at 25 °C? (Hint: Set up the Nernst equation for the reaction.)

Practice Exercise 18: In a certain zinc–copper cell,

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

the ion concentrations are $[Cu^{2+}] = 0.0100$ M and $[Zn^{2+}] = 1.0$ M. What is the cell potential at 25 °C?

Experimental cell potentials can be used to determine ion concentrations

One of the principal uses of the relationship between concentration and cell potential is for the measurement of concentrations of redox reactants and products in a galvanic cell. Experimental determination of cell potentials combined with modern developments in electronics has provided a means of monitoring and analyzing the concentrations of all sorts of substances in solution, even some that are not themselves ionic and that are not involved directly in electrochemical changes. In fact, the operation of a pH meter relies on the logarithmic relationship between hydrogen ion concentration and the potential of a special kind of electrode (Figure 19.8 on page 795)

EXAMPLE 19.12
Using the Nernst Equation to Determine Concentrations

To measure the concentration of Cu^{2+} in a large number of samples of water in which the copper ion concentration is expected to be quite small, an electrochemical cell was assembled that consists of a silver electrode, dipping into a 1.00 M solution of $AgNO_3$, connected by a salt bridge to a second half-cell containing a copper electrode. The copper half-cell was then filled with one water sample after another, with the cell potential being measured for each sample. In the analysis of one sample, the cell potential at 25 °C was measured to be 0.62 V. The copper electrode was observed to carry a negative charge, so it served as the anode. What was the concentration of copper ion in the sample?

ANALYSIS: In this problem, we've been given the cell potential, E_{cell}, and we can calculate $E°_{cell}$ from the standard reduction potentials in Table 19.1. The unknown quantity is one of the concentration terms in the Nernst equation that we use as our tool for solving this problem.

SOLUTION: The first step is to write the proper equation for the cell reaction, because we need it to compute $E°_{cell}$ and to construct the mass action expression for use in the Nernst equation. Because copper is the anode, it is being oxidized. This also means that Ag^+ is being reduced. Therefore, the equation for the cell reaction is

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

Two electrons are transferred, so $n = 2$ and the Nernst equation is

$$E_{cell} = E°_{cell} - \frac{RT}{2\mathcal{F}} \ln \frac{[Cu^{2+}]}{[Ag^+]^2}$$

The value of $E°_{cell}$ can be obtained from the tabulated standard reduction potentials in Table 19.1. Following our usual procedure and recognizing that silver ion is reduced,

$$E°_{cell} = E°_{Ag^+} - E°_{Cu^{2+}}$$
$$= (0.80 \text{ V}) - (0.34 \text{ V})$$
$$= 0.46 \text{ V}$$

Now we can substitute values into the Nernst equation and solve for the concentration ratio in the mass action expression.

$$0.62 \text{ V} = 0.46 \text{ V} - \frac{8.314 \text{ J } \cancel{mol^{-1}} \text{ K}^{-1} \times 298 \text{ K}}{2 \times 9.65 \times 10^4 \text{ C } \cancel{mol^{-1}}} \ln \frac{[Cu^{2+}]}{[Ag^+]^2}$$

Solving for $\ln ([Cu^{2+}]/[Ag^+]^2)$ gives

$$\ln \frac{[Cu^{2+}]}{[Ag^+]^2} = -12$$

Taking the antilog gives us the value of the mass action expression.

$$\frac{[Cu^{2+}]}{[Ag^+]^2} = 6 \times 10^{-6}$$

Since we know that the concentration of Ag^+ is 1.00 M, we can now solve for the Cu^{2+} concentration.

$$\frac{[Cu^{2+}]}{(1.00)^2} = 6 \times 10^{-6}$$
$$[Cu^{2+}] = 6 \times 10^{-6} \text{ M}$$

IS THE ANSWER REASONABLE? All we can do easily is check to be sure we've written the correct chemical equation, on which all the rest of the solution to the problem rests. Be careful about algebraic signs and that you select the proper value for R and the temperature in kelvins. Also, notice that we first solved for the logarithm of the ratio of concentration terms. Then, after taking the (natural) antilogarithm, we substitute the known value for $[Ag^+]$ and solve for $[Cu^{2+}]$.

As a final point, notice that the Cu^{2+} concentration is indeed very small, and that it can be obtained very easily by simply measuring the potential generated by the electrochemical cell. Determining the concentrations in many samples is also very simple—just change the water sample and measure the potential again.

☐ The ease of such operations and the fact that they lend themselves well to automation and computer analysis make electrochemical analyses especially attractive to scientists.

Practice Exercise 19: A galvanic cell is constructed with a copper electrode dipping into a 0.015 M solution of Cu^{2+} ions and a magnesium electrode immersed in a solution of Mg^{2+} ions. The cell potential is measured as 2.79 volts at 25 °C. What is the concentration of magnesium ions?

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

(Hint: Use the Nernst equation to solve for $[Mg^{2+}]$.)

Practice Exercise 20: In the analysis of two other water samples by the procedure described in Example 19.12, cell potentials (E_{cell}) of 0.57 V and 0.82 V were obtained. Calculate the Cu^{2+} ion concentration in each of these samples.

Practice Exercise 21: A galvanic cell was constructed by connecting a nickel electrode that was dipping into 1.20 M $NiSO_4$ solution to a chromium electrode that was dipping into a solution containing Cr^{3+} at an unknown concentration. The potential of the cell was measured to be 0.552 V, with the chromium serving as the anode. The standard cell potential for the system was determined to be 0.487 V. What was the concentration of Cr^{3+} in the solution of unknown concentration?

Concentration cells consist of two almost identical half-cells

The dependence of cell potential on concentration allows us to construct a galvanic cell from two half-cells composed of the same substances but having different concentrations of the solute species. An example would be a pair of copper electrodes dipping into solutions that have different concentrations of Cu^{2+}, say 0.10 M Cu^{2+} in one and 1.0 M in the other (Figure 19.9). When this cell operates, reactions take place that tend to bring the two Cu^{2+} concentrations toward the same value. Thus, in the half-cell containing 0.10 M Cu^{2+}, copper is oxidized, which adds Cu^{2+} to the more dilute solution. In the other cell, Cu^{2+} is reduced, removing Cu^{2+} from the more concentrated solution. This makes the more dilute half-cell the anode and the more concentrated half-cell the cathode.

$$Cu(s)|Cu^{2+}(0.10\ M)||Cu^{2+}(1.0\ M)|Cu(s)$$
$$\text{anode} \qquad\qquad\qquad \text{cathode}$$

The half-reactions in the spontaneous cell reaction are

$$Cu(s) \longrightarrow Cu^{2+}(0.10\ M) + 2e^-$$
$$Cu^{2+}(1.0\ M) + 2e^- \longrightarrow Cu(s)$$
$$\overline{}$$
$$Cu^{2+}(1.0\ M) \longrightarrow Cu^{2+}(0.10\ M)$$

The Nernst equation for this cell is

$$E_{cell} = E_{cell}^\circ - \frac{RT}{n\mathscr{F}}\ln\frac{[Cu^{2+}]_{dilute}}{[Cu^{2+}]_{conc}}$$

Because we're dealing with the same substances in the cell, $E_{cell}^\circ = 0$ V (exactly). When the cell operates, $n = 2$, and we'll take $T = 298$ K. Substituting values,

$$E_{cell} = 0\ V - \frac{8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298\ \text{K}}{2 \times 9.65 \times 10^4\ \text{C mol}^{-1}}\ln\left(\frac{0.10}{1.0}\right)$$
$$= 0.030\ V$$

In this concentration cell, one solution is ten times more concentrated than the other, yet the potential generated is only 0.03 V. In general, the potential generated by concentration differences are quite small. Yet they are significant in biological systems, where electrical potentials are generated across biological membranes by differences in ion concentrations (e.g., K^+). Membrane potentials are important in processes such as the transmission of nerve impulses.

These small differences in potential also illustrate that if Q, in a system that is not at standard state, is between 0.10 and 10 we can conclude that $E_{cell} \approx E_{cell}^\circ$ and we can generalize the results in Sections 19.2 and 19.3 when predicting spontaneous reactions.

FIG. 19.8 **Electrodes used with a pH meter.** The electrode on the left is called a *glass electrode*. It contains a silver wire, coated with AgCl, dipping into a dilute solution of HCl. This half-cell has a potential that depends on the difference between the $[H^+]$ inside and outside a thin glass membrane at the bottom of the electrode. On the right is a reference electrode that forms the other half-cell. The galvanic cell formed by the two electrodes produces a potential that is proportional to the pH of the solution into which they are dipped.

FIG. 19.9 **A concentration cell.** When the circuit is completed, reactions occur that tend to make the concentrations of Cu^{2+} the same in the two half-cells. Oxidation occurs in the more dilute half-cell, and reduction occurs in the more concentrated one.

| 19.6 | ELECTROLYSIS USES ELECTRICAL ENERGY TO CAUSE CHEMICAL REACTIONS |

In our preceding discussions, we've examined how spontaneous redox reactions can be used to generate electrical energy. We now turn our attention to the opposite process, the use of electrical energy to force nonspontaneous redox reactions to occur.

When electricity is passed through a molten (melted) ionic compound or through a solution of an electrolyte, a chemical reaction occurs that we call **electrolysis.** A typical electrolysis apparatus, called an **electrolysis cell** or **electrolytic cell,** is shown in Figure 19.10. This particular cell contains molten sodium chloride. (A substance undergoing electrolysis must be molten or in solution so its ions can move freely and conduction can occur.) *Inert electrodes*—electrodes that won't react with the molten NaCl—are dipped into the cell and then connected to a source of direct current (DC) electricity.

The DC source serves as an "electron pump," pulling electrons away from one electrode and pushing them through the external wiring onto the other electrode. The electrode from which electrons are removed becomes positively charged, while the other electrode becomes negatively charged. When electricity starts to flow, chemical changes begin to happen. At the positive electrode, oxidation occurs as electrons are pulled away from negatively charged chloride ions. Because of the nature of the chemical change, therefore, *the positive electrode becomes the anode*. The DC source pumps the electrons through the external electrical circuit to the negative electrode. Here reduction takes place as the electrons are forced onto positively charged sodium ions, so *the negative electrode is the cathode*.
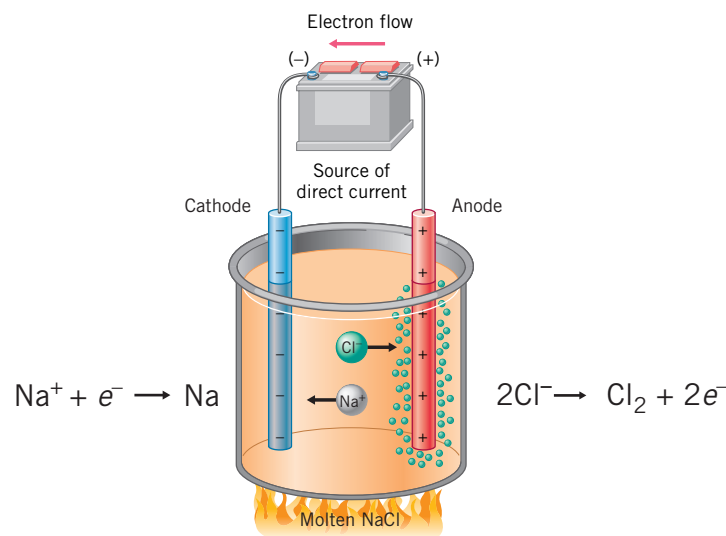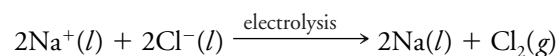
The chemical changes that occur at the electrodes can be described by chemical equations.

$$Na^+(l) + e^- \longrightarrow Na(l) \qquad \text{(cathode)}$$
$$2Cl^-(l) \longrightarrow Cl_2(g) + 2e^- \qquad \text{(anode)}$$
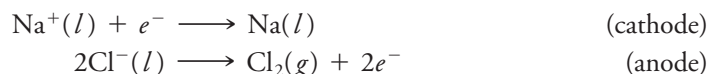
As in a galvanic cell, the overall reaction that takes place in the electrolysis cell is called the *cell reaction*. To obtain it, we add the individual electrode half-reactions together, making sure that the number of electrons gained in one half-reaction equals the number lost in the other.

$$2Na^+(l) + 2e^- \longrightarrow 2Na(l) \qquad \text{(cathode)}$$
$$2Cl^-(l) \longrightarrow Cl_2(g) + 2e^- \qquad \text{(anode)}$$
$$\overline{2Na^+(l) + 2Cl^-(l) + \cancel{2e^-} \longrightarrow 2Na(l) + Cl_2(g) + \cancel{2e^-}} \qquad \text{(cell reaction)}$$
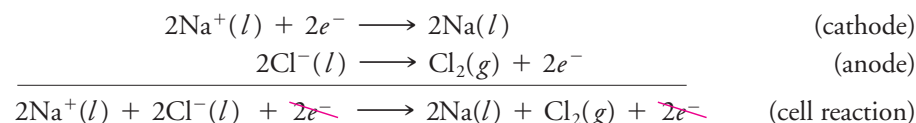
As you know, table salt is quite stable. It doesn't normally decompose because the reverse reaction, the reaction of sodium and chlorine to form sodium chloride, is highly spontaneous. Therefore, we often write the word *electrolysis* above the arrow in the equation to show that electricity is the driving force for this otherwise nonspontaneous reaction.

$$2Na^+(l) + 2Cl^-(l) \xrightarrow{\text{electrolysis}} 2Na(l) + Cl_2(g)$$

◻ To perform electrolysis, we must use direct current in which electrons move in only one direction, not in the oscillating, back and forth pattern of alternating current.

FIG. 19.10 **Electrolysis of molten sodium chloride.** In this electrolysis cell, the passage of an electric current decomposes molten sodium chloride into metallic sodium and gaseous chlorine. Unless the products are kept apart, they react on contact to re-form NaCl.

Electrolytic and galvanic cells have similarities and differences

In a galvanic cell, the spontaneous cell reaction deposits electrons on the anode and removes them from the cathode. As a result, the anode carries a slight negative charge and the cathode a slight positive charge. In most galvanic cells the reactants must be separated in separate compartments. In an *electrolysis cell*, the situation is reversed. Often the two electrodes are immersed in the same liquid. Also, the oxidation at the anode must be forced to occur, which requires that the anode be positive so it can remove electrons from the reactant at that electrode. On the other hand, the cathode must be made negative so it can force the reactant at the electrode to accept electrons.

Electrolytic Cell	**Galvanic Cell**
Cathode is negative (reduction).	Cathode is positive (reduction).
Anode is positive (oxidation).	Anode is negative (oxidation).
Anode and cathode are often in same compartment.	Anode and cathode are usually in separate compartments.

Even though the charges on the cathode and anode differ between electrolytic cells and galvanic cells, the ions in solution always move in the same direction. In both types of cells, positive ions (cations) move toward the cathode. They are attracted there by the negative charge on the cathode in an electrolysis cell; they diffuse toward the cathode in a galvanic cell to balance the charge of negative ions left behind when ions are reduced. Similarly, negative ions (anions) move toward the anode. They are attracted to the positive anode in an electrolysis cell, and they diffuse toward the anode in a galvanic cell to balance the charge of the positive ions entering the solution.

☐ By agreement among scientists, the names anode and cathode are assigned according to the nature of the reaction taking place at the electrode. If the reaction is oxidation, the electrode is called the anode; if it's reduction, the electrode is called the cathode.

Oxidation and reduction must occur for conduction to continue in an electrolytic cell

The electrical conductivity of a molten salt or a solution of an electrolyte is possible only because of the reactions that take place at the surface of the electrodes. For example, when charged electrodes are dipped into molten NaCl they become surrounded by a layer of ions of the opposite charge. Let's look closely at what happens at one of the electrodes, say the anode (Figure 19.11). Here the positive charge of the

Cl atoms combine to form Cl_2 molecules.

