

**One day sir, you may tax it.**

—MICHAEL FARADAY (1791–1867)

[In response to Mr. Gladstone, the British Chancellor of the Exchequer, when asked about the practical worth of electricity.]

CHAPTER

# 20

## Electrochemistry

This chapter's opening quote from Michael Faraday illustrates an important aspect of basic research (research for the sake of understanding how nature works). The Chancellor of the Exchequer (the British cabinet minister responsible for all financial matters) wanted to know how Michael Faraday's apparently esoteric investigations of electricity would ever be useful to the empire. Faraday responded in a way that the chancellor would understand—he pointed out the eventual financial payoff. Today electricity is a fundamental form of energy, powering our entire economy. Although basic research does not always lead to useful applications, much of the technology our society relies on has grown out of basic research. The history of modern science shows that we must first understand nature (the goal of basic research) before we can harness its power. In this chapter, we discuss oxidation-reduction reactions (first introduced in Chapter 5) and how we can exploit them to generate electricity. The applications range from the batteries that power flashlights to the fuel cells that may one day power our homes and automobiles.



The house shown in this image is completely powered by batteries that are recharged with solar cells, removing the need to connect to the electrical grid. With rapid advances in battery technology, houses like this could become commonplace.

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## 20.1 Lightning and Batteries

Lightning dramatically demonstrates the power of the flow of electrical charge. Many of the same principles, though in a much more controlled environment, are at work in a battery. The driving force for both lightning and the battery is the same, and we have encountered it before: Electrons flow *away* from negative charge and toward *positive* charge.



▲ Cloud-to-ground lightning

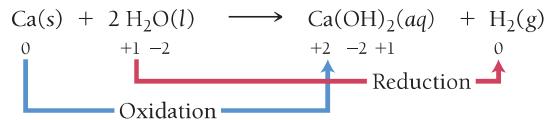
In a thundercloud, violent air currents cause water droplets and ice particles to collide. The collisions knock electrons off of molecules, creating positive and negative charges. The positive charges accumulate on small ice crystals that travel to the top of the thundercloud on rising air currents. The wet slushy bottom of the thundercloud becomes negatively charged. The resulting charge separation exists until a conductive path can form between the bottom of the cloud (negatively charged) and the top of the cloud (positively charged). The conductive path forms when the charge separation is so great that a channel of ionized air develops. This channel acts like a conductive wire, allowing a massive amount of charge to flow through it in order to equalize the charge separation. The massive flow of electrical charge is lightning.

Most lightning occurs within the thundercloud itself or from one thundercloud to another. However, if the thundercloud gets close enough to the ground, the earth underneath the cloud develops a positive charge in response to the negative charge at the base of the cloud. The channel of ionized air can then form between the cloud and the ground, resulting in the flow of charge from the base of the cloud to the earth in what is called cloud-to-ground lightning. Cloud-to-ground lightning is visible and dramatic to observers on the ground.

Batteries operate on many of the same principles that are at work in lightning. A battery is composed of substances that have different affinities for electrons. The substances are separated so that one end of the battery develops a positive charge and the other end develops a negative charge. The charge separation exists until a conductive path connects the two ends, providing a path through which charge can flow. A metal wire with an electrical load can provide such a path. When the wire is connected, electrons flow from the negative end of the battery—through the wire and through the electrical load—to the positive end. As the electrons flow through the electrical load, they can do electrical work, such as run a refrigerator or air conditioner. Battery technology has advanced dramatically in recent years, and you can now run your entire home from a bank of batteries such as the Tesla Powerwall. These batteries can recharge from solar cells, making it completely possible to live off the traditional electrical grid.

## 20.2 Balancing Oxidation–Reduction Equations

Recall from Section 5.9 that *oxidation* is the loss of electrons, and *reduction* is the gain of electrons. Recall also that we can identify oxidation–reduction reactions through changes in oxidation states: *oxidation corresponds to an increase in oxidation state, and reduction corresponds to a decrease in oxidation state*. For example, consider the following reaction between calcium and water:



Review Section 5.9 on assigning oxidation states.

Because calcium increases in oxidation state from 0 to +2, it is oxidized. Because hydrogen decreases in oxidation state from +1 to 0, it is reduced.

Balancing redox reactions can be more complicated than balancing other types of reactions because both the mass (or number of each type of atom) and the charge must be balanced. We can balance redox reactions occurring in aqueous solutions with a special procedure called the *half-reaction method of balancing*. In this procedure, we break down the overall equation into two half-reactions: one for oxidation and one for reduction. We then balance the half-reactions individually and add them together. The steps differ slightly for reactions occurring in acidic and in basic solution. Examples 20.1 and 20.2 demonstrate the method for an acidic solution, and Example 20.3 demonstrates the method for a basic solution.

## WATCH NOW!

 INTERACTIVE WORKED EXAMPLE VIDEO 20.2

**HOW TO:** Balance Aqueous Redox Equations in Acidic Solution Using the Half-Reaction Method  
**GENERAL PROCEDURE**

**Step 1** Assign oxidation states to all atoms and identify the substances being oxidized and reduced.

**Step 2** Separate the overall reaction into two half-reactions; one for oxidation and one for reduction.

**Step 3** Balance each half-reaction with respect to mass in the following order:

- Balance all elements other than H and O.
- Balance O by adding  $\text{H}_2\text{O}$ .
- Balance H by adding  $\text{H}^+$ .

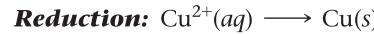
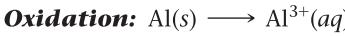
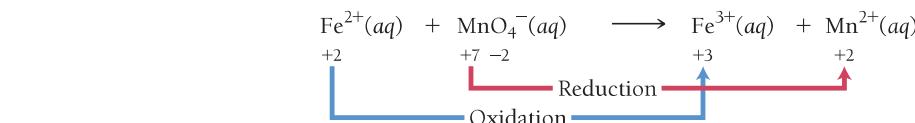
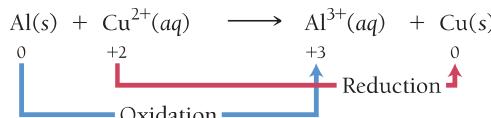
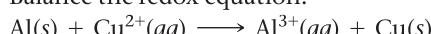
**Step 4** Balance each half-reaction with respect to charge by adding electrons. (Make the sum of the charges on both sides of the equation equal by adding as many electrons as necessary.)

**Step 5** Make the number of electrons in both half-reactions equal by multiplying one or both half-reactions by a small whole number.

**Step 6** Add the two half-reactions together, canceling electrons and other species as necessary.

**EXAMPLE 20.1****Half-Reaction Method of Balancing Aqueous Redox Equations in Acidic Solution**

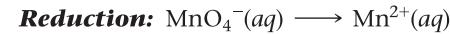
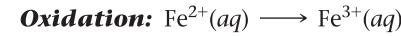
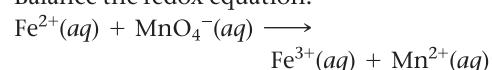
Balance the redox equation:



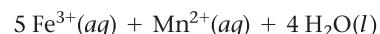
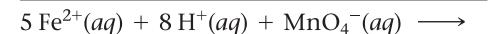
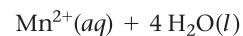
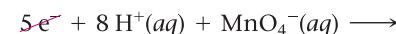
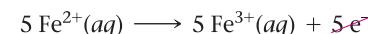
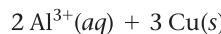
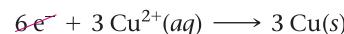
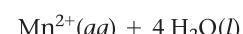
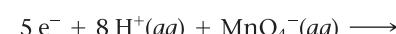
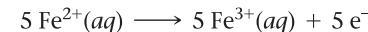
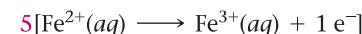
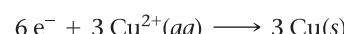
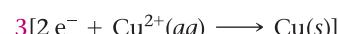
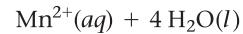
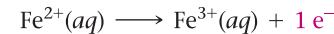
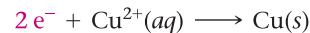
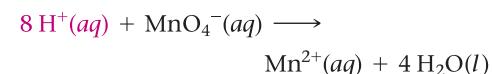
All elements are balanced, so proceed to the next step.

**EXAMPLE 20.2****Half-Reaction Method of Balancing Aqueous Redox Equations in Acidic Solution**

Balance the redox equation:



All elements other than H and O are balanced, so proceed to balance H and O.