Chloride ions, in contact with the anode, lose e^- to become Cl atoms.

Cl_2 molecules rise to the surface of the liquid.

Cl^- ions move toward the anode to replace others that have become Cl atoms.
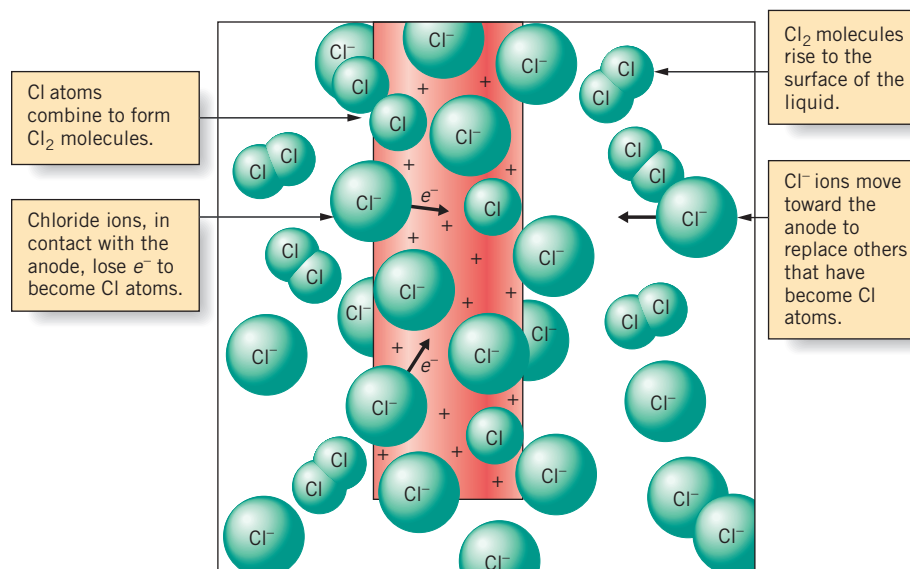
FIG. 19.11 **A microscopic view of changes at the anode in the electrolysis of molten NaCl.** The positive charge of the electrode attracts a coating of Cl^- ions. At the surface of the electrode, electrons are pulled from the ions, yielding neutral Cl atoms, which combine to form Cl_2 molecules that move away from the electrode and eventually rise to the surface as a gas.
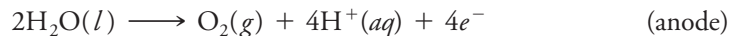
electrode attracts negative Cl^- ions, which form a coating on the electrode's surface. The charge on the anode pulls electrons from the ions, causing them to be oxidized and changing them into neutral Cl atoms that join to become Cl_2 molecules. Because the molecules are neutral, they are not held by the electrode and so move away from the electrode's surface. Their places are quickly taken by negative ions from the surrounding liquid, which tends to leave the surrounding liquid positively charged. Other negative ions from farther away move toward the anode to keep the liquid there electrically neutral. In this way, negative ions gradually migrate toward the anode. By a similar process, positive ions diffuse through the liquid toward the negatively charged cathode where they become reduced.

◻ Cations (positive ions) move toward the cathode and anions (negative ions) migrate toward the anode. This happens in both electrolytic and galvanic cells.

Electrolysis reactions in aqueous solutions can involve oxidation and/or reduction of water

When electrolysis is carried out in an aqueous solution, the electrode reactions are more difficult to predict because at the electrodes there are competing reactions. We have to consider not only the possible oxidation and reduction of the solute, but also the oxidation and reduction of water. For example, consider what happens when electrolysis is performed on a solution of potassium sulfate (Figure 19.12). The products are hydrogen and oxygen. At the cathode, water is reduced, not K^+.

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad \text{(cathode)}$$

At the anode, water is oxidized, not the sulfate ion.

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad \text{(anode)}$$

Color changes of an acid–base indicator dissolved in the solution confirm that the solution becomes basic around the cathode, where OH^- is formed, and acidic around the anode, where H^+ is formed (see Figure 19.13). In addition, the gases H_2 and O_2 can be separately collected.

We can understand why these redox reactions happen if we examine the standard reduction potential data from Table 19.1. For example, at the cathode we have the following competing reactions.

$$K^+(aq) + e^- \longrightarrow K(s) \qquad\qquad E^\circ_{K^+} = -2.92 \text{ V}$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad E^\circ_{H_2O} = -0.83 \text{ V}$$

Water has a much less negative (and therefore more positive) standard reduction potential than K^+, which means H_2O is much easier to reduce than K^+. As a result, when the

FIG. 19.12 **Electrolysis of an aqueous solution of potassium sulfate.** The products of the electrolysis are the gases hydrogen and oxygen as shown in the half-reactions for each half-cell.
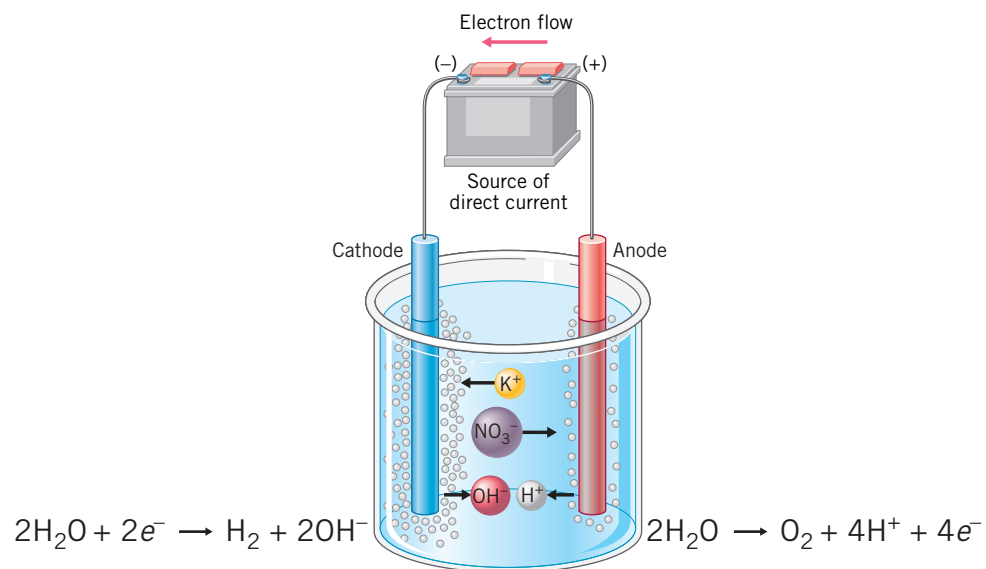
$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

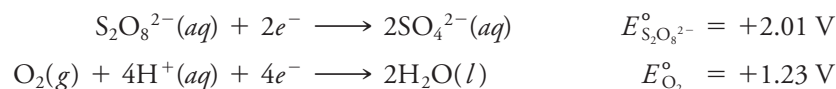(a)   (b)   (c)
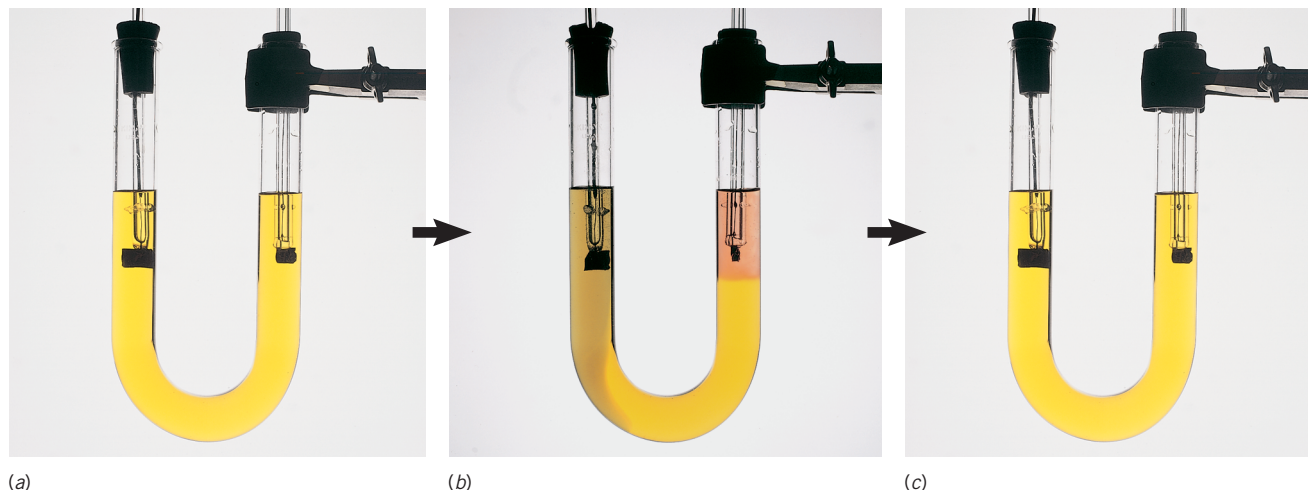
FIG. 19.13 **Electrolysis of an aqueous solution of potassium sulfate in the presence of acid–base indicators.** (*a*) The initial
yellow color indicates that the solution is neutral (neither acidic nor basic). (*b*) As the electrolysis proceeds, H^+ is produced at the
anode (along with O_2) and causes the solution there to become pink. At the cathode, H_2 is evolved and OH^- ions are formed, which
turns the solution around that electrode a bluish violet. (*c*) After the electrolysis is stopped and the solution is stirred, the color
becomes yellow again as the H^+ and OH^- ions formed by the electrolysis neutralize each other. *(Michael Watson)*

electrolysis is performed the more easily reduced substance is reduced and we observe H_2
being formed at the cathode.

At the anode we have the following possible oxidation half-reactions.

$$2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-}(aq) + 2e^-$$

$$2H_2O(l) \longrightarrow 4H^+(aq) + O_2(g) + 4e^-$$
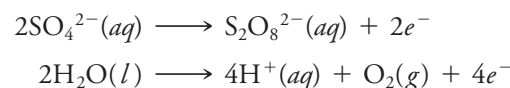
In Table 19.1, we find them written in the opposite direction:

$$S_2O_8^{2-}(aq) + 2e^- \longrightarrow 2SO_4^{2-}(aq) \qquad E^\circ_{S_2O_8^{2-}} = +2.01 \text{ V}$$

$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l) \qquad E^\circ_{O_2} = +1.23 \text{ V}$$

The E° values tell us that $S_2O_8^{2-}$ is much more easily reduced than O_2. But if $S_2O_8^{2-}$ is
the *more easily reduced*, then the product, SO_4^{2-}, must be *the less easily oxidized*. Stated
another way, *the half-reaction with the smaller standard reduction potential is more easily
reversed as an oxidation*. As a result, when electrolysis is performed, water is oxidized instead
of SO_4^{2-} and we observe O_2 being formed at the anode.
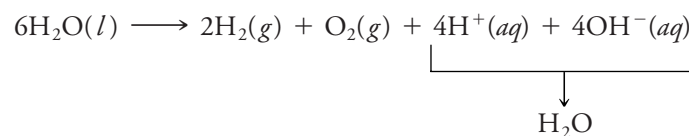
The overall cell reaction for the electrolysis of the K_2SO_4 solution can be obtained as
before. Because the number of electrons lost has to equal the number gained, the cathode
reaction must occur twice each time the anode reaction occurs once.

$$2 \times [2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq)] \qquad \text{(cathode)}$$

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad \text{(anode)}$$
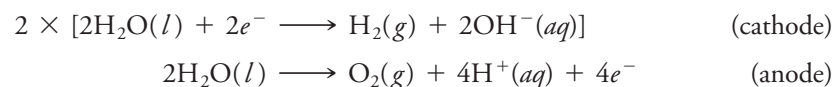
After adding, we combine the coefficients for water and cancel the electrons from both
sides to obtain the cell reaction.

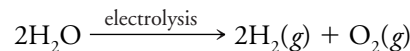$$6H_2O(l) \longrightarrow 2H_2(g) + O_2(g) + 4H^+(aq) + 4OH^-(aq)$$
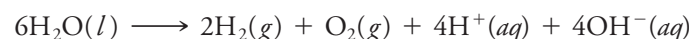
Notice that hydrogen ions and hydroxide ions are produced in equal numbers. In Figure
19.13, we see that when the solution is stirred, they combine to form water.

$$6H_2O(l) \longrightarrow 2H_2(g) + O_2(g) + 4H^+(aq) + 4OH^-(aq)$$

$$H_2O$$

The net change, then, is

$$2H_2O \xrightarrow{\text{electrolysis}} 2H_2(g) + O_2(g)$$

What function does potassium sulfate serve?
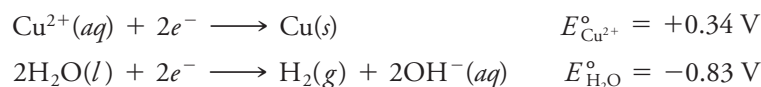
Although neither K^+ nor SO_4^{2-} are changed by the reaction, K_2SO_4 or some other electrolyte is needed for the electrolysis to proceed. Its function is to maintain electrical neutrality at the electrodes. At the anode, H^+ ions are formed and their charge can be balanced by mixing with SO_4^{2-} ions of the solute. Similarly, at the cathode the K^+ ions are able to mix with OH^- ions as they are formed, thereby balancing the charge and keeping the solution electrically neutral. In this way, at any moment, each small region of the solution is able to contain the same number of positive and negative charges and thereby remain neutral.

Often we can use standard reduction potentials to predict electrolysis products

TOOLS

Predicting electrolysis products
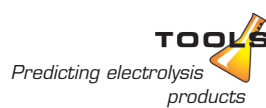
Suppose we wished to know what products are expected in the electrolysis of an aqueous solution of copper(II) bromide, $CuBr_2$. Let's examine the possible electrode half-reactions and their respective standard reduction potentials.

At the cathode, possible reactions are the reduction of copper ion and the reduction of water. From Table 19.1,
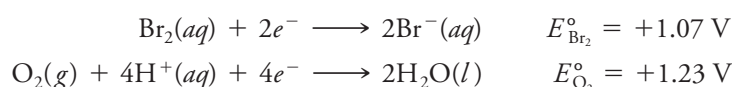
$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \qquad\qquad E°_{Cu^{2+}} = +0.34 \text{ V}$$

$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad E°_{H_2O} = -0.83 \text{ V}$$

The much more positive standard reduction potential for Cu^{2+} tells us to anticipate that Cu^{2+} will be reduced at the cathode.

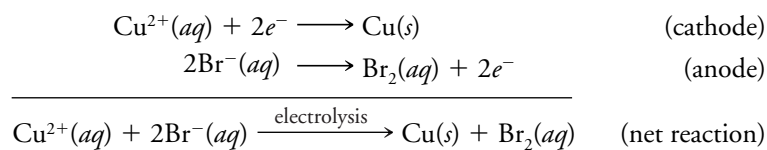At the anode, possible reactions are the oxidation of Br^- and the oxidation of water. The half-reactions are

$$2Br^-(aq) \longrightarrow Br_2(aq) + 2e^-$$

$$2H_2O(l) \longrightarrow O_2(g) + 4H^+(aq) + 4e^-$$
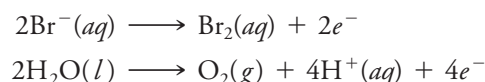
In Table 19.1 they are written as reductions with the following $E°$ values.

$$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq) \qquad E°_{Br_2} = +1.07 \text{ V}$$

$$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l) \qquad E°_{O_2} = +1.23 \text{ V}$$

The data tell us that O_2 is more easily reduced than Br_2, which means that Br^- is more easily oxidized than H_2O. Therefore, we expect that Br^- will be oxidized at the anode.

In fact, our predictions are confirmed when we perform the electrolysis. The cathode, anode, and net cell reactions are

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \qquad\qquad \text{(cathode)}$$

$$2Br^-(aq) \longrightarrow Br_2(aq) + 2e^- \qquad\qquad \text{(anode)}$$

$$\overline{\hspace{8cm}}$$

$$Cu^{2+}(aq) + 2Br^-(aq) \xrightarrow{\text{electrolysis}} Cu(s) + Br_2(aq) \qquad \text{(net reaction)}$$

EXAMPLE 19.13

Predicting the Products in an Electrolysis Reaction

Electrolysis is planned for an aqueous solution that contains a mixture of 0.50 *M* $ZnSO_4$ and 0.50 *M* $NiSO_4$. On the basis of standard reduction potentials, what products are expected to be observed at the electrodes? What is the expected net cell reaction?
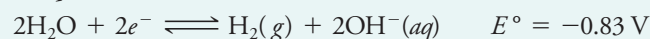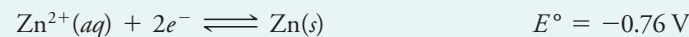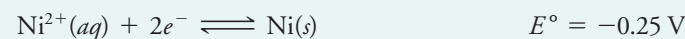
ANALYSIS: We need to consider the competing reactions at the cathode and the anode. At the cathode, the half-reaction with the most positive (or least negative) standard reduction potential will be the one expected to occur. At the anode, the half-reaction with the *least*
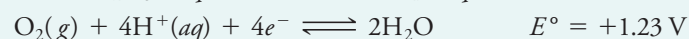
positive standard reduction potential is the one most easily reversed, and should occur as an oxidation.

SOLUTION: At the cathode, the competing reduction reactions involve the two cations and water. The reactions and their standard reduction potentials are

$$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s) \qquad\qquad E° = -0.25 \text{ V}$$
$$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s) \qquad\qquad E° = -0.76 \text{ V}$$
$$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq) \qquad E° = -0.83 \text{ V}$$

The least negative standard reduction potential is that of Ni^{2+}, so we expect that ion to be reduced at the cathode and solid nickel to be formed.

At the anode, the competing oxidation reactions are for water and SO_4^{2-} ion. In Table 19.1, substances oxidized are found on the right side of the half-reactions. The two half-reactions having these as products are

$$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq) \qquad E° = +2.01 \text{ V}$$
$$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O \qquad E° = +1.23 \text{ V}$$

The half-reaction with the least positive $E°$ (the second one here) is most easily reversed as an oxidation, so we expect the oxidation half-reaction to be

$$2H_2O \rightleftharpoons O_2(g) + 4H^+(aq) + 4e^-$$
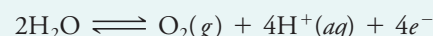
At the anode, we expect O_2 to be formed.

The predicted net cell reaction is obtained by combining the two expected electrode half-reactions, making the electron loss equal to the electron gain.

$$2H_2O \longrightarrow O_2(g) + 4H^+(aq) + 4e^- \qquad\qquad \text{(anode)}$$
$$\underline{2 \times [Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)]} \qquad\qquad\qquad \text{(cathode)}$$
$$2H_2O + 2Ni^{2+}(aq) \longrightarrow O_2(g) + 4H^+(aq) + 2Ni(s) \qquad \text{(net cell reaction)}$$
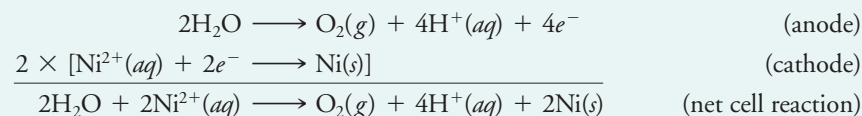
ARE THE ANSWERS REASONABLE? We can check the locations of the half-reactions in Table 19.1 to confirm our conclusions. For the reduction step, the higher up in the table a half-reaction is, the greater its tendency to occur as reduction. Among the competing half-reactions at the cathode, the one for Ni^{2+} is highest, so we expect that Ni^{2+} is the easiest to reduce and $Ni(s)$ should be formed at the cathode.

For the oxidation step, the lower down in the table a half-reaction is, the easier it is to reverse and cause to occur as oxidation. On this basis, the oxidation of water is easier than the oxidation of SO_4^{2-}, so we expect H_2O to be oxidized and O_2 to be formed at the anode.

Of course, we could also test our prediction by carrying out the electrolysis experimentally.

Practice Exercise 22: In the electrolysis of an aqueous solution containing Fe^{2+} and I^-, what product do we expect at the anode? (Hint: Write the three oxidation half-reactions possible at the anode.)
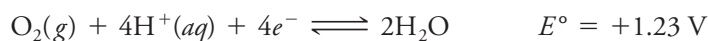
Practice Exercise 23: In the electrolysis of an aqueous solution containing both Cd^{2+} and Sn^{2+}, what product do we expect at the cathode? Under what conditions can the other ion be reduced?

## Using standard reduction potentials to predict electrolysis doesn't always work

Although we can use standard reduction potentials to predict electrolysis reactions most of the time, there are occasions when standard reduction potentials do not successfully predict electrolysis products. Sometimes concentrations, far from standard conditions, will change the sign of the cell potential. The formation of complex ions can also interfere and produce unexpected results. And sometimes the electrodes themselves are

the culprits. For example, in the electrolysis of aqueous NaCl using inert platinum electrodes, we find experimentally that Cl_2 is formed at the anode. Is this what we would have expected? Let's examine the standard reduction potentials of O_2 and Cl_2 to find out.

$$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq) \qquad E° = +1.36 \text{ V}$$

$$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O \qquad E° = +1.23 \text{ V}$$

Because of its less positive standard reduction potential, we would expect the oxygen half-reaction to be the easier to reverse (with water being oxidized to O_2). Thus, standard reduction potentials predict that O_2 should be formed, but experiment shows that Cl_2 is produced. The nature of the electrode surface and how it interacts with oxygen is part of the answer. Further explanation for why this happens is beyond the scope of this text, but the unexpected result does teach us that we must be cautious in predicting products in electrolysis reactions solely on the basis of standard reduction potentials.
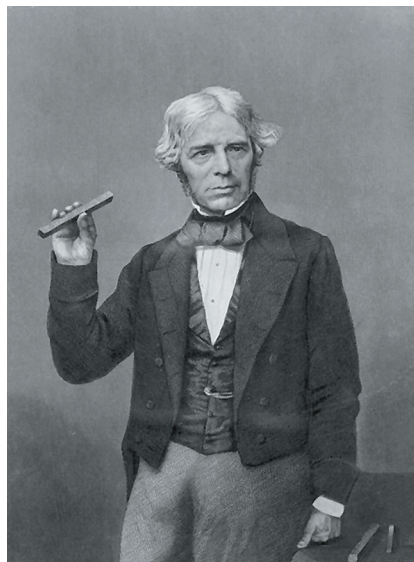
19.7 STOICHIOMETRY OF ELECTROCHEMICAL REACTIONS INVOLVES ELECTRIC CURRENT AND TIME

In about 1833, Michael Faraday discovered that the amount of chemical change that occurs during electrolysis is directly proportional to the amount of electrical charge that is passed through an electrolysis cell. For example, the reduction of copper ion at a cathode is given by the equation

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$$
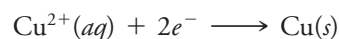
The equation tells us that to deposit one mole of metallic copper requires two moles of electrons. Thus, the half-reaction for an oxidation or reduction relates the amount of chemical substance consumed or produced to the amount of electrons that the electric current must supply. To use this information, however, we must be able to relate it to electrical measurements that can be made in the laboratory.

The SI unit of electric current is the **ampere (A)** and the SI unit of charge is the **coulomb (C).** A coulomb is the amount of charge that passes by a given point in a wire when an electric current of one ampere flows for one second. This means that coulombs are the product of amperes of current multiplied by seconds. Thus

$$1 \text{ coulomb} = 1 \text{ ampere} \times 1 \text{ second}$$

$$\boxed{1 \text{ C} = 1 \text{ A s}}$$

TOOLS

Coulombs are related to current in amperes and time in seconds.

For example, if a current of 4 A flows through a wire for 10 s, 40 C pass by a given point in the wire.

$$(4 \text{ A}) \times (10 \text{ s}) = 40 \text{ A s}$$
$$= 40 \text{ C}$$

As we noted earlier, it has been determined that 1 mol of electrons carries a charge of 9.65×10^4 C, which in honor of Michael Faraday is often called the Faraday constant, $\mathscr{F}$.

$$1 \text{ mol } e^- \Leftrightarrow 9.65 \times 10^4 \text{ C} \qquad \left(\begin{array}{c} \text{to three} \\ \text{significant figures} \end{array} \right)$$

$$1 \mathscr{F} = 9.65 \times 10^4 \text{ C/mol } e^-$$

Now we have a way to relate laboratory measurements to the amount of chemical change that occurs during an electrolysis. Measuring the current in amperes and the time in seconds allows us to calculate the charge sent through the system in coulombs. From this we can get the amount of electrons (in moles), which we can then use to calculate the amount of chemical change produced. The following examples demonstrate the principles involved for electrolysis, but similar calculations also apply to reactions in galvanic cells.

Michael Faraday (1791–1867), a British scientist and both a chemist and a physicist, made key discoveries leading to electric motors, generators, and transformers. *(Courtesy Edgar Fahs Smith Collection, University of Pennsylvania.)*

EXAMPLE 19.14
Calculations Related to Electrolysis

How many grams of copper are deposited on the cathode of an electrolytic cell if an electric current of 2.00 A is run through a solution of $CuSO_4$ for a period of 20.0 min?

ANALYSIS: The balanced half-reaction serves as our tool for relating chemical change to amounts of electricity. The ion being reduced is Cu^{2+}, so the half-reaction is

$$Cu^{2+} + 2e^- \longrightarrow Cu$$
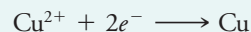
Therefore,

$$1 \text{ mol Cu} \Longleftrightarrow 2 \text{ mol } e^-$$
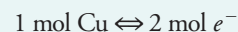
The product of current (in amperes) and time (in seconds) is the tool that will give us charge (in coulombs). We can relate this to the number of moles of electrons by the Faraday constant, another of our tools. Then, from the number of moles of electrons we calculate moles of copper, from which we calculate the mass of copper by using the atomic mass. Here's a diagram of the path to the solution.
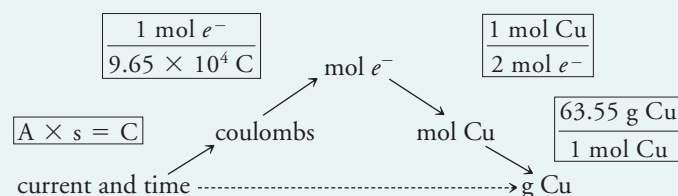
SOLUTION: First we convert minutes to seconds; 20.0 min $= 1.20 \times 10^3$ s. Then we multiply the current by the time to obtain the number of coulombs (1 A s $=$ 1 C).

$$(1.20 \times 10^3 \text{ s}) \times (2.00 \text{ A}) = 2.40 \times 10^3 \text{ A s}$$
$$= 2.40 \times 10^3 \text{ C}$$

Because 1 mol $e^- \Longleftrightarrow 9.65 \times 10^4$ C,

$$2.40 \times 10^3 \text{ C} \times \frac{1 \text{ mol } e^-}{9.65 \times 10^4 \text{ C}} = 0.02487 \text{ mol } e^-$$

□ In stepwise calculations we always carry one or more extra significant figures until the final result to minimize rounding errors.

Next, we use the relationship between mol e^- and mol Cu from the balanced half-reaction along with the atomic mass of copper.

$$0.02487 \text{ mol } e^- \times \left(\frac{1 \text{ mol Cu}}{2 \text{ mol } e^-}\right) \times \left(\frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}}\right) = 0.7903 \text{ g Cu}$$

With proper rounding, the electrolysis will deposit 0.790 g of copper on the cathode.

We could have combined all the steps in a single calculation by stringing together the various conversion factors and using the factor-label method to cancel units.

$$2.00 \text{ A} \times 20.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{1 \text{ mol } e^-}{9.65 \times 10^4 \text{ A s}} \times \frac{1 \text{ mol Cu}}{2 \text{ mol } e^-} \times \frac{63.55 \text{ g Cu}}{1 \text{ mol Cu}} = 0.790 \text{ g Cu}$$

IS THE ANSWER REASONABLE? As before, we round all numbers to one significant figure to estimate the answer.

$$\text{g Cu} = 2.00 \text{ A} \times 20.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{1 \text{ mol } e^-}{10 \times 10^4 \text{ A s}} \times \frac{1 \text{ mol Cu}}{2 \text{ mol } e^-} \times \frac{60 \text{ g Cu}}{1 \text{ mol Cu}}$$

$$= \frac{40 \times 3600}{200000} = \frac{40 \times 0.36}{20} = 0.72 \text{ g Cu}$$

This is very close to our answer and we are even more confident that the calculation was correct when we check the cancellation of units.

E X A M P L E   1 9 . 1 5

Calculations Related to Electrolysis

Electrolysis provides a useful way to deposit a thin metallic coating on an electrically conducting surface. This technique is called electroplating. How much time would it take in minutes to deposit 0.500 g of metallic nickel on a metal object using a current of 3.00 A? The nickel is reduced from the +2 oxidation state.

ANALYSIS: We need an equation for the reduction. Because the nickel is reduced to the free metal from the +2 state, we can write

$$Ni^{2+} + 2e^- \longrightarrow Ni(s)$$
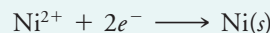
This gives the relationship

$$1 \text{ mol Ni} \Leftrightarrow 2 \text{ mol } e^-$$
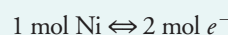
We wish to deposit 0.500 g of Ni, which we can convert to moles. Then we can calculate the number of moles of electrons required, which in turn is used with the tool for the Faraday constant to determine the number of coulombs required. Another of our tools tells us that this is the product of amperes and seconds, so we can calculate the time needed to deposit the metal. The calculation can be diagrammed as follows.
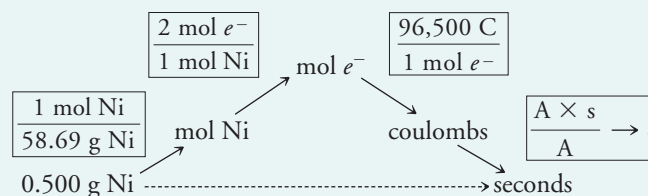
SOLUTION: First, we calculate the number of moles of electrons required (keeping at least one extra significant figure).

$$0.500 \text{ g Ni} \times \left(\frac{1 \text{ mol Ni}}{58.69 \text{ g Ni}} \right) \times \left(\frac{2 \text{ mol } e^-}{1 \text{ mol Ni}} \right) = 0.01704 \text{ mol } e^-$$

Then we calculate the number of coulombs needed.

$$0.01704 \text{ mol } e^- \times \left(\frac{9.65 \times 10^4 \text{ C}}{1 \text{ mol } e^-} \right) = 1.644 \times 10^3 \text{ C} = 1.644 \times 10^3 \text{ A s}$$

◻ Once we've calculated the number of coulombs required, we can calculate the time required if we know the current, or the current needed to perform the electrolysis in a given time.