—Continued on the next page

Continued—

**Step 7** Verify that the reaction is balanced with respect to both mass and charge.

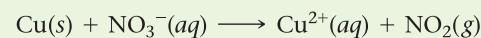
Reactants	Products
2 Al	2 Al
3 Cu	3 Cu
+6 charge	+6 charge

Reactants	Products
5 Fe	5 Fe
8 H	8 H
1 Mn	1 Mn
4 O	4 O
+17 charge	+17 charge

**FOR PRACTICE 20.1** Balance the redox reaction in acidic solution:



**FOR PRACTICE 20.2** Balance the redox reaction in acidic solution:



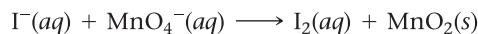
When a redox reaction occurs in basic solution, we balance the reaction in a similar manner, except that we add an additional step to neutralize any  $\text{H}^+$  with  $\text{OH}^-$ . The  $\text{H}^+$  and the  $\text{OH}^-$  combine to form  $\text{H}_2\text{O}$  as shown in Example 20.3.

### WATCH NOW!

### INTERACTIVE WORKED EXAMPLE 20.3

## EXAMPLE 20.3 Balancing Redox Reactions Occurring in Basic Solution

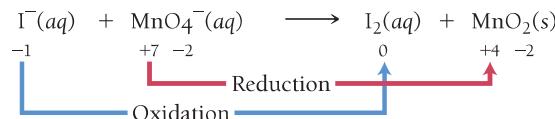
Balance the equation occurring in basic solution:



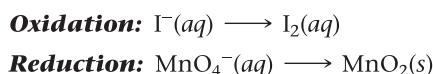
### SOLUTION

To balance redox reactions occurring in basic solution, follow the half-reaction method outlined in Examples 20.1 and 20.2, but add an extra step to neutralize the acid with  $\text{OH}^-$  as shown in step 3.

1. Assign oxidation states.

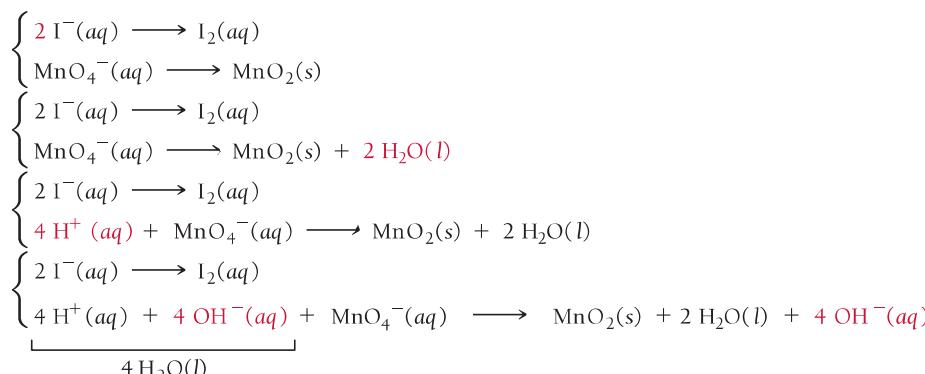


2. Separate the overall reaction into two half-reactions.



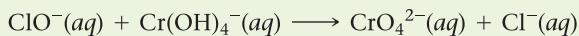
3. Balance each half-reaction with respect to mass.

- Balance all elements other than H and O.
- Balance O by adding  $\text{H}_2\text{O}$ .
- Balance H by adding  $\text{H}^+$ .
- Neutralize  $\text{H}^+$  by adding enough  $\text{OH}^-$  to neutralize each  $\text{H}^+$ . Add the same number of  $\text{OH}^-$  ions to each side of the equation.



4. Balance each half-reaction with respect to charge.	$2 \text{I}^-(aq) \longrightarrow \text{I}_2(aq) + 2 \text{e}^-$ $4 \text{H}_2\text{O}(l) + \text{MnO}_4^-(aq) + 3 \text{e}^- \longrightarrow \text{MnO}_2(s) + 2 \text{H}_2\text{O}(l) + 4 \text{OH}^-(aq)$												
5. Make the number of electrons in both half-reactions equal.	$3[2 \text{I}^-(aq) \longrightarrow \text{I}_2(aq) + 2 \text{e}^-]$ $6 \text{I}^-(aq) \longrightarrow 3 \text{I}_2(aq) + 6 \text{e}^-$ $2[4 \text{H}_2\text{O}(l) + \text{MnO}_4^-(aq) + 3 \text{e}^- \longrightarrow \text{MnO}_2(s) + 2 \text{H}_2\text{O}(l) + 4 \text{OH}^-(aq)]$ $8 \text{H}_2\text{O}(l) + 2 \text{MnO}_4^-(aq) + 6 \text{e}^- \longrightarrow 2 \text{MnO}_2(s) + 4 \text{H}_2\text{O}(l) + 8 \text{OH}^-(aq)$												
6. Add the half-reactions together.	$6 \text{I}^-(aq) \longrightarrow 3 \text{I}_2(aq) + 6 \text{e}^-$ <del><math>48 \text{H}_2\text{O}(l) + 2 \text{MnO}_4^-(aq) + 6 \text{e}^- \longrightarrow 2 \text{MnO}_2(s) + 4 \text{H}_2\text{O}(l) + 8 \text{OH}^-(aq)</math></del> $6 \text{I}^-(aq) + 4 \text{H}_2\text{O}(l) + 2 \text{MnO}_4^-(aq) \longrightarrow 3 \text{I}_2(aq) + 2 \text{MnO}_2(s) + 8 \text{OH}^-(aq)$												
7. Verify that the reaction is balanced.	<table border="1"> <thead> <tr> <th>Reactants</th> <th>Products</th> </tr> </thead> <tbody> <tr> <td>6 I</td> <td>6 I</td> </tr> <tr> <td>8 H</td> <td>8 H</td> </tr> <tr> <td>2 Mn</td> <td>2 Mn</td> </tr> <tr> <td>12 O</td> <td>12 O</td> </tr> <tr> <td>-8 charge</td> <td>-8 charge</td> </tr> </tbody> </table>	Reactants	Products	6 I	6 I	8 H	8 H	2 Mn	2 Mn	12 O	12 O	-8 charge	-8 charge
Reactants	Products												
6 I	6 I												
8 H	8 H												
2 Mn	2 Mn												
12 O	12 O												
-8 charge	-8 charge												

**FOR PRACTICE 20.3** Balance the following redox reaction occurring in basic solution:



## 20.3

### Voltaic (or Galvanic) Cells: Generating Electricity from Spontaneous Chemical Reactions

**Electrical current** is the flow of electric charge. Electrons flowing through a wire or ions flowing through a solution both constitute electrical current. Since redox reactions involve the transfer of electrons from one substance to another, these reactions have the potential to generate electrical current, as we discussed in Section 20.1.

For example, consider the spontaneous redox reaction:



When Zn metal is placed in a  $\text{Cu}^{2+}$  solution, the greater tendency of zinc to lose electrons results in Zn being oxidized and  $\text{Cu}^{2+}$  being reduced. Electrons are transferred directly from the Zn to the  $\text{Cu}^{2+}$  (Figure 20.1►). Although the actual process is more complicated, we can imagine that—on the atomic scale—a zinc atom within the zinc metal transfers two electrons to a copper ion in solution. The zinc atom then becomes a zinc ion dissolved in the solution. The copper ion accepts the two electrons and is deposited on the zinc as solid copper.

Suppose we were to separate the zinc atoms and copper ions and force the electron transfer to occur another way—not directly from the zinc atom to the copper ion, but through a wire connecting the two half-reactions. The flowing electrons would constitute an electrical current and could be used to do electrical work.