This tells us that the product of current multiplied by time equals 1.644×10^3 A s. The current is 3.00 A. Dividing 1.644×10^3 A s by 3.00 A gives the time required in seconds, which we then convert to minutes.

$$\left(\frac{1.644 \times 10^3 \text{ A s}}{3.00 \text{ A}} \right) \times \left(\frac{1 \text{ min}}{60 \text{ s}} \right) = 9.133 \text{ min}$$

Properly rounded, this becomes 9.13 min. We could also have combined the calculations in a single string of conversion factors.

$$0.500 \text{ g Ni} \times \frac{1 \text{ mol Ni}}{58.69 \text{ g Ni}} \times \frac{2 \text{ mol } e^-}{1 \text{ mol Ni}} \times \frac{9.65 \times 10^4 \text{ A s}}{1 \text{ mol } e^-} \times \frac{1}{3.00 \text{ A}} \times \frac{1 \text{ min}}{60 \text{ s}} = 9.13 \text{ min}$$

IS THE ANSWER REASONABLE? As in the preceding example, let's round all numbers to one digit:

$$0.500 \text{ g Ni} \times \frac{1 \text{ mol Ni}}{60 \text{ g Ni}} \times \frac{2 \text{ mol } e^-}{1 \text{ mol Ni}} \times \frac{10 \times 10^4 \text{ A s}}{1 \text{ mol } e^-} \times \frac{1}{3.00 \text{ A}} \times \frac{1 \text{ min}}{60 \text{ s}} = \frac{100000 \text{ min}}{3600 \times 3} = \frac{100000 \text{ min}}{10000} = 10 \text{ min}$$

This result, along with the proper cancellation of units, indicates our calculations and setup were correct.

Practice Exercise 24: How many moles of hydroxide ion will be produced at the cathode during the electrolysis of water with a current of 4.00 A for a period of 200 s? The cathode reaction is

$$2e^- + 2H_2O \longrightarrow H_2 + 2OH^-$$

(Hint: The stepwise diagram in Example 19.15 will be helpful.)

Practice Exercise 25: How many minutes will it take for a current of 10.0 A to deposit 3.00 g of gold from a solution of $AuCl_3$?

Practice Exercise 26: What current must be supplied to deposit 3.00 g of gold from a solution of $AuCl_3$ in 20.0 min?

Practice Exercise 27: Suppose the solutions in the galvanic cell depicted in Figure 19.2 (page 771) have a volume of 125 mL and suppose the cell is operated for a period of 1.25 hr with a constant current of 0.100 A flowing through the external circuit. By how much will the concentration of the copper ion increase during that time?

19.8 PRACTICAL APPLICATIONS OF ELECTROCHEMISTRY

Electrochemistry has many applications both in science and in our everyday lives. In this limited space, we can only touch on some of the more common and important examples.
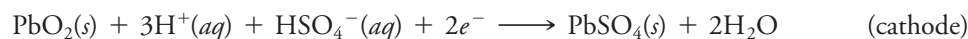
Batteries are practical examples of galvanic cells

One of the most familiar uses of galvanic cells, popularly called *batteries*, is the generation of portable electrical energy.[8] These devices are classified as being either **primary cells** (cells not designed to be recharged; they are discarded after their energy is depleted) or **secondary cells** (cells designed for repeated use; they are able to be recharged).
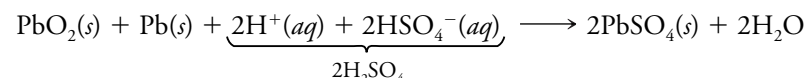
The lead storage battery is used in most automobiles

The common **lead storage battery** used to start an automobile is composed of a number of secondary cells, each having a potential of about 2 V, that are connected in series so that their voltages are additive. Most automobile batteries contain six such cells and give about 12 V, but 6, 24, and 32 V batteries are also available.

A typical lead storage battery is illustrated in Figure 19.14. The anode of each cell is composed of a set of lead plates, the cathode consists of another set of plates that hold a coating of PbO_2, and the electrolyte is sulfuric acid. When the battery is discharging the electrode reactions are
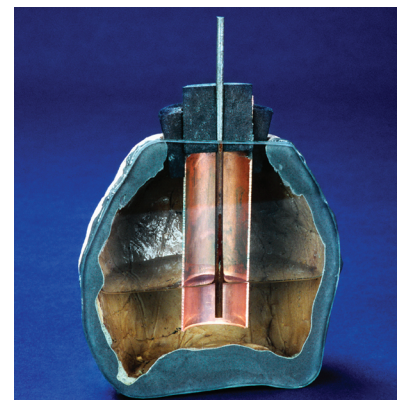
$$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O \qquad \text{(cathode)}$$

$$Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2e^- \quad \text{(anode)}$$

The net reaction taking place in each cell is

$$PbO_2(s) + Pb(s) + \underbrace{2H^+(aq) + 2HSO_4^-(aq)}_{2H_2SO_4} \longrightarrow 2PbSO_4(s) + 2H_2O$$

As the cell discharges, the sulfuric acid concentration decreases, which causes the density of the electrolyte to drop. The state of charge of the battery can be monitored with a **hydrometer,** which consists of a rubber bulb that is used to draw the battery fluid into


The oldest known electric battery in existence, discovered in 1938 in Baghdad, Iraq, consists of a copper tube surrounding an iron rod. If filled with an acidic liquid such as vinegar, the cell could produce a small electric current. *(Smith College Museum of Ancient Inventions.)*
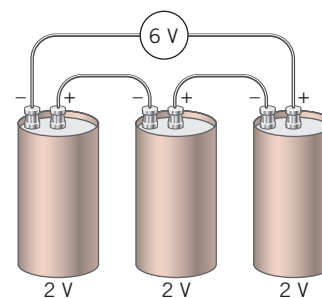
If three 2 volt cells are connected in series, their voltages are additive to provide a total of 6 volts. In today's autos, 12 volt batteries containing six cells are the norm.

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[8] Strictly speaking, a cell is a single electrochemical unit consisting of a cathode and an anode. A battery is a collection of cells connected in series.

FIG. 19.14 **Lead storage battery.** A 12 volt lead storage battery, such as those used in most automobiles, consists of six cells like the one shown here. Notice that the anode and cathode each consist of several plates connected together. This allows the cell to produce the large currents necessary to start a car.
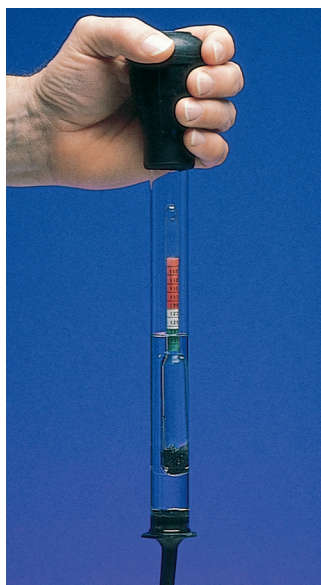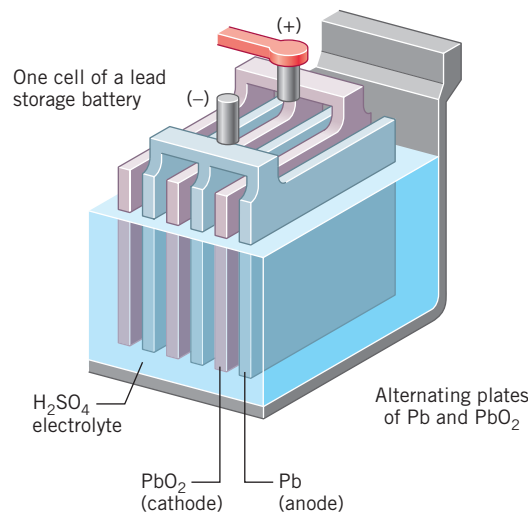
FIG. 19.15 **A battery hydrometer.** Battery acid is drawn into the glass tube. The depth to which the float sinks is inversely proportional to the concentration of the acid and, therefore, to the state of charge of the battery. *(OPC, Inc.)*

a glass tube containing a float (see Figure 19.15). The depth to which the float sinks is inversely proportional to the density of the liquid—the deeper the float sinks, the lower is the density of the acid and the weaker is the charge on the battery. The narrow neck of the float is usually marked to indicate the state of charge of the battery.

The principal advantage of the lead storage battery is that the cell reactions that occur spontaneously during discharge can be reversed by the application of a voltage from an external source. In other words, the battery can be recharged by electrolysis. The reaction for battery recharge is

$$2PbSO_4(s) + 2H_2O \xrightarrow{\text{electrolysis}} PbO_2(s) + Pb(s) + 2H^+(aq) + 2HSO_4^-(aq)$$
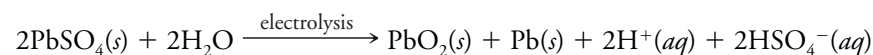
Improper recharging of lead–acid batteries can produce potentially explosive H_2 gas. Most modern lead storage batteries use a lead–calcium alloy as the anode. That reduces the need to have the individual cells vented, and the battery can be sealed, thereby preventing spillage of the corrosive electrolyte.

The zinc–manganese dioxide cell is our familiar dry cell

The ordinary, relatively inexpensive 1.5 V dry cell is the **zinc–manganese dioxide cell,** or **Leclanché cell** (named after its inventor George Leclanché). It is a primary cell used to power flashlights, remote TV, VCR, and DVD controllers, toys, and the like, but it is not really dry (see Figure 19.16). Its outer shell is made of zinc, which serves as the anode. The cathode—the positive terminal of the battery—consists of a carbon (graphite) rod surrounded by a moist paste of graphite powder, manganese dioxide, and ammonium chloride.

The anode reaction is simply the oxidation of zinc.

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \qquad \text{(anode)}$$
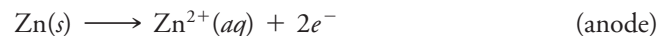
The cathode reaction is complex, and a mixture of products is formed. One of the major reactions is

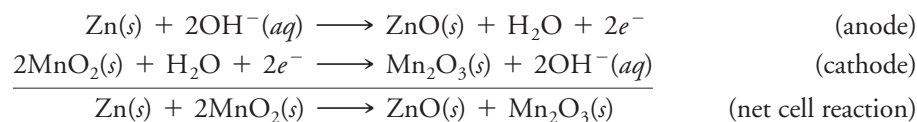$$2MnO_2(s) + 2NH_4^+(aq) + 2e^- \longrightarrow Mn_2O_3(s) + 2NH_3(aq) + H_2O \quad \text{(cathode)}$$

The ammonia that forms at the cathode reacts with some of the Zn^{2+} produced from the anode to form a complex ion, $Zn(NH_3)_4^{2+}$. Because of the complexity of the cathode half-cell reaction, no simple overall cell reaction can be written.

A more popular version of the Leclanché battery uses a basic, or *alkaline* electrolyte and is called an **alkaline battery** or **alkaline dry cell.** It too uses Zn and MnO_2 as reactants, but under basic conditions (Figure 19.17). The half-cell reactions are
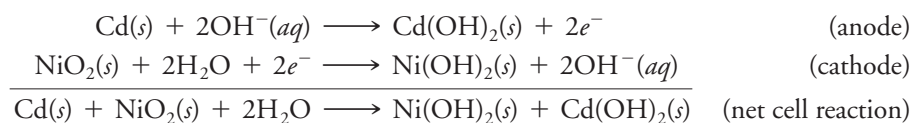
◻ The alkaline battery is also a primary cell.
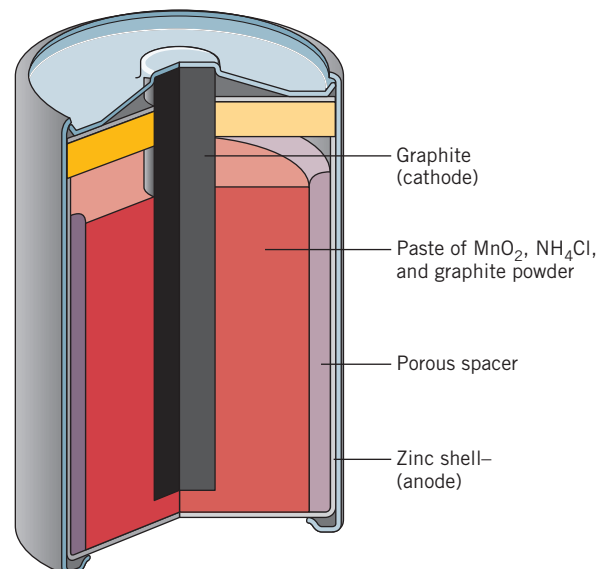
FIG. 19.16 A cutaway view of a zinc–carbon dry cell (Leclanché cell).

$$Zn(s) + 2OH^-(aq) \longrightarrow ZnO(s) + H_2O + 2e^- \quad \text{(anode)}$$
$$2MnO_2(s) + H_2O + 2e^- \longrightarrow Mn_2O_3(s) + 2OH^-(aq) \quad \text{(cathode)}$$
$$\overline{Zn(s) + 2MnO_2(s) \longrightarrow ZnO(s) + Mn_2O_3(s)} \quad \text{(net cell reaction)}$$

and the voltage is about 1.54 V. It has a longer shelf-life and is able to deliver higher currents for longer periods than the less expensive zinc–carbon cell.

The nickel–cadmium storage cell is rechargeable

The **nickel–cadmium storage cell,** or **nicad battery,** is a secondary cell that produces a potential of about 1.4 V, which is slightly lower than that of the zinc–carbon cell. The electrode reactions in the cell during discharge are

$$Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^- \quad \text{(anode)}$$
$$NiO_2(s) + 2H_2O + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq) \quad \text{(cathode)}$$
$$\overline{Cd(s) + NiO_2(s) + 2H_2O \longrightarrow Ni(OH)_2(s) + Cd(OH)_2(s)} \quad \text{(net cell reaction)}$$
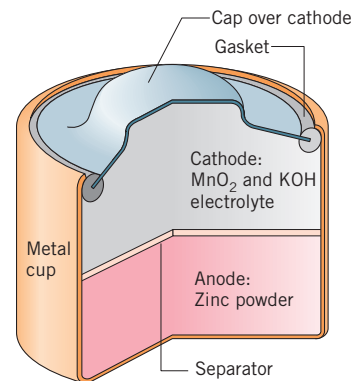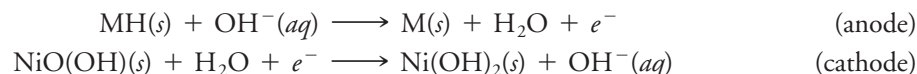
The nickel–cadmium battery can be recharged, in which case the anode and cathode reactions above are reversed to remake the reactants. The battery also can be sealed to prevent leakage, which is particularly important in electronic devices.

Nickel–cadmium batteries work especially well in applications such as portable power tools, CD players, and even electric cars. They have a high **energy density** (available energy per unit volume), they are able to release the energy quickly, and they can be rapidly recharged.

Nickel–metal hydride batteries store more energy than nicad batteries

These secondary cells, which are often referred to as Ni–MH batteries, have been used extensively in recent years to power devices such as cell phones, camcorders, and even electric vehicles. They are similar in many ways to the alkaline nickel–cadmium cells discussed above, except for the anode reactant, which is hydrogen. This is possible because certain metal alloys [e.g., $LaNi_5$ (an alloy of lanthanum and nickel) and Mg_2Ni (an alloy of magnesium and nickel)] have the ability to absorb and hold substantial amounts of hydrogen, and that the hydrogen can be made to participate in reversible electrochemical reactions. The term *metal hydride* is used to describe the hydrogen-holding alloy.

The cathode in the Ni–MH cell is NiO(OH), a compound of nickel in the +3 oxidation state, and the electrolyte is a solution of KOH. Using the symbol MH to stand for the metal hydride, the reactions in the cell during discharge are

$$MH(s) + OH^-(aq) \longrightarrow M(s) + H_2O + e^- \quad \text{(anode)}$$
$$NiO(OH)(s) + H_2O + e^- \longrightarrow Ni(OH)_2(s) + OH^-(aq) \quad \text{(cathode)}$$

FIG. 19.17 A simplified diagram of an alkaline zinc–carbon dry cell.

☐ If a battery can supply large amounts of energy and is contained in a small package, it will have a desirably high energy density.

☐ There are compounds of hydrogen with metals such as sodium that actually contain the *hydride ion*, H^-. The metal "hydrides" described here are not of that type.

The overall cell reaction is

$$MH(s) + NiO(OH)(s) \longrightarrow Ni(OH)_2(s) + M(s) \qquad E°_{cell} = 1.35 \text{ V}$$

When the cell is recharged, the reactions are reversed.

The principal advantage of the Ni–MH cell over the Ni–Cd cell is that it can store about 50% more energy in the same volume. This means, for example, that comparing cells of the same size and weight, a nickel–metal hydride cell can power a laptop computer or a cell phone about 50% longer than a nickel–cadmium cell.

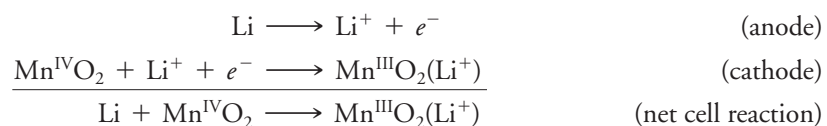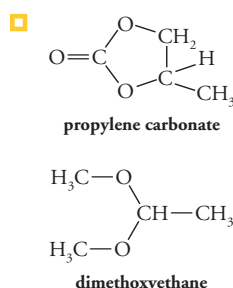### Lithium batteries combine high energy with low weight

Lithium has the most negative standard reduction potential of any metal (Table 19.1), so it has a lot of appeal as an anode material. Furthermore, lithium is a very lightweight metal, so a cell employing lithium as a reactant would also be lightweight. The major problem with using lithium in a galvanic cell is that the metal reacts vigorously with water to produce hydrogen gas and lithium hydroxide.

$$2Li(s) + 2H_2O \longrightarrow 2LiOH(aq) + H_2(g)$$
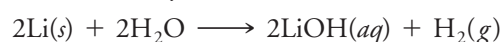
Therefore, to employ lithium in a galvanic cell scientists had to find a way to avoid aqueous electrolytes. This became possible in the 1970s with the introduction of organic solvents and solvent mixtures that were able dissolve certain lithium salts and thereby serve as electrolytes.

Today's lithium batteries fall into two categories, primary batteries that can be used once and then discarded when fully discharged, and rechargeable cells.

One of the most common nonrechargeable cells is the **lithium–manganese dioxide battery,** which accounts for about 80% of all primary lithium cells. This cell uses a solid lithium anode and a cathode made of heat-treated MnO_2. The electrolyte is a mixture of propylene carbonate and dimethoxyethane (see structures in the margin) containing a dissolved lithium salt such as $LiClO_4$. The cell reactions are as follows (superscripts are the oxidation numbers of the manganese):

$$Li \longrightarrow Li^+ + e^- \qquad \text{(anode)}$$

$$\underline{Mn^{IV}O_2 + Li^+ + e^- \longrightarrow Mn^{III}O_2(Li^+)} \qquad \text{(cathode)}$$

$$Li + Mn^{IV}O_2 \longrightarrow Mn^{III}O_2(Li^+) \qquad \text{(net cell reaction)}$$

This cell produces a voltage of about 3.4 V, which is more than twice that of an alkaline dry cell, and because of the light weight of the lithium, it produces more than twice as much energy for a given weight. These cells are used in applications that require a higher current drain or energy pulses (e.g., photoflash).

Lithium ion cells are rechargeable

Rechargeable lithium batteries found in many cell phones, digital cameras, and laptop computers do not contain metallic lithium. They are called **lithium ion cells** and use lithium ions instead. In fact, the cell's operation doesn't actually involve true oxidation and reduction. Instead, it uses the transport of Li^+ ions through the electrolyte from one electrode to the other accompanied by the transport of electrons through the external circuit to maintain charge balance. Here's how it works.

It was discovered that Li^+ ions are able to slip between layers of atoms in certain crystals such as graphite[9] and $LiCoO_2$ (a process called **intercalation**). When the cell is constructed, it is in its "uncharged" state, with no Li^+ ions between the layers of carbon atoms in the graphite. When the cell is charged (Figure 19.18a), Li^+ ions leave $LiCoO_2$ and travel through the electrolyte to the graphite (represented below by the formula C_6).

Initial charging:

$$LiCoO_2 + C_6 \longrightarrow Li_{1-x}CoO_2 + Li_xC_6$$
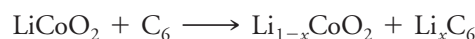
When the cell spontaneously discharges to provide electrical power (Figure 19.18b), Li^+ ions move back through the electrolyte to the cobalt oxide while electrons move through

propylene carbonate

dimethoxyethane

☐ Pronounced in-*ter*-ca-*la*-tion. Rhymes with *percolation*.

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[9] Graphite is one of the forms of elemental carbon and consists of layers of joined benzene-like rings.

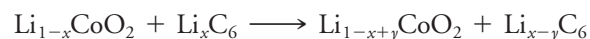**Charge cycle**
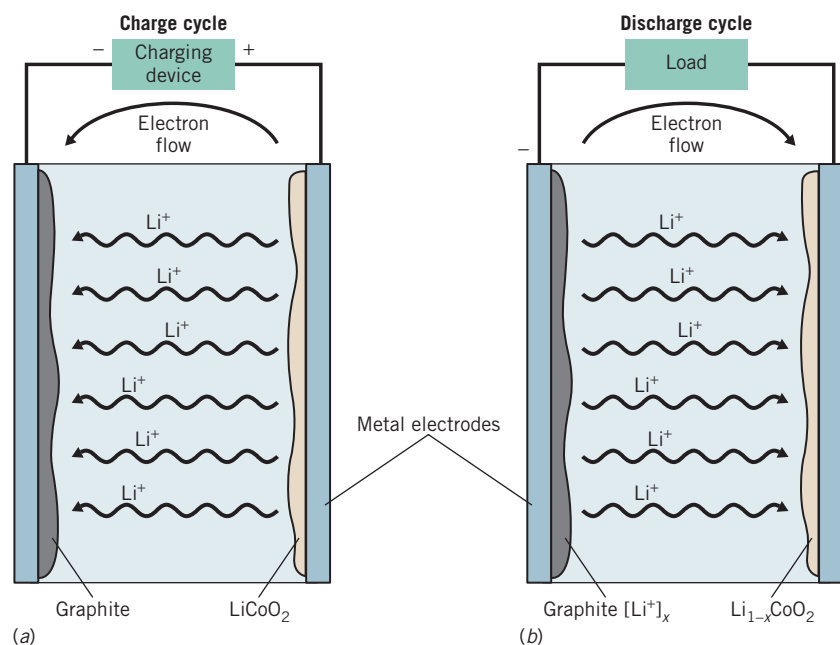
Discharge cycle

FIG. 19.18 **Lithium ion cell.** (*a*) During the charging cycle, an external voltage forces electrons through the external circuit and causes lithium ions to travel from the $LiCoO_2$ electrode to the graphite electrode. (*b*) During discharge, the lithium ions spontaneously migrate back to the $LiCoO_2$ electrode, and electrons flow through the external circuit to balance the charge.

the external circuit from the graphite electrode to the cobalt oxide electrode. If we represent the amount of Li^+ transferring by *y*, the discharge "reaction" is

Discharge:

$$Li_{1-x}CoO_2 + Li_xC_6 \longrightarrow Li_{1-x+y}CoO_2 + Li_{x-y}C_6$$

Thus, the charging and discharging cycles simply sweep Li^+ ions back and forth between the two electrodes, with the electrons flowing through the external circuit to keep the charge in balance.

Fuel cells operate with a continuous supply of reactants

The galvanic cells we've discussed until now can only produce power for a limited time because the electrode reactants are eventually depleted. Fuel cells are different; they are electrochemical cells in which the electrode reactants are supplied continuously and are able to operate without theoretical limit as long as the supply of reactants is maintained. This makes fuel cells an attractive source of power where long-term generation of electrical energy is required.

Figure 19.19 illustrates an early design of a hydrogen–oxygen **fuel cell.** The electrolyte, a hot (~200 °C) concentrated solution of potassium hydroxide in the center
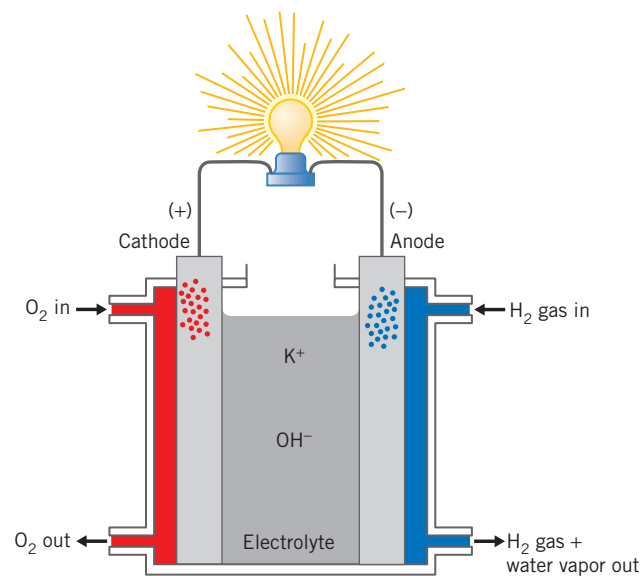
FIG. 19.19 **A hydrogen–oxygen fuel cell.**

compartment, is in contact with two porous electrodes that contain a catalyst (usually platinum) to facilitate the electrode reactions. Gaseous hydrogen and oxygen under pressure are circulated so as to come in contact with the electrodes. At the cathode, oxygen is reduced.

$$O_2(g) + 2H_2O + 4e^- \longrightarrow 4OH^-(aq) \qquad \text{(cathode)}$$

At the anode, hydrogen is oxidized to water.

$$H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O + 2e^- \qquad \text{(anode)}$$

Part of the water formed at the anode leaves as steam mixed with the circulating hydrogen gas. The net cell reaction, after making electron loss equal to electron gain, is

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O \qquad \text{(net cell reaction)}$$

Hydrogen–oxygen fuel cells are an attractive alternative to gasoline powered engines in part because they are essentially pollution-free—the only product of the reaction is harmless water. Fuel cells are also quite thermodynamically efficient, converting as much as 75% of the available energy to useful work, compared to approximately 25 to 30% for gasoline and diesel engines. Among the major obstacles are the energy costs of generating the hydrogen fuel and problems in providing storage and distribution of the highly flammable H_2.

Electrolysis has many industrial applications

Besides being a useful tool in the chemistry laboratory, electrolysis has many important industrial applications. Here we will briefly examine the chemistry of electroplating and the production of some of our most common chemicals.

Electroplating deposits metal on a surface

Electroplating, which was mentioned in Examples 19.14 and 19.15, is a procedure in which electrolysis is used to apply a thin (generally 0.03 to 0.05 mm thick) ornamental or protective coating of one metal over another. It is a common technique for improving the appearance and durability of metal objects. For instance, a thin, shiny coating of metallic chromium is applied over steel objects to make them attractive and to prevent rusting.
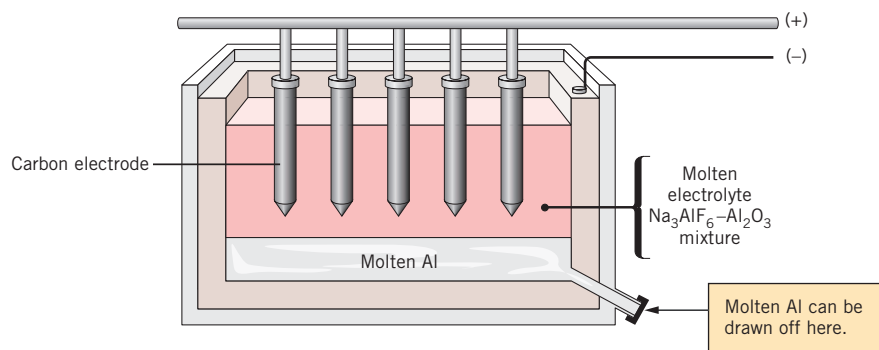
The exact composition of the electroplating bath varies, depending on the metal to be deposited, and it can affect the appearance and durability of the finished surface. For example, silver deposited from a solution of silver nitrate ($AgNO_3$) does not stick to other metal surfaces very well. However, if it is deposited from a solution of silver cyanide containing $Ag(CN)_2^-$, the coating adheres well and is bright and shiny. Other metals that are electroplated from a cyanide bath are gold and cadmium. Nickel, which can also be applied as a protective coating, is plated from a nickel sulfate solution, and chromium is plated from a chromic acid (H_2CrO_4) solution.

This motorcycle sparkles with chrome plating that was deposited by electrolysis. The shiny hard coating of chromium is both decorative and a barrier to corrosion. *(Syracuse Newspapers/ The Image Works.)*

□ Aluminum is used today as a structural metal, in alloys, and in such products as aluminum foil, electrical wire, window frames, and kitchen pots and pans.

Aluminum is produced from aluminum oxide

Aluminum is a useful but highly reactive metal. It is so difficult to reduce that ordinary metallurgical methods for obtaining it do not work. Early efforts to produce aluminum by electrolysis failed because its anhydrous halide salts (those with no water of hydration) are difficult to prepare and are volatile, tending to evaporate rather than melt. On the other hand, its oxide, Al_2O_3, has such a high melting point (over 2000 °C) that no practical method of melting it could be found.
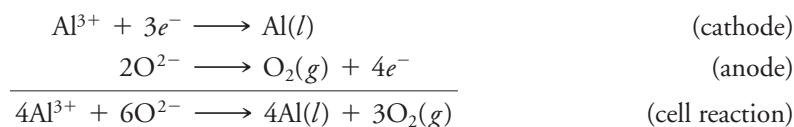
In 1886, Charles M. Hall discovered that Al_2O_3 dissolves in the molten form of a mineral called cryolite, Na_3AlF_6, to give a conducting mixture with a relatively low melting point from which aluminum could be produced electrolytically. The process was also discovered by Paul Héroult in France at nearly the same time, and today this method for producing aluminum is usually called the **Hall–Héroult process** (see Figure 19.20). Purified aluminum oxide, which is obtained from an ore called *bauxite*, is dissolved in molten cryolite in which the oxide dissociates to give Al^{3+} and O^{2-} ions. At the cathode,

Molten
electrolyte
Na_3AlF_6–Al_2O_3
mixture

Molten Al

Molten Al can be
drawn off here.

FIG. 19.20 **Production of aluminum by electrolysis.** In the apparatus used to produce aluminum electrolytically by the Hall–Héroult process, Al_2O_3 is dissolved in molten cryolite, Na_3AlF_6. Al^{3+} is reduced to metallic Al and O^{2-} is oxidized to O_2, which reacts with the carbon anodes to give CO_2. Periodically, molten aluminum is drawn off at the bottom of the cell and additional Al_2O_3 is added to the cryolite. The carbon anodes also must be replaced from time to time as they are consumed by their reaction with O_2.

aluminum ions are reduced to produce the free metal, which forms as a layer of molten aluminum below the less dense solvent. At the carbon anodes, oxide ion is oxidized to give free O_2.

$$Al^{3+} + 3e^- \longrightarrow Al(l) \qquad \text{(cathode)}$$
$$2O^{2-} \longrightarrow O_2(g) + 4e^- \qquad \text{(anode)}$$
$$\overline{4Al^{3+} + 6O^{2-} \longrightarrow 4Al(l) + 3O_2(g)} \qquad \text{(cell reaction)}$$

The oxygen formed at the anode attacks the carbon electrodes (producing CO_2), so the electrodes must be replaced frequently.

The production of aluminum consumes enormous amounts of electrical energy and is therefore very costly, not only in terms of dollars but also in terms of energy resources. For this reason, recycling of aluminum has a high priority as we seek to minimize our use of energy.

Sodium is made by electrolysis of sodium chloride

Sodium is prepared by the electrolysis of molten sodium chloride (see Section 19.6). The metallic sodium and the chlorine gas that form must be kept apart or they will react violently and re-form NaCl. A specialized apparatus called a **Downs cell** accomplishes this separation.