#### WATCH NOW!

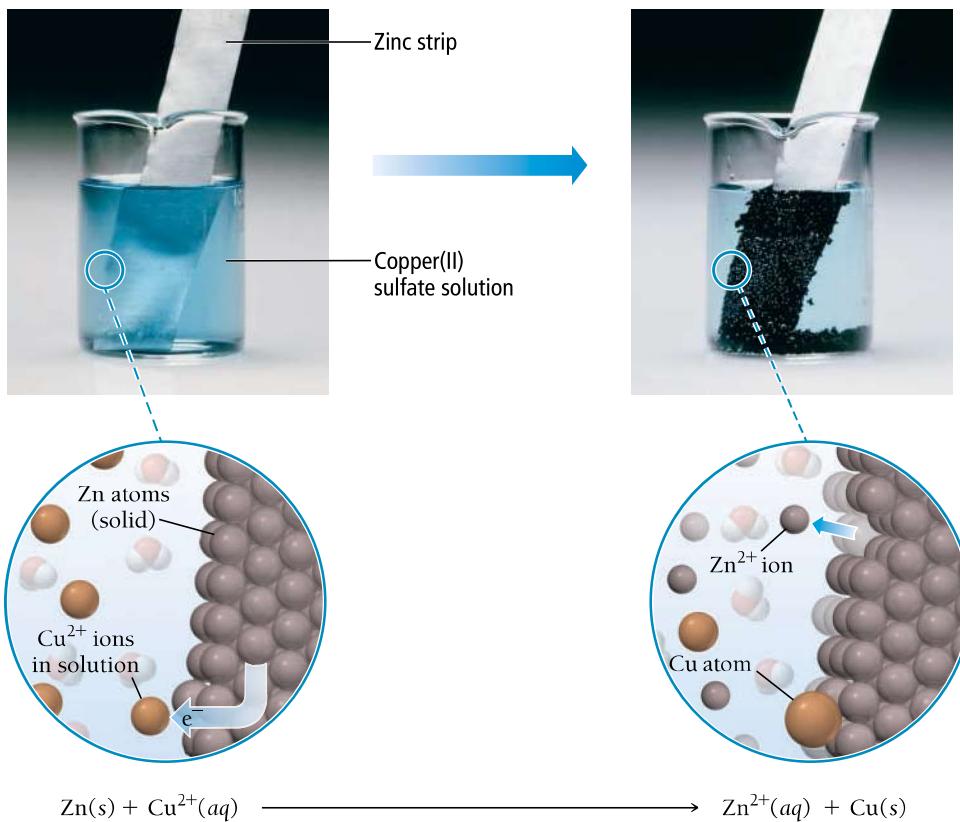
#### KEY CONCEPT VIDEO 20.3



**► FIGURE 20.1 A Spontaneous Oxidation–Reduction Reaction**

When zinc is immersed in a solution containing copper ions, the zinc atoms transfer electrons to the copper ions. The zinc atoms are oxidized and dissolve in the solution. The copper ions are reduced and are deposited on the electrode.

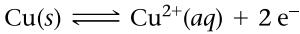
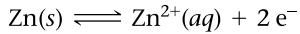
**A Spontaneous Redox Reaction:  $\text{Zn} + \text{Cu}^{2+}$**



### The Voltaic Cell

The generation of electricity through redox reactions is carried out in a device called an **electrochemical cell**. A **voltaic (or galvanic) cell** is an electrochemical cell that *produces* electrical current from a *spontaneous* chemical reaction. A second type of electrochemical cell, called an **electrolytic cell**, *consumes* electrical current-to drive a *nonspontaneous* chemical reaction. We discuss voltaic cells in this section and electrolytic cells in Section 20.8.

In the voltaic cell in Figure 20.2►, a solid strip of zinc is placed in a  $\text{Zn}(\text{NO}_3)_2$  solution to form a **half-cell**. A solid strip of copper placed in a  $\text{Cu}(\text{NO}_3)_2$  solution forms a second half-cell. The strips act as **electrodes**, conductive surfaces through which electrons can enter or leave the half-cells. Each metal strip reaches equilibrium with its ions in solution according to these half-reactions:



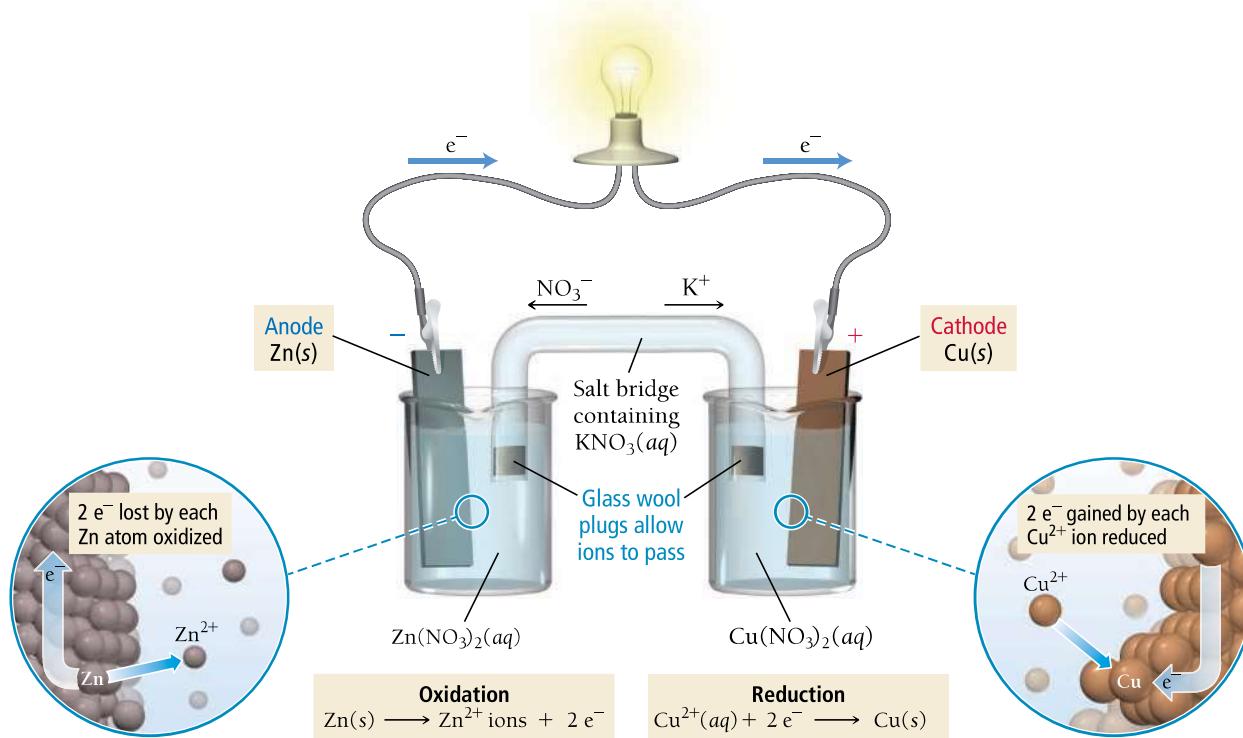
The continual flow of electrical current in a voltaic cell requires a pathway by which counterions can flow to neutralize charge buildup; this is discussed later.

The idea that one electrode in a voltaic cell becomes more negatively charged relative to the other electrode due to differences in ionization tendencies is central to understanding how a voltaic cell works.

However, the position of these equilibria is not the same for both metals. As we have just seen, the zinc has a greater tendency to ionize than the copper, so the zinc half-reaction lies further to the right. As a result, the zinc electrode becomes negatively charged relative to the copper electrode.

If the two half-cells are connected by a wire running from the zinc—through a light-bulb or other electrical device—to the copper, electrons spontaneously flow from the zinc electrode (which is more negatively charged, and therefore, repels electrons) to the copper electrode. As the electrons flow away from the zinc electrode, the  $\text{Zn}/\text{Zn}^{2+}$  equilibrium shifts to the right (according to Le Châtelier's principle) and oxidation occurs. As electrons flow to the copper electrode, the  $\text{Cu}/\text{Cu}^{2+}$  equilibrium shifts to the left, and reduction occurs. The flowing electrons constitute an electrical current that lights the bulb.

## A Voltaic Cell



**▲ FIGURE 20.2 A Voltaic Cell** The tendency of zinc to transfer electrons to copper results in a flow of electrons through the wire that lights the bulb. The movement of electrons from the zinc anode to the copper cathode creates a positive charge buildup at the zinc half-cell and a negative charge buildup at the copper half-cell. The flow of ions within the salt bridge neutralizes this charge buildup, allowing the reaction to continue.

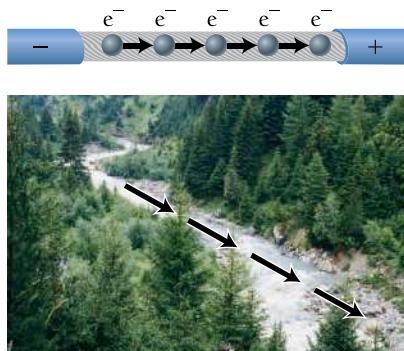
## Current and Potential Difference

We can understand electrical current and why it flows by analogy with water current in a stream (Figure 20.3►). The *rate of electrons flowing* through a wire is analogous to the *rate of water moving* through a stream. Electrical current is measured in units of **amperes (A)**, also called amps. One ampere represents the flow of one coulomb (a measure of electrical charge) per second:

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

Because an electron has a charge of  $1.602 \times 10^{-19} \text{ C}$ , 1 A corresponds to the flow of  $6.242 \times 10^{18}$  electrons per second.

The ampere is often abbreviated as *amp*.



The *driving force* for electrical current is analogous to the driving force for water current. Water current is driven by a difference in gravitational potential energy (caused by a gravitational field). Streams flow downhill, from higher to lower potential energy. Electrical current is also driven by a difference in potential energy (caused by an electric field resulting from the charge difference on the two electrodes) called **potential difference**. *Potential difference is a measure of the difference in potential energy (usually in joules) per unit of charge (coulombs)*. The SI unit of potential difference is the **volt (V)**, which is equal to one joule per coulomb:

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

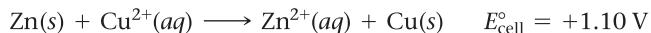
In other words, a potential difference of one volt indicates that a charge of one coulomb experiences an energy difference of one joule between the two electrodes.

A large potential difference corresponds to a large difference in charge between the two electrodes, and therefore, a strong tendency for electron flow (analogous to a steeply descending streambed). Potential difference, since it gives rise to the force that results in the motion of electrons, is also referred to as **electromotive force (emf)**.

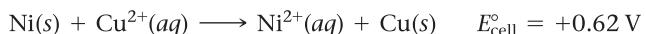
**▲ FIGURE 20.3 An Analogy for Electrical Current** Just as water flows downhill in response to a difference in gravitational potential energy, electrons flow through a conductor in response to an electrical potential difference, creating an electrical current.

In a voltaic cell, the potential difference between the two electrodes is the **cell potential ( $E_{\text{cell}}$ )** or **cell emf**. The cell potential depends on the relative tendencies of the reactants to undergo oxidation and reduction. Combining the oxidation of a substance with a strong tendency to undergo oxidation and the reduction of a substance with a strong tendency to undergo reduction produces a large difference in charge between the two electrodes, and therefore, a high positive cell potential.

In general, cell potential also depends on the concentrations of the reactants and products in the cell and the temperature (which we will assume to be 25 °C unless otherwise noted). Under standard conditions (1 M concentration for reactants in solution and 1 atm pressure for gaseous reactants), the cell potential is called the **standard cell potential ( $E_{\text{cell}}^{\circ}$ )** or **standard emf**. For example, the standard cell potential in the zinc and copper cell described previously is 1.10 volts:



If the zinc is replaced with nickel (which has a lower tendency to be oxidized), the cell potential is lower:



The cell potential is a measure of the overall tendency of the redox reaction to occur spontaneously—the lower the cell potential, the lower the tendency to occur. A negative cell potential indicates that the forward reaction is not spontaneous.

### ANSWER NOW!

### 20.1 Cc Conceptual Connection



## POTENTIAL DIFFERENCE AND ELECTRICAL CURRENT

Which statement best captures the difference between volts and amps?

- (a) The volt is a unit that quantifies the difference in electrical potential energy, and the amp is a unit that quantifies the flow of electrical current.
- (b) The amp is a unit that quantifies the difference in electrical potential energy, and the volt is a unit that quantifies the flow of electrical current.
- (c) The volt and amp are two different units used to measure the same thing, the flow of electrical current.

Note that the anode and cathode need not actually be negatively and positively charged, respectively. The anode is the electrode with the relatively *more* negative (or less positive) charge.

## Anode, Cathode, and Salt Bridge

In all electrochemical cells, we call the electrode where oxidation occurs the **anode** and the electrode where reduction occurs the **cathode**. In a voltaic cell, the anode is the more negatively charged electrode, and we label it with a negative (−) sign. The cathode of a voltaic cell is the more positively charged electrode, and we label it with a (+) sign. Electrons flow from the anode to the cathode (from negative to positive) through the wires connecting the electrodes.

As electrons flow out of the anode, positive ions ( $\text{Zn}^{2+}$  in the preceding example) form in the oxidation half-cell, resulting in a buildup of *positive charge* in the *solution*. As electrons flow into the cathode, positive ions ( $\text{Cu}^{2+}$  in the preceding example) are reduced at the reduction half-cell, resulting in a buildup of *negative charge* in the *solution*.

If the movement of electrons from anode to cathode were the only flow of charge, the buildup of the opposite charge in the solution would stop electron flow almost immediately. The cell needs a pathway by which counterions can flow between the half-cells without the solutions in the half-cells totally mixing. One such pathway is a **salt bridge**, an inverted, U-shaped tube that contains a strong electrolyte such as  $\text{KNO}_3$  and connects the two half-cells (see Figure 20.2). The electrolyte is usually suspended in a gel and held within the tube by permeable stoppers. The salt bridge allows a flow of ions that neutralizes the charge buildup in the solution. *The negative ions within the salt bridge flow to neutralize the accumulation of positive charge at the anode, and the positive ions flow to neutralize the accumulation of negative charge at the cathode.* In other words, the salt bridge completes the circuit, allowing electrical current to flow.

## VOLTAIC CELLS

In a voltaic cell, in which direction do electrons flow?

- (a) from higher potential energy to lower potential energy
- (b) from the cathode to the anode
- (c) from lower potential energy to higher potential energy



ANSWER NOW!



## Electrochemical Cell Notation

We represent electrochemical cells with a compact notation called a *cell diagram* or *line notation*. For example, we represent the electrochemical cell discussed previously in which Zn is oxidized to Zn<sup>2+</sup> and Cu<sup>2+</sup> is reduced to Cu as follows:



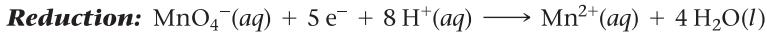
In this representation,

- the oxidation half-reaction is on the left and the reduction is on the right. A double vertical line, indicating the salt bridge, separates the two half-reactions.
- substances in different phases are separated by a single vertical line, which represents the boundary between the phases.
- for some redox reactions, the reactants and products of one or both of the half-reactions may be in the same phase. In these cases (as shown in the example below), we separate the reactants and products from each other with a comma in the line diagram. Such cells use an inert electrode, such as platinum (Pt) or graphite, as the anode or cathode (or both).

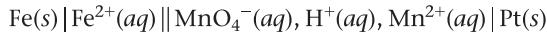
Consider the redox reaction in which Fe(s) is oxidized and MnO<sub>4</sub><sup>-</sup>(aq) is reduced:



The half-reactions for this overall reaction are:



Notice that in the reduction half-reaction the principal species are all in the aqueous phase. In this case, the electron transfer needs an electrode on which to occur. An inert platinum electrode is employed, and the electron transfer takes place at its surface. Using line notation, we represent the electrochemical cell corresponding to the above reaction as:



The Pt(s) on the far right indicates that an inert platinum electrode acts as the cathode in this reaction, as depicted in Figure 20.4►.

## 20.4

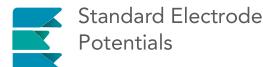
## Standard Electrode Potentials

As we have just seen, the standard cell potential ( $E_{\text{cell}}^\circ$ ) for an electrochemical cell depends on the specific half-reactions occurring in the half-cells and is a measure of the potential energy difference (per unit charge) between the two electrodes. We can think of the electrode in each half-cell as having its own individual potential, called the **standard electrode potential**. The overall standard cell potential ( $E_{\text{cell}}^\circ$ ) is the difference between the two standard electrode potentials.

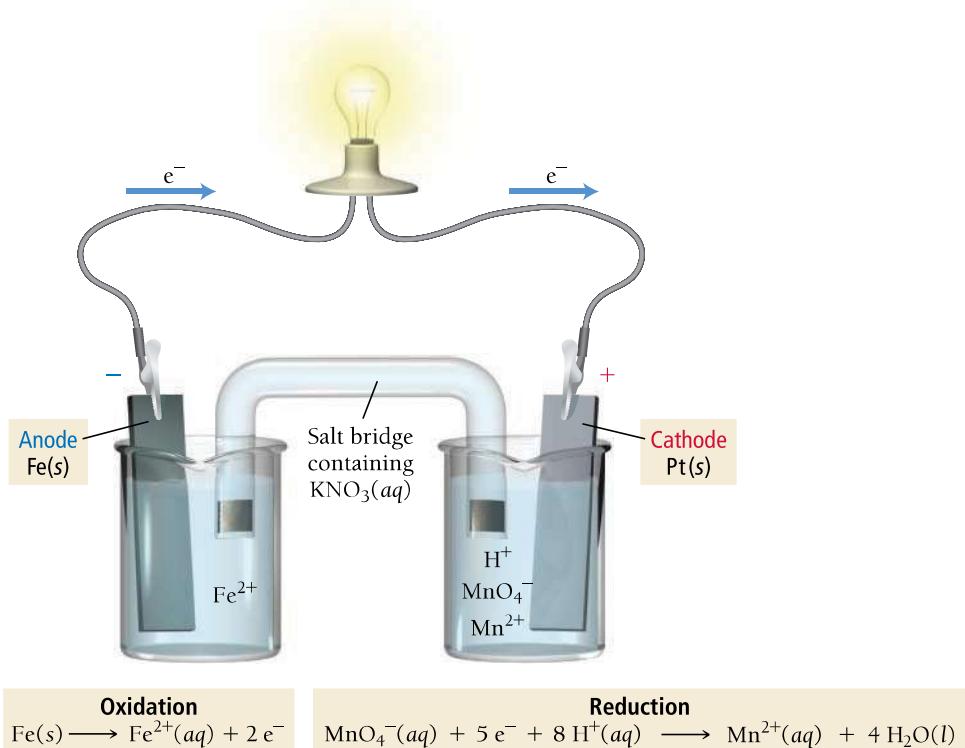
We can better understand this idea with an analogy. Consider two water tanks with different water levels connected by a common pipe, as shown in Figure 20.5►. The water in each tank has its own level and corresponding potential energy. When the tanks are connected, water flows from the tank with the higher level (higher potential energy) to the tank with a lower water level (lower potential energy). Similarly, each half-cell in an electrochemical cell has its own charge and corresponding electrode potential. *When the cells are connected, electrons flow from the electrode with more negative charge (greater potential energy) to the electrode with less negative charge (less potential energy).*