Both sodium and chlorine are commercially important. Chlorine is used largely to manufacture plastics such as polyvinyl chloride (PVC), many solvents, and industrial chemicals. A small percentage of the annual chlorine production is used to chlorinate drinking water.

Sodium has been used in the manufacture of tetraethyl lead, an octane booster for gasoline that has been phased out in the United States but which is still used in many other countries. Sodium is also used in the production of energy efficient sodium vapor lamps, which give street lights and other commercial lighting a bright yellow-orange color.

Refining of copper makes it suitable for electrical wire

When copper is first obtained from its ore, it is about 99% pure. The impurities—mostly silver, gold, platinum, iron, and zinc—decrease the electrical conductivity of the copper enough that even 99% pure copper must be further refined before it can be used in electrical wire.

The impure copper is used as the anode in an electrolysis cell that contains a solution of copper sulfate and sulfuric acid as the electrolyte (see Figure 19.21). The cathode is a thin sheet of very pure copper. When the cell is operated at the correct voltage, only copper and impurities more easily oxidized than copper (iron and zinc) dissolve at the anode. The less active metals simply fall off the electrode and settle to the bottom of the container. At the cathode, copper ions are reduced, but the zinc ions and iron ions remain

☐ The spectacular reaction of chlorine and sodium is captured in Figure 2.24 on page 62.

☐ PVC is used to make a large variety of products, from raincoats to wire insulation to pipes and conduits for water and sanitary systems. In the United States, the annual demand for PVC plastics is about 15 billion pounds.

FIG. 19.21 **Purification of copper by electrolysis.** Impure copper anodes dissolve and pure copper is deposited on the cathodes. Metals less easily oxidized than copper settle to the bottom of the apparatus as "anode mud," while metals less easily reduced than copper remain in solution.
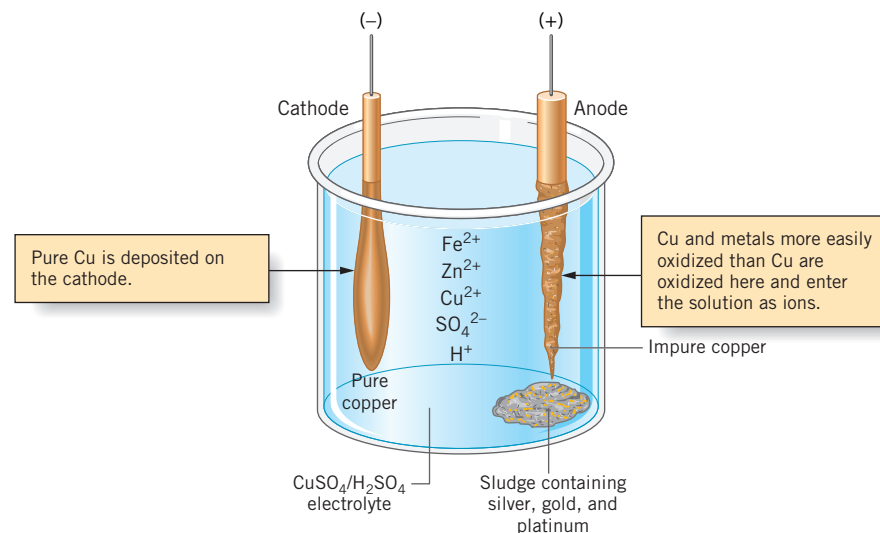
◻ Copper refining provides one-fourth of the silver and one-eighth of the gold produced annually in the United States.

in solution because they are more difficult to reduce than copper. Gradually, the impure copper anode dissolves and the copper cathode, about 99.96% pure, grows larger. The accumulating sludge—called anode mud—is removed periodically, and the value of the silver, gold, and platinum recovered from it virtually pays for the entire refining operation.

Electrolysis of brine produces several important chemicals

One of the most important commercial electrolysis reactions is the electrolysis of concentrated aqueous sodium chloride solutions called **brine.** At the cathode, water is much more easily reduced than sodium ion, so H_2 forms.

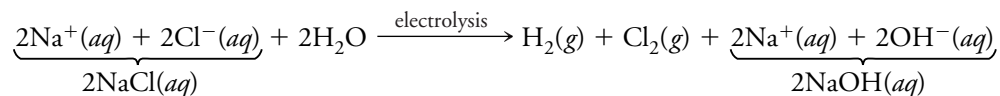$$2H_2O(l) + 2e^- \longrightarrow H_2(g) + 2OH^-(aq) \qquad \text{(cathode)}$$
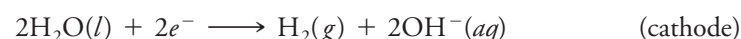
As we noted earlier, even though water is more easily oxidized than chloride ion, complicating factors at the electrodes actually allow chloride ion to be oxidized instead. At the anode, therefore, we observe the formation of Cl_2.

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e^- \qquad \text{(anode)}$$
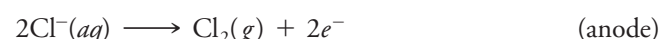
The net cell reaction is therefore

$$2Cl^-(aq) + 2H_2O(l) \longrightarrow H_2(g) + Cl_2(g) + 2OH^-(aq)$$

If we include the sodium ion, already in the solution as a spectator ion and not involved in the electrolysis directly, we can see why this is such an important reaction.


Copper refining. Copper cathodes, 99.96% pure, are pulled from the electrolytic refining tanks at Kennecott's Utah copper refinery. It takes about 28 days for the impure copper anodes to dissolve and deposit the pure metal on the cathodes. *(Courtesy ASARCO, Inc.)*

$$\underbrace{2Na^+(aq) + 2Cl^-(aq)}_{2NaCl(aq)} + 2H_2O \xrightarrow{\text{electrolysis}} H_2(g) + Cl_2(g) + \underbrace{2Na^+(aq) + 2OH^-(aq)}_{2NaOH(aq)}$$

Thus, the electrolysis converts inexpensive salt to valuable chemicals: H_2, Cl_2, and NaOH. The hydrogen is used to make other chemicals, including hydrogenated vegetable oils. The chlorine is used for the purposes mentioned earlier. Among the uses of sodium hydroxide, one of industry's most important bases, are the manufacture of soap and paper, the neutralization of acids in industrial reactions, and the purification of aluminum ores.

In the industrial electrolysis of brine, it is necessary to capture the H_2 and Cl_2 separately to prevent them from mixing and reacting (explosively). Second, the NaOH from the reaction is contaminated with unreacted NaCl. Third, if Cl_2 is left in the presence of NaOH, the solution becomes contaminated by hypochlorite ion (OCl^-), which forms by the reaction of Cl_2 with OH^-.

◻ Sodium hydroxide is commonly known as *lye* or *caustic soda.*

$$Cl_2(g) + 2OH^-(aq) \longrightarrow Cl^-(aq) + OCl^-(aq) + H_2O$$
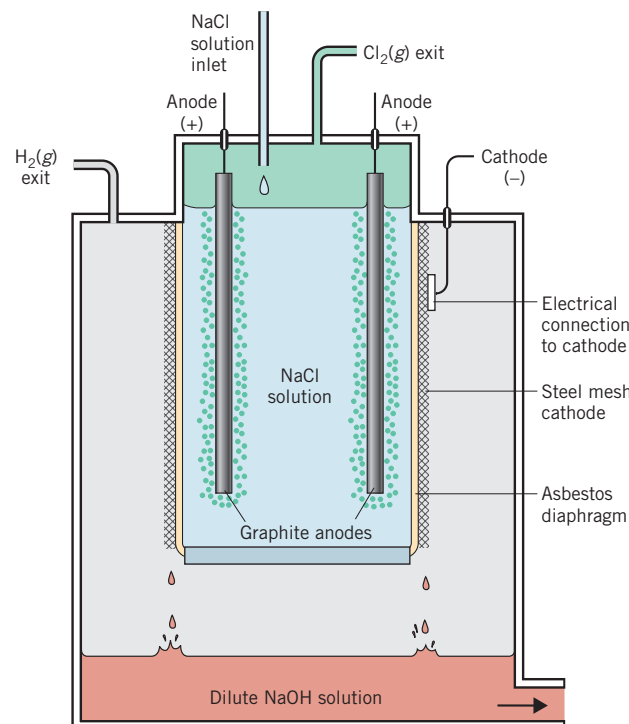
FIG. 19.22 **A diaphragm cell used in the commercial production of NaOH by the electrolysis of aqueous NaCl.** This is a cross section of a cylindrical cell in which the NaCl solution is surrounded by an asbestos diaphragm supported by a steel mesh cathode. (From J. E. Brady and G. E. Humiston, *General Chemistry: Principles and Structure*, 4th ed. Copyright © 1986, John Wiley & Sons, New York. Used by permission.)

In one manufacturing operation, however, the Cl_2 is not removed as it forms, and its reaction with hydroxide ion is used to manufacture aqueous sodium hypochlorite. For this purpose, the solution is stirred vigorously during the electrolysis so that very little Cl_2 escapes. As a result, a stirred solution of NaCl gradually changes during electrolysis to a solution of NaOCl, a dilute (5%) solution of which is sold as liquid laundry bleach (e.g., Clorox).

Most of the pure NaOH manufactured today is made in an apparatus called a **diaphragm cell.** The design varies somewhat, but Figure 19.22 illustrates its basic features. The cell consists of an iron wire mesh cathode that encloses a porous asbestos shell—the diaphragm. The NaCl solution is added to the top of the cell and seeps slowly through the diaphragm. When it contacts the iron cathode, hydrogen is evolved and is pumped out of the surrounding space. The solution, now containing dilute NaOH, drips off the cell into the reservoir below. Meanwhile, within the cell, chlorine is generated at the anodes dipping into the NaCl solution. Because there is no OH^- in this solution, the Cl_2 can't react to form OCl^- ion and simply bubbles out of the solution and is captured.

SUMMARY

Galvanic Cells. A **galvanic cell** is composed of two **half-cells,** each containing an **electrode** in contact with an electrolyte reactant. A spontaneous redox reaction is thus divided into separate oxidation and reduction half-reactions, with the electron transfer occurring through an external electrical circuit. Reduction occurs at the **cathode;** oxidation occurs at the **anode.** In a galvanic cell, the cathode is positively charged and the anode is negatively charged. The half-cells must be connected electrolytically by a **salt bridge** to complete the electrical circuit, which permits electrical neutrality to be maintained by allowing cations to move toward the cathode and anions toward the anode.

The **potential** (expressed in volts) produced by a cell is equal to the **standard cell potential** when all ion concentrations are 1.00 *M* and the partial pressures of any gases involved equal 1.00 atm and the temperature is 25.0 °C. The **standard cell potential** is the difference between the **standard reduction potentials** of the half-cells. In the spontaneous reaction, the half-cell with the higher standard reduction potential undergoes reduction and forces the other to undergo oxidation. The standard reduction potentials of isolated half-cells can't be measured, but values are assigned by choosing the **hydrogen electrode** as a reference electrode; its standard reduction potential is assigned a value of exactly 0 V. Species more easily reduced than H^+ have positive standard reduction potentials; those less easily reduced have negative standard reduction potentials. Standard reduction potentials can be used to predict the cell reaction. They can also be used to

predict spontaneous redox reactions not occurring in galvanic cells and to predict whether or not a given reaction is spontaneous. Often, they can be used to determine the products of electrolysis reactions. Standard reduction potentials are used to calculate E°_{cell}. Since reduction potentials under nonstandard conditions are often numerically close to standard reduction potentials, we can usually use standard reduction potentials to make predictions about reactions with nonstandard conditions. The predictions above about spontaneous reactions, cell reactions, electrolysis products, and reactions outside of galvanic cells are usually valid under non-standard conditions also.

Thermodynamics and Cell Potentials. The values of ΔG° and K_{c} for a reaction can be calculated from E°_{cell}. They all involve the **faraday, $\mathcal{F}$,** a constant equal to the number of **coulombs (C)** of charge per mole of electrons (1 $\mathcal{F}$ = 96,500 C/mol e^-). The Nernst equation relates the cell potential to the standard cell potential and the reaction quotient. It allows the cell potential to be calculated for ion concentrations other than 1.00 M. The important equations are summarized as

$$\Delta G^{\circ} = -n\mathcal{F}E^{\circ}_{\text{cell}} = -RT \ln K_{\text{c}}$$

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{RT}{n\mathcal{F}} \ln Q$$

Electrolysis. In an **electrolytic cell,** a flow of electricity causes an otherwise nonspontaneous reaction to occur. A negatively charged **cathode** causes reduction of one reactant and a positively charged **anode** causes oxidation of another. Ion movement instead of electron transport occurs in the electrolyte. The electrode reactions are determined by which species is most easily reduced and which is most easily oxidized, but in aqueous solutions complex surface effects at the electrodes can alter the natural order.

In the electrolysis of water, an electrolyte must be present to maintain electrical neutrality at the electrodes.

Quantitative Aspects of Electrochemical Reactions. The product of current (**amperes**) and time (seconds) gives coulombs. This relationship and the half-reactions that occur at the anode or cathode permit us to relate the amount of chemical change to measurements of current and time.

Practical Galvanic Cells. The **lead storage battery** and the **nickel–cadmium (nicad) battery** are **secondary cells** and are rechargeable. The state of charge of the lead storage battery can be tested with a **hydrometer,** which measures the density of the sulfuric acid electrolyte. The **zinc–manganese dioxide cell** (the **Leclanché cell** or common dry cell) and the common **alkaline battery** (which uses essentially the same reactions as the less expensive dry cell) are **primary cells** and are not rechargeable. The rechargeable **nickel–metal hydride** (Ni–MH) battery uses hydrogen contained in a metal alloy as its anode reactant and has a higher **energy density** than the **nicad battery.** Primary **lithium–manganese dioxide cells** and rechargeable **lithium ion cells** produce a large cell potential and have a very high energy density. Lithium ion cells store and release energy by transferring lithium ions between electrodes where the Li^+ ions are **intercalated** between layers of atoms in the electrode materials. **Fuel cells,** which have high thermodynamic efficiencies, are able to provide continuous power because they consume fuel that can be fed continuously.

Applications of Electrolysis. **Electroplating,** the production of aluminum, the refining of copper, and the electrolysis of molten and aqueous sodium chloride are examples of practical applications of electrolysis.

T🔬OLS FOR PROBLEM SOLVING

The table below lists the concepts that you've learned in this chapter which can be applied as tools in solving problems. Study each one carefully so that you know what each is used for. When faced with solving a problem, recall what each tool does and consider whether it will be helpful in finding a solution. This will aid you in selecting the tools you need. If necessary, refer to this table when working on the Review Questions and Review Problems that follow.

Electrode reactions *(page 772)* Chemists have agreed to call the electrode at which oxidation occurs the anode. The cathode is the electrode where reduction occurs.

Standard reduction potentials relate to E°_{cell} In a galvanic cell, the difference between two standard reduction potentials equals the standard cell potential *(page 776)*.

$$E^{\circ}_{\text{cell}} = \left(\begin{array}{c} \text{standard reduction potential} \\ \text{of the substance reduced} \end{array} \right) - \left(\begin{array}{c} \text{standard reduction potential} \\ \text{of the substance oxidized} \end{array} \right)$$

Standard cell potentials are always positive and the reaction that gives us a positive standard cell potential will be a spontaneous reaction at standard state *(page 786)*. Comparing standard reduction potentials also lets us predict the electrode reactions in electrolysis *(page 800)*.

Standard cell potentials are related to thermodynamic quantities The relationship between the standard cell potential, E°_{cell}, and the standard free energy, ΔG°, is $\Delta G^{\circ} = -n\mathcal{F}E^{\circ}_{\text{cell}}$ *(page 788)*

The relationship between the standard cell potential, E°_{cell}, and the equilibrium constant, K_{c}, is $E^{\circ}_{\text{cell}} = \dfrac{RT}{n\mathcal{F}} \ln K_{\text{c}}$ *(page 789)*.