## WATCH NOW!

### KEY CONCEPT VIDEO 20.4

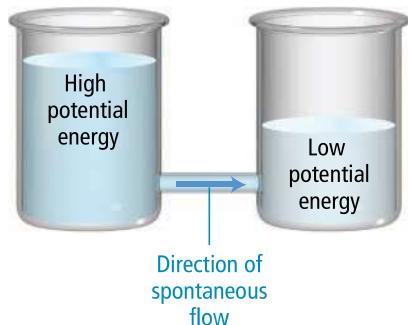


### Inert Platinum Electrode



**► FIGURE 20.4 Inert Platinum Electrode**

**Electrode** When the participants in a half-reaction are all in the aqueous phase, a conductive surface is needed for electron transfer to take place. In such cases, an inert electrode of graphite or platinum is often used. In this electrochemical cell, an iron strip acts as the anode and a platinum strip acts as the cathode. Iron is oxidized at the anode, and  $\text{MnO}_4^-$  is reduced at the cathode.



**▲ FIGURE 20.5 An Analogy for Electrode Potential**

One limitation of this analogy is that, unlike the water level in a tank, we cannot measure the electrode potential in a half-cell directly—we can only measure the overall potential that occurs when two half-cells are combined in a whole cell. However, we can arbitrarily assign a potential of zero to the electrode in a *particular* type of half-cell and then measure all other electrode potentials relative to that zero.

The half-cell electrode that is normally chosen to have a potential of zero is the **standard hydrogen electrode (SHE)**. This half-cell consists of an inert platinum electrode immersed in 1 M HCl with hydrogen gas at 1 atm bubbling through the solution, as shown in Figure 20.6►. When the SHE acts as the cathode, the following half-reaction occurs:

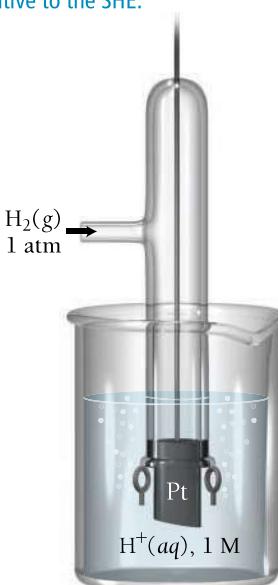


If we connect the standard hydrogen electrode to an electrode in another half-cell of interest, we can measure the potential difference (or voltage) between the two electrodes. Because we assigned the standard hydrogen electrode zero voltage, we can now determine the electrode potential of the other half-cell.

For example, consider the electrochemical cell in Figure 20.7►. In this electrochemical cell, Zn is oxidized to  $\text{Zn}^{2+}$  and  $\text{H}^+$  is reduced to  $\text{H}_2$  under standard conditions (all solutions are 1 M in concentration, and all gases are 1 atm in pressure) and at 25 °C.

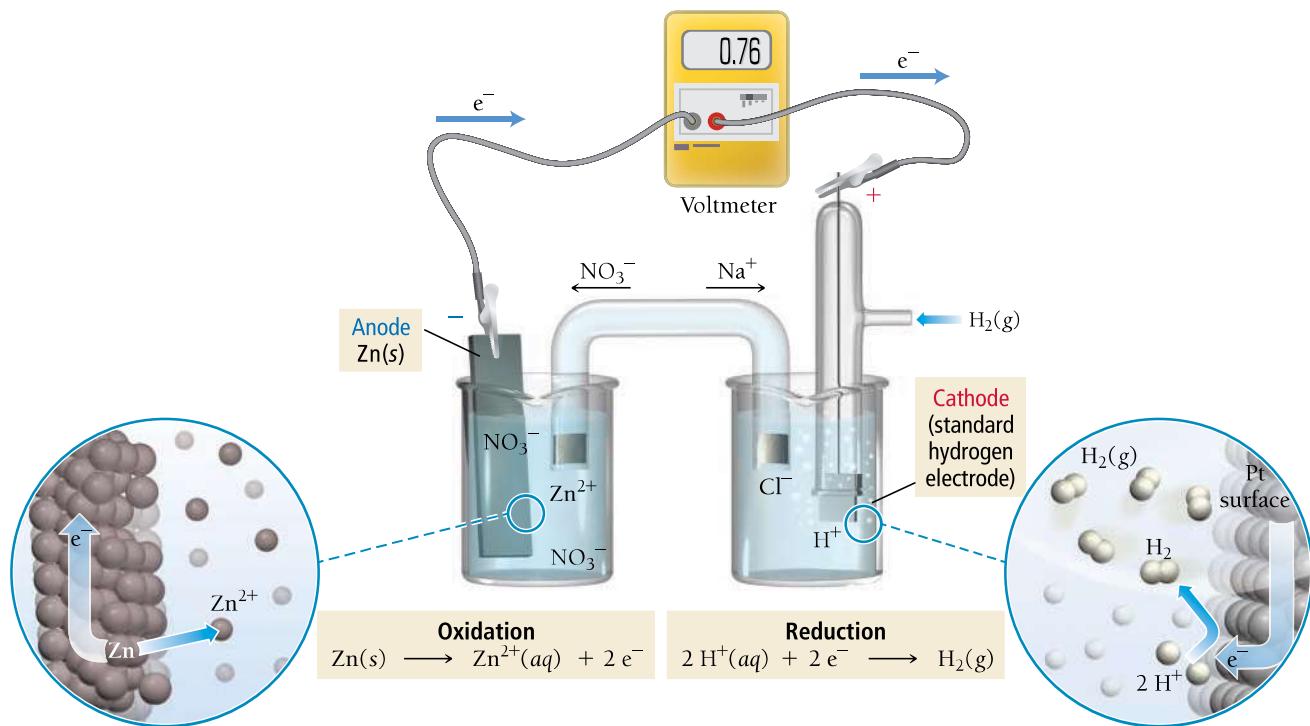
### Standard Hydrogen Electrode (SHE)

We arbitrarily assign the SHE an electrode potential of zero. All other electrode potentials are then measured relative to the SHE.



**▲ FIGURE 20.6 The Standard Hydrogen Electrode**

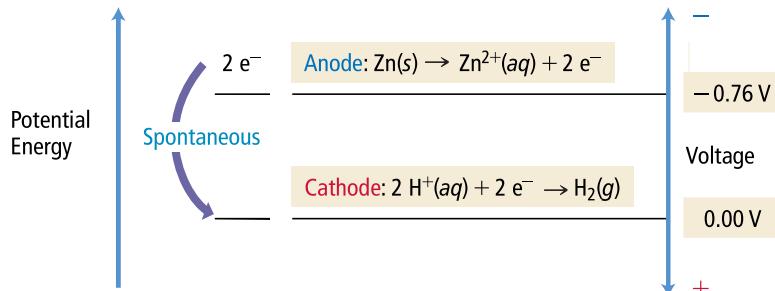
## Measuring Half-Cell Potential with the SHE



Electrons travel from the anode (where oxidation occurs) to the cathode (where reduction occurs), so we define  $E_{\text{cell}}^{\circ}$  as *the difference in voltage between the cathode (final state) and the anode (initial state)*:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{final}}^{\circ} - E_{\text{initial}}^{\circ} \\ &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \end{aligned}$$

The measured cell potential for this cell is +0.76 V. The anode (in this case, Zn/Zn<sup>2+</sup>) is at a more negative voltage (higher potential energy) than the cathode (in this case, the SHE). Therefore, electrons spontaneously flow from the anode to the cathode. We can diagram the potential energy and the voltage as follows:



Referring back to our water tank analogy, the zinc half-cell is like the water tank with the higher water level, and electrons therefore flow from the zinc electrode to the standard hydrogen electrode.