Standard cell potentials are also needed in the Nernst equation (below) to relate concentrations of species in galvanic cells to the cell potential.

Nernst equation *(page 790)* The Nernst equation lets us relate the cell potential, E_{cell}, the standard cell potential, E°_{cell}, and concentration data.

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{n\mathscr{F}} \ln Q$$

We can also calculate the concentration of a species in solution from E°_{cell} and a measured value for E_{cell}.

Faraday constant *(page 788)* Besides being a constant in the equations above, the Faraday constant allows us to relate coulombs (obtained from the product of current and time) to moles of chemical change in electrochemical reactions.

$$1 \mathscr{F} = 9.65 \times 10^4 \text{ C/mol } e^-$$

Coulombs *(page 802)* Coulombs, C, can be experimentally determined as the current, in amperes, A, multiplied by time, in seconds. Combined with the faraday, the moles of electrons can be determined.

$$1 \text{ coulomb (C)} = 1 \text{ ampere (A)} \times 1 \text{ second (s)}$$

QUESTIONS, PROBLEMS, AND EXERCISES

Answers to problems whose numbers are printed in color are given in Appendix B. More challenging problems are marked with asterisks. ILW = Interactive Learningware solution is available at www.wiley.com/college/brady. (OH) = an Office Hours video is available for this problem.

REVIEW QUESTIONS

Galvanic Cells

19.1 What is a *galvanic cell*? What is a *half-cell*?

19.2 What is the function of a *salt bridge*?

19.3 In the copper–silver cell, why must the Cu^{2+} and Ag^+ solutions be kept in separate containers?

19.4 Which redox processes take place at the anode and cathode in a galvanic cell? What is the sign of the electrical charges on the anode and cathode in a galvanic cell?

19.5 In a galvanic cell, do electrons travel from anode to cathode, or from cathode to anode? Explain.

19.6 Explain how the movement of the ions relative to the electrodes is the same in both galvanic and electrolytic cells.

19.7 Aluminum will displace tin from solution according to the equation $2Al(s) + 3Sn^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Sn(s)$. What would be the individual half-cell reactions if this were the cell reaction in a galvanic cell? Which metal would be the anode and which the cathode?

Cell Potentials and Reduction Potentials

19.8 What is the difference between a *cell potential* and a *standard cell potential*?

19.9 How are standard reduction potentials combined to give the standard cell potential for a spontaneous reaction?

19.10 Describe the hydrogen electrode. What is the value of its standard reduction potential?

19.11 What do the positive and negative signs of reduction potentials tell us?

19.12 If $E^{\circ}_{Cu^{2+}}$ had been chosen as the standard reference electrode and had been assigned a potential of 0.00 V, what would the reduction potential of the hydrogen electrode be relative to it?

19.13 If you set up a galvanic cell using metals not found in Table 19.1, what experimental information will tell you which is the anode and which is the cathode in the cell?

Using Standard Reduction Potentials

19.14 Compare Table 5.2 with Table 19.1. What can you say about the basis for the activity series for metals?

19.15 Make a sketch of a galvanic cell for which the cell notation is
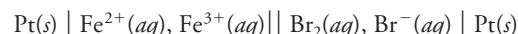
$$Fe(s) \mid Fe^{3+}(aq) \| Ag^+(aq) \mid Ag(s)$$

(a) Label the anode and the cathode.

(b) Indicate the charge on each electrode.

(c) Indicate the direction of electron flow in the external circuit.

(d) Write the equation for the net cell reaction.

19.16 Make a sketch of a galvanic cell in which inert platinum electrodes are used in the half-cells for the system

$$Pt(s) \mid Fe^{2+}(aq), Fe^{3+}(aq) \| Br_2(aq), Br^-(aq) \mid Pt(s)$$

Label the diagram and indicate the composition of the electrolytes in the two cell compartments. Show the signs of the electrodes and label the anode and cathode. Write the equation for the net cell reaction.

Cell Potentials and Thermodynamics

19.17 Write the equation that relates the standard cell potential to the standard free energy change for a reaction.

19.18 What is the equation that relates the equilibrium constant to the cell potential?

19.19 Show how the equation that relates the equilibrium constant to the cell potential (Equation 19.7) can be derived from the Nernst equation (Equation 19.8).

The Effect of Concentration on Cell Potential

19.20 The cell reaction during the discharge of a lead storage battery is

$$Pb(s) + PbO_2(s) + 2H^+(aq) + 2HSO_4^-(aq) \longrightarrow$$
$$2PbSO_4(s) + 2H_2O$$
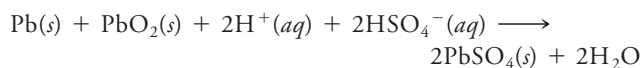
The standard cell potential is 2.05 V. What is the correct form of the Nernst equation for the reaction at 25 °C?

19.21 What is a *concentration cell*? Why is the $E°_{cell}$ for such a cell equal to zero?

Electrolysis

19.22 What electrical charges do the anode and the cathode carry in an electrolytic cell? What does the term *inert electrode* mean?

19.23 Why must electrolysis reactions occur at the electrodes in order for electrolytic conduction to continue?

19.24 Why must NaCl be melted before it is electrolyzed to give Na and Cl_2? Write the anode, cathode, and overall cell reactions for the electrolysis of molten NaCl.

19.25 Write half-reactions for the oxidation and the reduction of water.

19.26 What happens to the pH of the solution near the cathode and anode during the electrolysis of K_2SO_4? What function does K_2SO_4 serve in the electrolysis of a K_2SO_4 solution?

Stoichiometric Relationships in Electrolysis

19.27 What is a *faraday*? What relationships relate faradays to current and time measurements?

19.28 Using the same current, which will require the greater length of time, depositing 0.10 mol Cu from a Cu^{2+} solution, or depositing 0.10 mol of Cr from a Cr^{3+} solution? Explain your reasoning.

19.29 An electric current is passed through two electrolysis cells connected in series (so the same amount of current passes through each of them). One cell contains Cu^{2+} and the other contains Ag^+. In which cell will the larger number of moles of metal be deposited? Explain your answer.

19.30 An electric current is passed through two electrolysis cells connected in series (so the same amount of current passes through each of them). One cell contains Cu^{2+} and the other contains Fe^{2+}. In which cell will the greater mass of metal be deposited? Explain your answer.

Practical Galvanic Cells

19.31 What are the anode and cathode reactions during the discharge of a lead storage battery? How can a battery produce a potential of 12 V if the cell reaction has a standard potential of only 2 V?

19.32 What are the anode and cathode reactions during the charging of a lead storage battery?

19.33 How is a hydrometer constructed? How does it measure density? Why can a hydrometer be used to check the state of charge of a lead storage battery?

19.34 What reactions occur at the electrodes in the ordinary dry cell?

19.35 What chemical reactions take place at the electrodes in an alkaline dry cell?

19.36 Give the half-cell reactions and the cell reaction that take place in a nicad battery during discharge. What are the reactions that take place during the charging of the cell?

19.37 How is hydrogen held as a reactant in a nickel–metal hydride battery? Write the chemical formula for a typical alloy used in this battery. What is the electrolyte?

19.38 What are the anode, cathode, and net cell reactions that take place in a nickel–metal hydride battery during discharge? What are the reactions when the battery is charged?

19.39 Give two reasons why lithium is such an attractive anode material for use in a battery. What are the problems associated with using lithium for this purpose?

19.40 What are the electrode materials in a typical primary lithium cell? Write the equations for the anode, cathode, and cell reactions.

19.41 What are the electrode materials in a typical lithium ion cell? Explain what happens when the cell is charged. Explain what happens when the cell is discharged.

19.42 Write the cathode, anode, and net cell reaction in a hydrogen–oxygen fuel cell.

19.43 What advantages do fuel cells offer over conventional means of obtaining electrical power by the combustion of fuels?

Applications of Electrolysis

19.44 What is *electroplating*? Sketch an apparatus to electroplate silver.

19.45 Describe the Hall–Héroult process for producing metallic aluminum. What half–reaction occurs at the anode? What half-reaction occurs at the cathode? What is the overall cell reaction?

19.46 In the Hall–Héroult process, why must the carbon anodes be replaced frequently?

19.47 How is metallic sodium produced? What are some uses of metallic sodium? Write equations for the anode and cathode reactions.

19.48 Describe the electrolytic refining of copper. What economic advantages offset the cost of electricity for this process? What chemical reactions occur at the anode and the cathode?

19.49 Describe the electrolysis of aqueous sodium chloride. How do the products of the electrolysis compare for stirred and unstirred reactions? Write chemical equations for the reactions that occur at the electrodes.

REVIEW PROBLEMS

Cell Notation

19.50 Write the half-reactions and the balanced cell reaction for the following galvanic cells.

(a) $Cd(s)|Cd^{2+}(aq)||Au^{3+}(aq)|Au(s)$

(b) $Fe(s)|Fe^{2+}(aq)||Br_2(aq), Br^-(aq)|Pt(s)$

(c) $Cr(s)|Cr^{3+}(aq)||Cu^{2+}(aq)|Cu(s)$

OH 19.51 Write the half-reactions and the balanced cell reaction for the following galvanic cells.

(a) $Zn(s)|Zn^{2+}(aq)||Cr^{3+}(aq)|Cr(s)$

(b) $Pb(s), PbSO_4(s)|HSO_4^-(aq), H^+(aq)||H^+(aq),$
$$HSO_4^-(aq)|PbO_2(s), PbSO_4(s)$$

(c) $Mg(s)|Mg^{2+}(aq)||Sn^{2+}(aq)|Sn(s)$

19.52 Write the cell notation for the following galvanic cells. For half-reactions in which all the reactants are in solution or are gases, assume the use of inert platinum electrodes.

(a) $NO_3^-(aq) + 4H^+(aq) + 3Fe^{2+}(aq) \longrightarrow$
$$3Fe^{3+}(aq) + NO(g) + 2H_2O$$

(b) $Cl_2(g) + 2Br^-(aq) \longrightarrow Br_2(aq) + 2Cl^-(aq)$

(c) $Au^{3+}(aq) + 3Ag(s) \longrightarrow Au(s) + 3Ag^+(aq)$

19.53 Write the cell notation for the following galvanic cells. For half-reactions in which all the reactants are in solution or are gases, assume the use of inert platinum electrodes.

(a) $Cd^{2+}(aq) + Fe(s) \longrightarrow Cd(s) + Fe^{2+}(aq)$

(b) $NiO_2(s) + 4H^+(aq) + 2Ag(s) \longrightarrow$
$$Ni^{2+}(aq) + 2H_2O + 2Ag^+(aq)$$

(c) $Mg(s) + Cd^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cd(s)$

Using Reduction Potentials

19.54 For each pair of substances, use Table 19.1 to choose the better reducing agent.

(a) $Sn(s)$ or $Ag(s)$ (c) $Co(s)$ or $Zn(s)$

(b) $Cl^-(aq)$ or $Br^-(aq)$ (d) $I^-(aq)$ or $Au(s)$

19.55 For each pair of substances, use Table 19.1 to choose the better oxidizing agent.

(a) $NO_3^-(aq)$ or $MnO_4^-(aq)$ (c) $PbO_2(s)$ or $Cl_2(g)$

(b) $Au^{3+}(aq)$ or $Co^{2+}(aq)$ (d) $NiO_2(s)$ or $HOCl(aq)$

OH 19.56 Use the data in Table 19.1 to calculate the standard cell potential for each of the following reactions:

(a) $NO_3^-(aq) + 4H^+(aq) + 3Fe^{2+}(aq) \longrightarrow$
$$3Fe^{3+}(aq) + NO(g) + 2H_2O$$

(b) $Br_2(aq) + 2Cl^-(aq) \longrightarrow Cl_2(g) + 2Br^-(aq)$

(c) $Au^{3+}(aq) + 3Ag(s) \longrightarrow Au(s) + 3Ag^+(aq)$

19.57 Use the data in Table 19.1 to calculate the standard cell potential for each of the following reactions:

(a) $Cd^{2+}(aq) + Fe(s) \longrightarrow Cd(s) + Fe^{2+}(aq)$

(b) $NiO_2(s) + 4H^+(aq) + 2Ag(s) \longrightarrow$
$$Ni^{2+}(aq) + 2H_2O + 2Ag^+(aq)$$

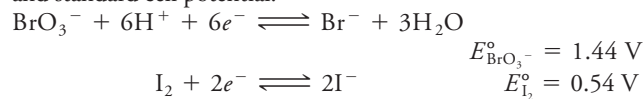(c) $Mg(s) + Cd^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cd(s)$

19.58 From the positions of the half-reactions in Table 19.1, determine whether the following reactions are spontaneous under standard state conditions.

(a) $2Au^{3+} + 6I^- \longrightarrow 3I_2 + 2Au$

(b) $H_2SO_3 + H_2O + Br_2 \longrightarrow 4H^+ + SO_4^{2-} + 2Br^-$
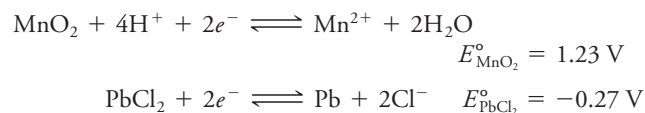
(c) $3Ca + 2Cr^{3+} \longrightarrow 2Cr + 3Ca^{2+}$

19.59 Use the data in Table 19.1 to determine which of the following reactions should occur spontaneously under standard state conditions.

(a) $Br_2 + 2Cl^- \longrightarrow Cl_2 + 2Br^-$

(b) $3Fe^{2+} + 2NO + 4H_2O \longrightarrow 3Fe + 2NO_3^- + 8H^+$

(c) $Ni^{2+} + Fe \longrightarrow Fe^{2+} + Ni$

ILW 19.60 From the half-reactions below, determine the cell reaction and standard cell potential.

$BrO_3^- + 6H^+ + 6e^- \rightleftharpoons Br^- + 3H_2O$
$$E^\circ_{BrO_3^-} = 1.44 \text{ V}$$

$I_2 + 2e^- \rightleftharpoons 2I^-$ $E^\circ_{I_2} = 0.54 \text{ V}$

19.61 What is the standard cell potential and the net reaction in a galvanic cell that has the following half-reactions?

$MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$
$$E^\circ_{MnO_2} = 1.23 \text{ V}$$

$PbCl_2 + 2e^- \rightleftharpoons Pb + 2Cl^-$ $E^\circ_{PbCl_2} = -0.27 \text{ V}$

OH 19.62 What will be the spontaneous reaction among H_2SO_3, $S_2O_3^{2-}$, HOCl, and Cl_2? The half-reactions involved are

$2H_2SO_3 + 2H^+ + 4e^- \rightleftharpoons S_2O_3^{2-} + 3H_2O$
$$E^\circ_{H_2SO_3} = 0.40 \text{ V}$$

$2HOCl + 2H^+ + 2e^- \rightleftharpoons Cl_2 + 2H_2O$ $E^\circ_{HOCl} = 1.63 \text{ V}$
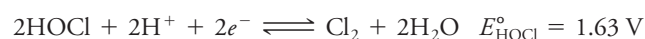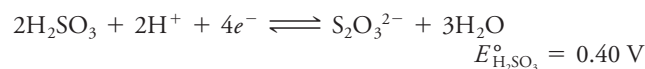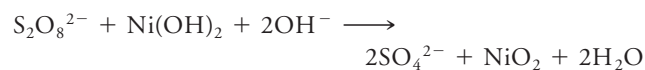
19.63 What will be the spontaneous reaction among Br_2, I_2, Br^-, and I^-?