Because we assigned the SHE a potential of zero (0.00 V), we can determine the electrode potential for the Zn/Zn<sup>2+</sup> half-cell (the anode) from the measured cell potential ( $E_{\text{cell}}^{\circ}$ ):

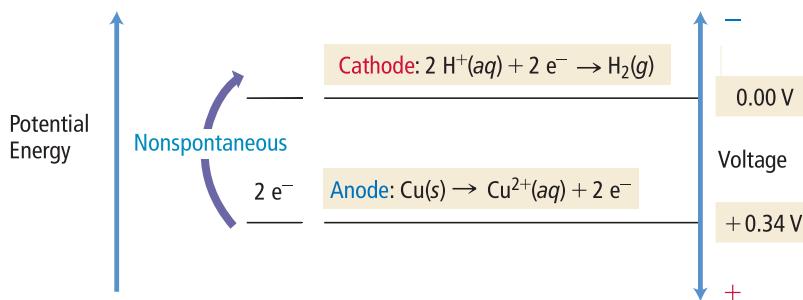
$$\begin{aligned} E_{\text{cell}}^{\circ} &= E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} \\ 0.76 \text{ V} &= 0.00 \text{ V} - E_{\text{anode}}^{\circ} \\ E_{\text{anode}}^{\circ} &= -0.76 \text{ V} \end{aligned}$$

The potential for the Zn/Zn<sup>2+</sup> electrode is *negative*. The negative potential indicates that an electron at the Zn/Zn<sup>2+</sup> electrode has greater potential energy than it does at the SHE. Remember that the more negative the electrode potential is, the greater the potential energy of an electron at that electrode (because negative charge repels electrons).

**▲ FIGURE 20.7 Measuring Electrode Potential** Because the electrode potential of the SHE is zero, the electrode potential for the oxidation of Zn is equal to the cell potential.

What happens if we connect an electrode in which the electron has *more positive* potential (than the standard hydrogen electrode) to the standard hydrogen electrode? That electrode would then have a more *positive* voltage (lower potential energy for an electron).

For example, suppose we connect the standard hydrogen electrode to a Cu electrode immersed in a 1 M  $\text{Cu}^{2+}$  solution. The measured cell potential for this cell is  $-0.34\text{ V}$ . The anode (defined as  $\text{Cu}/\text{Cu}^{2+}$ ) is at a more positive voltage (lower potential energy) than the cathode (the SHE). Therefore, electrons will *not* spontaneously flow from the anode to the cathode. We can diagram the potential energy and the voltage of this cell as follows:



The copper half-cell is like the water tank with the lower water level, and electrons *do not* spontaneously flow from the copper electrode to the standard hydrogen electrode.

We can again determine the electrode potential for the  $\text{Cu}/\text{Cu}^{2+}$  half-cell (the anode) from the measured cell potential:

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$-0.34\text{ V} = 0.00\text{ V} - E_{\text{anode}}^{\circ}$$

$$E_{\text{anode}}^{\circ} = +0.34\text{ V}$$

The potential for the  $\text{Cu}/\text{Cu}^{2+}$  electrode is *positive*. The positive potential indicates that an electron at the  $\text{Cu}/\text{Cu}^{2+}$  electrode has *lower* potential energy than it does at the SHE. The more positive the electrode potential, the lower the potential energy of an electron at that electrode (because positive charge attracts electrons).

By convention, standard electrode potentials are written for *reduction* half-reactions. We write the standard electrode potentials for the two half-reactions just discussed as:



We can see that the  $\text{Cu}/\text{Cu}^{2+}$  electrode is positive relative to the SHE (and therefore, tends to draw electrons *away* from the SHE) and that the  $\text{Zn}/\text{Zn}^{2+}$  electrode is negative relative to the SHE (and therefore, tends to repel electrons toward the SHE). Table 20.1 lists the standard electrode potentials for a number of common half-reactions.

#### **Summarizing Standard Electrode Potentials:**

- The electrode potential of the standard hydrogen electrode (SHE) is exactly zero.
- The electrode in any half-cell with a greater tendency to undergo reduction is positively charged relative to the SHE and therefore has a positive  $E^{\circ}$ .
- The electrode in any half-cell with a lesser tendency to undergo reduction (or greater tendency to undergo oxidation) is negatively charged relative to the SHE and therefore has a negative  $E^{\circ}$ .
- The cell potential of any electrochemical cell ( $E_{\text{cell}}^{\circ}$ ) is the difference between the electrode potentials of the cathode and the anode ( $E_{\text{cell}}^{\circ} = E_{\text{cat}}^{\circ} - E_{\text{an}}^{\circ}$ ).
- $E_{\text{cell}}^{\circ}$  is positive for spontaneous reactions and negative for nonspontaneous reactions.

Multiplying a half-reaction by some constant to balance a redox reaction *does not* affect the value of  $E^{\circ}$  for the half-reaction.

**TABLE 20.1** Standard Electrode Potentials at 25 °C

Reduction Half-Reaction		$E^\circ(V)$
High tendency towards reduction		
$\text{F}_2(g) + 2 \text{e}^- \rightarrow 2 \text{F}^-(aq)$	2.87	Low tendency towards oxidation
$\text{H}_2\text{O}_2(aq) + 2 \text{H}^+(aq) + 2 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(l)$	1.78	
$\text{PbO}_2(s) + 4 \text{H}^+(aq) + \text{SO}_4^{2-}(aq) + 2 \text{e}^- \rightarrow \text{PbSO}_4(s) + 2 \text{H}_2\text{O}(l)$	1.69	
$\text{MnO}_4^-(aq) + 4 \text{H}^+(aq) + 3 \text{e}^- \rightarrow \text{MnO}_2(s) + 2 \text{H}_2\text{O}(l)$	1.68	
$\text{MnO}_4^-(aq) + 8 \text{H}^+(aq) + 5 \text{e}^- \rightarrow \text{Mn}^{2+}(aq) + 4 \text{H}_2\text{O}(l)$	1.51	
$\text{Au}^{3+}(aq) + 3 \text{e}^- \rightarrow \text{Au}(s)$	1.50	
$\text{PbO}_2(s) + 4 \text{H}^+(aq) + 2 \text{e}^- \rightarrow \text{Pb}^{2+}(aq) + 2 \text{H}_2\text{O}(l)$	1.46	
$\text{Cl}_2(g) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(aq)$	1.36	
$\text{Cr}_2\text{O}_7^{2-}(aq) + 14 \text{H}^+(aq) + 6 \text{e}^- \rightarrow 2 \text{Cr}^{3+}(aq) + 7 \text{H}_2\text{O}(l)$	1.33	
$\text{O}_2(g) + 4 \text{H}^+(aq) + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(l)$	1.23	
$\text{MnO}_2(s) + 4 \text{H}^+(aq) + 2 \text{e}^- \rightarrow \text{Mn}^{2+}(aq) + 2 \text{H}_2\text{O}(l)$	1.21	
$\text{IO}_3^-(aq) + 6 \text{H}^+(aq) + 5 \text{e}^- \rightarrow \frac{1}{2}\text{I}_2(aq) + 3 \text{H}_2\text{O}(l)$	1.20	
$\text{Br}_2(l) + 2 \text{e}^- \rightarrow 2 \text{Br}^-(aq)$	1.09	
$\text{VO}_2^+(aq) + 2 \text{H}^+(aq) + \text{e}^- \rightarrow \text{VO}^{2+}(aq) + \text{H}_2\text{O}(l)$	1.00	
$\text{NO}_3^-(aq) + 4 \text{H}^+(aq) + 3 \text{e}^- \rightarrow \text{NO}(g) + 2 \text{H}_2\text{O}(l)$	0.96	
$\text{ClO}_2(g) + \text{e}^- \rightarrow \text{ClO}_2^-(aq)$	0.95	
$\text{Ag}^+(aq) + \text{e}^- \rightarrow \text{Ag}(s)$	0.80	
$\text{Fe}^{3+}(aq) + \text{e}^- \rightarrow \text{Fe}^{2+}(aq)$	0.77	
$\text{O}_2(g) + 2 \text{H}^+(aq) + 2 \text{e}^- \rightarrow \text{H}_2\text{O}_2(aq)$	0.70	
$\text{MnO}_4^-(aq) + \text{e}^- \rightarrow \text{MnO}_4^{2-}(aq)$	0.56	
$\text{I}_2(s) + 2 \text{e}^- \rightarrow 2 \text{I}^-(aq)$	0.54	
$\text{Cu}^+(aq) + \text{e}^- \rightarrow \text{Cu}(s)$	0.52	
$\text{O}_2(g) + 2 \text{H}_2\text{O}(l) + 4 \text{e}^- \rightarrow 4 \text{OH}^-(aq)$	0.40	
$\text{Cu}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Cu}(s)$	0.34	
$\text{SO}_4^{2-}(aq) + 4 \text{H}^+(aq) + 2 \text{e}^- \rightarrow \text{H}_2\text{SO}_3(aq) + \text{H}_2\text{O}(l)$	0.20	
$\text{Cu}^{2+}(aq) + \text{e}^- \rightarrow \text{Cu}^+(aq)$	0.16	
$\text{Sn}^{4+}(aq) + 2 \text{e}^- \rightarrow \text{Sn}^{2+}(aq)$	0.15	
$2 \text{H}^+(aq) + 2 \text{e}^- \rightarrow \text{H}_2(g)$	0	
$\text{Fe}^{3+}(aq) + 3 \text{e}^- \rightarrow \text{Fe}(s)$	-0.036	
$\text{Pb}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Pb}(s)$	-0.13	
$\text{Sn}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Sn}(s)$	-0.14	
$\text{Ni}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Ni}(s)$	-0.23	
$\text{Cd}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Cd}(s)$	-0.40	
$\text{Fe}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Fe}(s)$	-0.45	
$\text{Cr}^{3+}(aq) + \text{e}^- \rightarrow \text{Cr}^{2+}(aq)$	-0.50	
$\text{Cr}^{3+}(aq) + 3 \text{e}^- \rightarrow \text{Cr}(s)$	-0.73	
$\text{Zn}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Zn}(s)$	-0.76	
$2 \text{H}_2\text{O}(l) + 2 \text{e}^- \rightarrow \text{H}_2(g) + 2 \text{OH}^-(aq)$	-0.83	
$\text{Mn}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Mn}(s)$	-1.18	
$\text{Al}^{3+}(aq) + 3 \text{e}^- \rightarrow \text{Al}(s)$	-1.66	
$\text{Mg}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Mg}(s)$	-2.37	
$\text{Na}^+(aq) + \text{e}^- \rightarrow \text{Na}(s)$	-2.71	
$\text{Ca}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Ca}(s)$	-2.76	
$\text{Ba}^{2+}(aq) + 2 \text{e}^- \rightarrow \text{Ba}(s)$	-2.90	
$\text{K}^+(aq) + \text{e}^- \rightarrow \text{K}(s)$	-2.92	
$\text{Li}^+(aq) + \text{e}^- \rightarrow \text{Li}(s)$	-3.04	

Low tendency towards reduction

High tendency towards oxidation

Example 20.4 illustrates how to calculate the potential of an electrochemical cell from the standard electrode potentials of the half-reactions.

**WATCH NOW!**

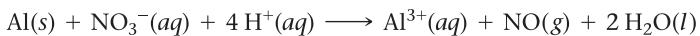
**INTERACTIVE WORKED EXAMPLE 20.4**

### EXAMPLE 20.4

### Calculating Standard Potentials for Electrochemical Cells from Standard Electrode Potentials of the Half-Reactions



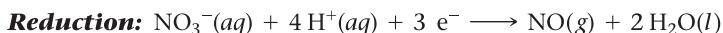
Use tabulated standard electrode potentials to calculate the standard cell potential for the following reaction occurring in an electrochemical cell at 25 °C. (The equation is balanced.)



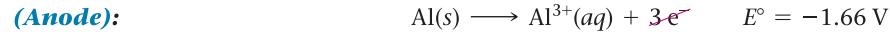
#### SOLUTION

Begin by separating the reaction into oxidation and reduction half-reactions. (In this case, you can readily see that Al(s) is oxidized. In cases where it is not so apparent, you may want to assign oxidation states to determine the correct half-reactions.)

Look up the standard electrode potentials for each half-reaction in Table 20.1. Add the half-cell reactions together to obtain the overall redox equation. Calculate the standard cell potential by subtracting the electrode potential of the anode from the electrode potential of the cathode.



**Oxidation**



**Reduction**



$$E_{\text{cell}}^\circ = E_{\text{cat}}^\circ - E_{\text{an}}^\circ$$

$$= 0.96 \text{ V} - (-1.66 \text{ V})$$

$$= 2.62 \text{ V}$$

**FOR PRACTICE 20.4** Use tabulated standard electrode potentials to calculate the standard cell potential for the following reaction occurring in an electrochemical cell at 25 °C. (The equation is balanced.)



**ANSWER NOW!**



### 20.3 Cc Conceptual Connection

**STANDARD ELECTRODE POTENTIALS** An electrode has a negative electrode potential. Which statement is correct regarding the potential energy of an electron at this electrode?

- (a) An electron at this electrode has a lower potential energy than it has at a standard hydrogen electrode.
- (b) An electron at this electrode has a higher potential energy than it has at a standard hydrogen electrode.
- (c) An electron at this electrode has the same potential energy as it has at a standard hydrogen electrode.

### Predicting the Spontaneous Direction of an Oxidation–Reduction Reaction

To determine the spontaneous direction of an oxidation–reduction reaction, we examine the electrode potentials of the two relevant half-reactions in Table 20.1. The half-reaction with the more *negative* electrode potential tends to lose electrons and therefore tends to

undergo oxidation. (Remember that negative charge repels electrons.) The half-reaction having the more *positive* electrode potential tends to gain electrons, and therefore, undergo reduction. (Remember that positive charge attracts electrons.)

For example, consider the two reduction half-reactions:



The following mnemonics (NIO and PIR) help to predict the spontaneous direction of redox reactions:

**N.I.O.**—More **N**egative **I**s **O**xidation

**P.I.R.**—More **P**ositive **I**s **R**eduction

Because the manganese half-reaction has a more negative electrode potential, it repels electrons and proceeds in the reverse direction (oxidation). Because the nickel half-reaction has the more positive (or less negative) electrode potential, it attracts electrons and proceeds in the forward direction.

We can confirm this by calculating the standard electrode potential for manganese acting as the anode (oxidation) and nickel acting as the cathode (reduction):

**Oxidation (Anode):**



**Reduction (Cathode):**



$$\begin{array}{c} \text{Ni}^{2+}(aq) + \text{Mn}(s) \longrightarrow \text{Ni}(s) + \text{Mn}^{2+}(aq) \\ \hline E_{\text{cell}}^\circ = E_{\text{cat}}^\circ - E_{\text{an}}^\circ \\ = -0.23 \text{ V} - (-1.18 \text{ V}) \\ = 0.95 \text{ V} \end{array}$$

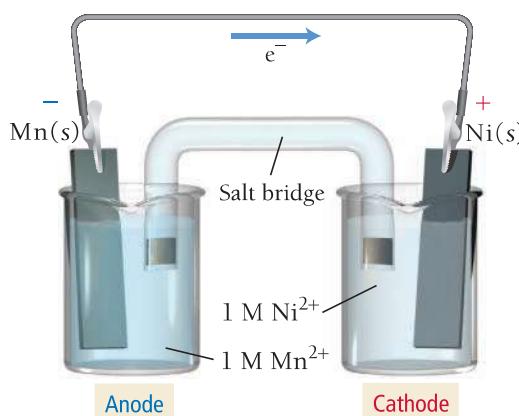
The overall cell potential is positive, indicating a spontaneous reaction. Consider the electrochemical cell corresponding to this spontaneous redox reaction in Figure 20.8▼. We draw the manganese half-cell on the left as the anode and the nickel half-cell on the right as the cathode. Electrons flow from the anode to the cathode.

Another way to predict the spontaneity of a redox reaction is to note the relative positions of the two half-reactions in Table 20.1. The table lists half-reactions in order of *decreasing* electrode potential, so the half-reactions near the top of the table—those having large *positive* electrode potentials—attract electrons, and therefore, tend to occur in the forward direction. Half-reactions near the bottom of the table—those having large *negative* electrode potentials—repel electrons, and therefore, tend to occur in the reverse direction. In other words, as we move down Table 20.1, the half-reactions become less likely to occur in the forward direction and more likely to occur in the reverse direction. As a result, *any reduction half-reaction listed is spontaneous when paired with the reverse of a half-reaction that appears below it in Table 20.1*.

For example, if we return to our two previous half-reactions involving manganese and nickel, we can see that the manganese half-reaction is below the nickel half-reaction in Table 20.1:



Therefore, the nickel reaction occurs in the forward direction (reduction), and the manganese reaction occurs in the reverse direction (oxidation).