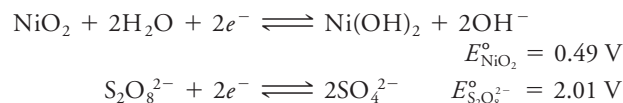**19.64** Will the following reaction occur spontaneously under standard state conditions?

$$SO_4^{2-} + 4H^+ + 2I^- \longrightarrow H_2SO_3 + I_2 + H_2O$$

Use E°_{cell} calculated from data in Table 19.1 to answer the question.

19.65 Determine whether the reaction

$S_2O_8^{2-} + Ni(OH)_2 + 2OH^- \longrightarrow$
$$2SO_4^{2-} + NiO_2 + 2H_2O$$

will occur spontaneously under standard state conditions. Use E°_{cell} calculated from the data below to answer the question.

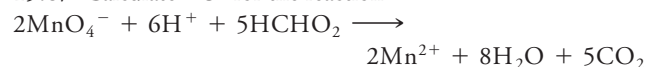$NiO_2 + 2H_2O + 2e^- \rightleftharpoons Ni(OH)_2 + 2OH^-$
$$E^\circ_{NiO_2} = 0.49 \text{ V}$$

$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $E^\circ_{S_2O_8^{2-}} = 2.01 \text{ V}$

Cell Potentials and Thermodynamics

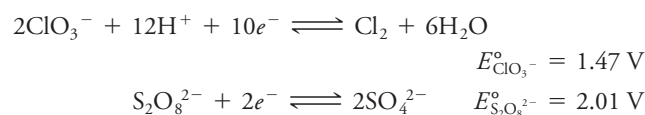**ILW 19.66** Calculate ΔG° for the following reaction *as written*.

$$2Br^- + I_2 \longrightarrow 2I^- + Br_2$$

OH 19.67 Calculate ΔG° for the reaction
$2MnO_4^- + 6H^+ + 5HCHO_2 \longrightarrow$
$$2Mn^{2+} + 8H_2O + 5CO_2$$
for which $E^\circ_{cell} = 1.69 \text{ V}$.

19.68 Given the following half-reactions and their standard reduction potentials, calculate (a) E°_{cell}, (b) ΔG° for the cell reaction, and (c) the value of K_c for the cell reaction.
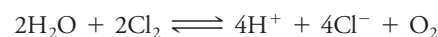
$2ClO_3^- + 12H^+ + 10e^- \rightleftharpoons Cl_2 + 6H_2O$
$$E^\circ_{ClO_3^-} = 1.47 \text{ V}$$

$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $E^\circ_{S_2O_8^{2-}} = 2.01 \text{ V}$

19.69 Calculate K_c for the system,

$$Ni^{2+} + Co \rightleftharpoons Ni + Co^{2+}$$

Use the data in Table 19.1. Assume $T = 298$ K.

19.70 The system $2AgI + Sn \rightleftharpoons Sn^{2+} + 2Ag + 2I^-$ has a calculated E°_{cell} of -0.015 V. What is the value of K_c for this system?

19.71 Determine the value of K_c at 25 °C for the reaction

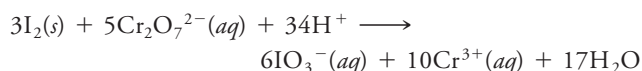$$2H_2O + 2Cl_2 \rightleftharpoons 4H^+ + 4Cl^- + O_2$$

The Effect of Concentration on Cell Potential

19.72 The cell reaction

$$NiO_2(s) + 4H^+(aq) + 2Ag(s) \longrightarrow$$
$$Ni^{2+}(aq) + 2H_2O + 2Ag^+(aq)$$
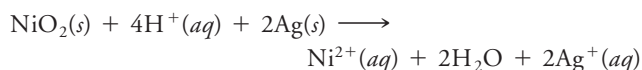
has $E^\circ_{cell} = 2.48$ V. What will be the cell potential at a pH of 2.00 when the concentrations of Ni^{2+} and Ag^+ are each 0.030 M?

19.73 The E°_{cell} is 0.135 V for the reaction

$$3I_2(s) + 5Cr_2O_7{}^{2-}(aq) + 34H^+ \longrightarrow$$
$$6IO_3{}^-(aq) + 10Cr^{3+}(aq) + 17H_2O$$

What is E_{cell} if $[Cr_2O_7{}^{2-}] = 0.010$ M, $[H^+] = 0.10$ M, $[IO_3{}^-] = 0.00010$ M, and $[Cr^{3+}] = 0.0010$ M?

OH ***19.74** A cell was set up having the following reaction.

$$Mg(s) + Cd^{2+}(aq) \longrightarrow Mg^{2+}(aq) + Cd(s)$$
$$E^\circ_{cell} = 1.97 \text{ V}$$
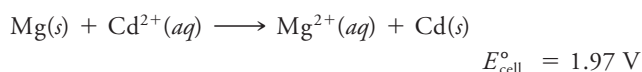
The magnesium electrode was dipping into a 1.00 M solution of $MgSO_4$ and the cadmium electrode was dipping into a solution of unknown Cd^{2+} concentration. The potential of the cell was measured to be 1.54 V. What was the unknown Cd^{2+} concentration?

*19.75 A silver wire coated with AgCl is sensitive to the presence of chloride ion because of the half-cell reaction

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^- \qquad E^\circ_{AgCl} = 0.2223 \text{ V}$$
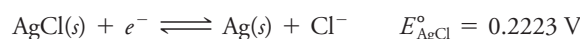
A student, wishing to measure the chloride ion concentration in a number of water samples, constructed a galvanic cell using the AgCl electrode as one half-cell and a copper wire dipping into 1.00 M $CuSO_4$ solution as the other half-cell. In one analysis, the potential of the cell was measured to be 0.0895 V with the copper half-cell serving as the cathode. What was the chloride ion concentration in the water? (Take $E^\circ_{Cu^{2+}} = +0.3419$ V.)

*19.76 At 25 °C, a galvanic cell was set up having the following half-reactions.

$$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s) \qquad E^\circ_{Fe^{2+}} = -0.447 \text{ V}$$
$$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s) \qquad E^\circ_{Cu^{2+}} = +0.3419 \text{ V}$$
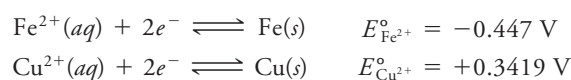
The copper half-cell contained 100 mL of 1.00 M $CuSO_4$. The iron half-cell contained 50.0 mL of 0.100 M $FeSO_4$. To the iron half-cell was added 50.0 mL of 0.500 M NaOH solution. The mixture was stirred and the cell potential was measured to be 1.175 V. Calculate the value of K_{sp} for $Fe(OH)_2$.

*19.77 Suppose a galvanic cell was constructed at 25 °C using a Cu/Cu^{2+} half-cell (in which the molar concentration of Cu^{2+} was 1.00 M) and a hydrogen electrode having a partial pressure of H_2 equal to 1 atm. The hydrogen electrode dipped into a solution of unknown hydrogen ion concentration, and the two half-cells were connected by a salt bridge. The precise value of $E^\circ_{Cu^{2+}}$ is +0.3419 V.

(a) Derive an equation for the pH of the solution with the unknown hydrogen ion concentration, expressed in terms of E_{cell} and E°_{cell}.

(b) If the pH of the solution were 5.15, what would be the observed potential of the cell?

(c) If the potential of the cell were 0.645 V, what would be the pH of the solution?

19.78 What is the potential of a concentration cell at 25.0 °C if it consists of silver electrodes dipping into two different solutions of $AgNO_3$, one with a concentration of 0.015 M and the other with a concentration of 0.50 M?

19.79 What would be the potential of the cell in the preceding problem if the temperature of the cell were 50 °C?

Quantitative Aspects of Electrochemical Reactions

19.80 How many moles of electrons are required to (a) reduce 0.20 mol Fe^{2+} to Fe, (b) oxidize 0.70 mol Cl^- to Cl_2, (c) reduce 1.50 mol Cr^{3+} to Cr, (d) oxidize 1.0×10^{-2} mol Mn^{2+} to $MnO_4{}^-$?

19.81 How many moles of electrons are required to (a) produce 5.00 g Mg from molten $MgCl_2$, (b) form 41.0 g Cu from a $CuSO_4$ solution?

ILW **19.82** How many grams of $Fe(OH)_2$ are produced at an iron anode when a basic solution undergoes electrolysis at a current of 8.00 A for 12.0 min?

19.83 How many grams of Cl_2 would be produced in the electrolysis of molten NaCl by a current of 4.25 A for 35.0 min?

ILW **19.84** How many hours would it take to produce 75.0 g of metallic chromium by the electrolytic reduction of Cr^{3+} with a current of 2.25 A?

19.85 How many hours would it take to generate 35.0 g of lead from $PbSO_4$ during the charging of a lead storage battery using a current of 1.50 A? The half-reaction is

$$Pb + HSO_4{}^- \longrightarrow PbSO_4 + H^+ + 2e^-$$
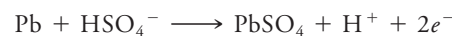
OH **19.86** How many amperes would be needed to produce 60.0 g of magnesium during the electrolysis of molten $MgCl_2$ in 2.00 hr?

19.87 A large electrolysis cell that produces metallic aluminum from Al_2O_3 by the Hall–Héroult process is capable of yielding 900 lb (409 kg) of aluminum in 24 hr. What current is required?

*19.88 The electrolysis of 250 mL of a brine solution (NaCl) was carried out for a period of 20.00 min with a current of 2.00 A in an apparatus that prevented Cl_2 from reacting with other products of the electrolysis. The resulting solution was titrated with 0.620 M HCl. How many milliliters of the HCl solution was required for the titration?

*19.89 An unstirred solution of 2.00 M NaCl was electrolyzed for a period of 25.0 min and then titrated with 0.250 M HCl. The titration required 15.5 mL of the acid. What was the average current in amperes during the electrolysis?

*19.90 A solution of NaCl in water was electrolyzed with a current of 2.50 A for 15.0 min. How many milliliters of Cl_2 gas would be formed if it was collected over water at 25 °C and a total pressure of 750 torr?

*19.91 How many milliliters of dry gaseous H_2, measured at 20 °C and 735 torr, would be produced at the cathode in the electrolysis of dilute H_2SO_4 with a current of 0.750 A for 15.00 min?

Predicting Electrolysis Reactions

19.92 If electrolysis is carried out on an aqueous solution of aluminum sulfate, what products are expected at the electrodes? Write the equation for the net cell reaction.

19.93 If electrolysis is carried out on an aqueous solution of cadmium iodide, what products are expected at the electrodes? Write the equation for the net cell reaction.

OH **19.94** What products would we expect at the electrodes if a solution containing both KBr and $CuSO_4$ were electrolyzed? Write the equation for the net cell reaction.

19.95 What products would we expect at the electrodes if a solution containing both $BaCl_2$ and CuI_2 were electrolyzed? Write the equation for the net cell reaction.

ADDITIONAL EXERCISES

*__19.96__ A watt is a unit of electrical power and is equal to one joule per second (1 watt $= 1$ J s^{-1}). How many hours can a calculator drawing 2.0×10^{-3} watt be operated by a mercury battery having a cell potential equal to 1.34 V if a mass of 1.00 g of HgO is available at the cathode? The cell reaction is

$$HgO(s) + Zn(s) \longrightarrow ZnO(s) + Hg(l)$$

*__19.97__ Suppose that a galvanic cell were set up having the net cell reaction

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

The Ag^+ and Zn^{2+} concentrations in their respective half-cells initially are 1.00 M, and each half-cell contains 100 mL of electrolyte solution. If this cell delivers current at a constant rate of 0.10 A, what will the cell potential be after 15.00 hr?

*__19.98__ The value of K_{sp} for AgBr is 5.0×10^{-13}. What will be the potential of a cell constructed of a standard hydrogen electrode as one half-cell and a silver wire coated with AgBr dipping into 0.10 M HBr as the other half-cell? For the Ag/AgBr electrode,

$$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-(aq) \qquad E°_{AgBr} = +0.070 \text{ V}$$

*__19.99__ A student set up an electrolysis apparatus and passed a current of 1.22 A through a 3 M H_2SO_4 solution for 30.0 min. The H_2 formed at the cathode was collected and found to have a volume, over water at 27 °C, of 288 mL at a total pressure of 767 torr. Use the data to calculate the charge on the electron, expressed in coulombs.

*__19.100__ A hydrogen electrode is immersed in a 0.10 M solution of acetic acid at 25 °C. The electrode is connected to another consisting of an iron nail dipping into 0.10 M $FeCl_2$. What will be the measured potential of this cell? Assume $P_{H_2} = 1.00$ atm.

*__19.101__ What current would be required to deposit 1.00 m^2 of chrome plate having a thickness of 0.050 mm in 4.50 hr from a solution of H_2CrO_4? The density of chromium is 7.19 g cm^{-3}.

19.102 A solution containing vanadium (chemical symbol V) in an unknown oxidation state was electrolyzed with a current of 1.50 A for 30.0 min. It was found that 0.475 g of V was deposited on the cathode. What was the original oxidation state of the vanadium ion?

*__19.103__ What masses of H_2 and O_2 in grams would have to react each second in a fuel cell at 110 °C to provide 1.00 kilowatt (kW) of power if we assume a thermodynamic efficiency of 70%? (Hint: Use data in Chapters 6 and 18 to compute the value of

$\Delta G°$ for the reaction $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$ at 110 °C. 1 watt $= 1$ J s^{-1}.)

*__19.104__ A Ag/AgCl electrode dipping into 1.00 M HCl has a standard reduction potential of $+0.2223$ V. The half-reaction is

$$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$$
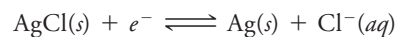
A second Ag/AgCl electrode is dipped into a solution containing Cl^- at an unknown concentration. The cell generates a potential of 0.0478 V, with the electrode in the solution of unknown concentration having a negative charge. What is the molar concentration of Cl^- in the unknown solution?

19.105 Consider the following galvanic cell

$$Ag(s)|Ag^+(0.00030\ M)||Fe^{3+}(0.0011\ M), Fe^{2+}(0.040\ M)|Pt(s)$$
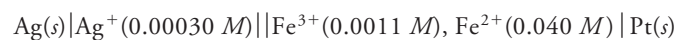
Calculate the cell potential. Determine the sign of the electrodes in the cell. Write the equation for the spontaneous cell reaction.

EXERCISES IN CRITICAL THINKING

19.106 In biochemical systems the normal standard state that requires $[H^+] = 1.00$ M is not realistic. (a) Which half-reactions in Table 19.1 will have different potentials if pH $= 7.00$ is defined as the standard state for hydronium ions? (b) What will the new standard reduction potentials be at pH $= 7.00$ for those reactions? These are called $E°'_{cell}$ with the prime indicating the potential at pH $= 7.00$.

19.107 Calculate a new version of Table 19.1 using the lithium half-reaction to define zero. Does this change the results of any problems involving standard cell potentials?

19.108 In Problem 19.79 the potential at 50 °C was calculated. Does the change in molarity of the solutions, due to the change in density of water, have an effect on the potentials?

19.109 There are a variety of methods available for generating electricity. List as many methods as you can think of. Rank each of the methods based on your knowledge of (a) the efficiency of the method and (b) the environmental pollution caused by each method.

19.110 Using the cost of electricity in your area, how much will it cost to produce a case of 24 soda cans, each weighing 0.45 ounces? Assume that alternating current can be converted to direct current with 100% efficiency.

*__19.111__ Most flashlights use two or more batteries in series. Use the concepts of galvanic cells in this chapter to explain why a flashlight with two new batteries and one "dead" battery will give only a dim light if any light is obtained at all.

*__19.112__ If two electrolytic cells are placed in series, the same number of electrons must pass through both cells. One student argues you can get twice as much product if two cells are placed in series compared to a single cell and therefore the cost of production (i.e., the cost of electricity) will decrease greatly and profits will increase. Is the student correct? Explain your reasoning based on the principles of electrochemistry.