**◀ FIGURE 20.8 Mn/Ni<sup>2+</sup> Electrochemical Cell** The reduction of Mn<sup>2+</sup> is listed below the reduction of Ni<sup>2+</sup> in Table 20.1, so the reduction of Ni<sup>2+</sup> is spontaneous when paired with the oxidation of Mn.

Recall from Section 5.9 that an oxidizing agent causes the oxidation of another substance (and is itself reduced) and that a reducing agent causes the reduction of another substance (and is itself oxidized).

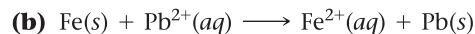
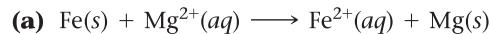
### Summarizing the Prediction of Spontaneous Direction for Redox Reactions:

- The half-reaction with the more *positive* electrode potential attracts electrons more strongly and undergoes reduction. (Substances listed at the top of Table 20.1 tend to undergo reduction; they are good oxidizing agents.)
- The half-reaction with the more *negative* electrode potential repels electrons more strongly and undergoes oxidation. (Substances listed near the bottom of Table 20.1 tend to undergo oxidation; they are good reducing agents.)
- Any reduction reaction in Table 20.1 is spontaneous when paired with the *reverse* of any of the reactions listed below it on the table.

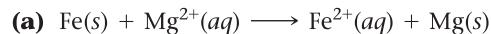
### EXAMPLE 20.5

### Predicting Spontaneous Redox Reactions and Sketching Electrochemical Cells

Without calculating  $E_{\text{cell}}^{\circ}$ , predict whether each of the redox reactions is spontaneous. If the reaction is spontaneous as written, make a sketch of the electrochemical cell in which the reaction could occur. If the reaction is not spontaneous as written, write an equation for the spontaneous direction in which the reaction would occur and sketch the electrochemical cell in which the spontaneous reaction would occur. In your sketches, make sure to label the anode (which should be drawn on the left), the cathode, and the direction of electron flow.



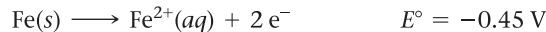
#### SOLUTION



This reaction involves the reduction of  $\text{Mg}^{2+}$ :



and the oxidation of Fe:

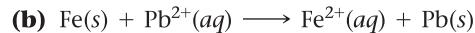


However, the magnesium half-reaction has the more negative electrode potential and therefore repels electrons more strongly and undergoes oxidation. The iron half-reaction has the more positive electrode potential and therefore attracts electrons more strongly and undergoes reduction. So the reaction as written is *not* spontaneous. (The reaction pairs the reduction of  $\text{Mg}^{2+}$  with the reverse of a half-reaction *above it* in Table 20.1—such pairings are not spontaneous.)

However, the reverse reaction is spontaneous:



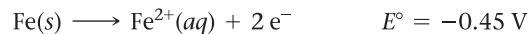
The corresponding electrochemical cell is shown in Figure 20.9.



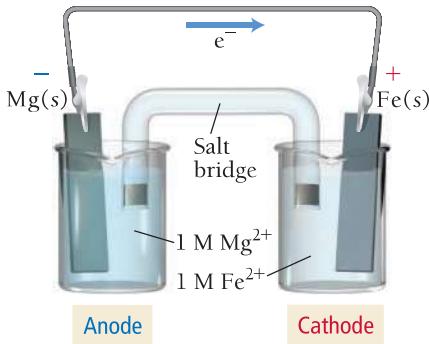
This reaction involves the reduction of  $\text{Pb}^{2+}$ :



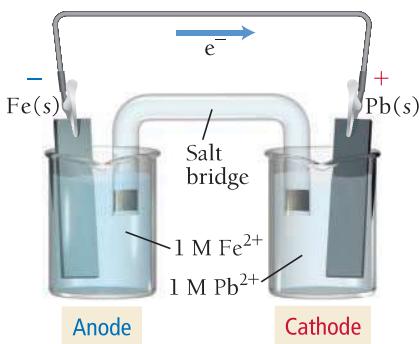
and the oxidation of iron:



The iron half-reaction has the more negative electrode potential and therefore repels electrons and undergoes oxidation. The lead half-reaction has the more positive electrode potential and therefore attracts electrons and undergoes reduction. Therefore, the reaction *is* spontaneous as written. (The reaction pairs the reduction of  $\text{Pb}^{2+}$  with the reverse of a half-reaction *below it* in Table 20.1—such pairings are always spontaneous.) The corresponding electrochemical cell is shown in Figure 20.10.

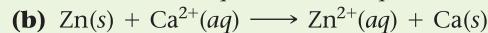
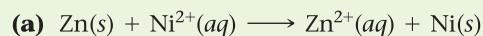


**▲ FIGURE 20.9** Mg/Fe<sup>2+</sup> Electrochemical Cell



**▲ FIGURE 20.10** Fe/Pb<sup>2+</sup> Electrochemical Cell

**FOR PRACTICE 20.5** Are the following redox reactions spontaneous under standard conditions?



**SELECTIVE OXIDATION**

A solution contains both NaI and NaBr. Which oxidizing agent could you add to the solution to selectively oxidize  $\text{I}^-(aq)$  but not  $\text{Br}^-(aq)$ ?

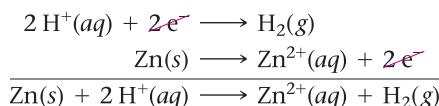
- (a)  $\text{Cl}_2$       (b)  $\text{H}_2\text{O}_2$       (c)  $\text{CuCl}_2$       (d)  $\text{HNO}_3$



ANSWER NOW!

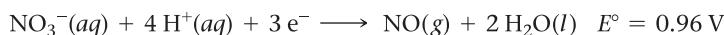
**Predicting Whether a Metal Will Dissolve in Acid**

In Chapter 17, we learned that acids dissolve metals. Most acids dissolve metals by the reduction of  $\text{H}^+$  ions to hydrogen gas and the corresponding oxidation of the metal to its ion. For example, if solid Zn is dropped into hydrochloric acid, the following reaction occurs:

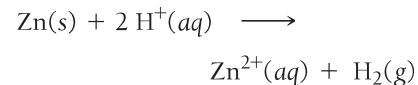


We observe the reaction as the dissolving of the zinc and the bubbling of hydrogen gas. The zinc is oxidized and the  $\text{H}^+$  ions are reduced. Notice that this reaction involves the pairing of a reduction half-reaction (the reduction of  $\text{H}^+$ ) with the reverse of a half-reaction that falls below it in Table 20.1. Therefore, this reaction is spontaneous. What happens, however, if we pair the reduction of  $\text{H}^+$  with the oxidation of Cu? The reaction is not spontaneous because it involves pairing the reduction of  $\text{H}^+$  with the reverse of a half-reaction that is listed *above it* in the table. Consequently, copper does not react with  $\text{H}^+$  and does not dissolve in acids such as HCl. In general, *metals whose reduction half-reactions are listed below the reduction of  $\text{H}^+$  to  $\text{H}_2$  in Table 20.1 dissolve in acids, while metals listed above it do not.*

An important exception to this rule is nitric acid ( $\text{HNO}_3$ ), which can oxidize metals through the reduction half-reaction:



Since this half-reaction is above the reduction of  $\text{H}^+$  in Table 20.1,  $\text{HNO}_3$  can oxidize metals (such as copper) that can't be oxidized by HCl.



▲ When zinc is immersed in hydrochloric acid, the zinc is oxidized, forming ions that become solvated in the solution. Hydrogen ions are reduced, forming bubbles of hydrogen gas.

**METALS DISSOLVING IN ACIDS**

Which metal dissolves in  $\text{HNO}_3$  but not in HCl?

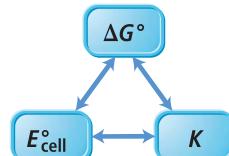
- (a) Fe      (b) Au      (c) Ag



ANSWER NOW!

**20.5****Cell Potential, Free Energy, and the Equilibrium Constant**

We have seen that a positive standard cell potential ( $E_{\text{cell}}^\circ$ ) corresponds to a spontaneous oxidation-reduction reaction. And we know (from Chapter 19) that the spontaneity of a reaction is determined by the sign of  $\Delta G^\circ$ . Therefore,  $E_{\text{cell}}^\circ$  and  $\Delta G^\circ$  must be related. We also know from Section 19.10 that  $\Delta G^\circ$  for a reaction is related to the equilibrium constant ( $K$ ) for the reaction. Since  $E_{\text{cell}}^\circ$  and  $\Delta G^\circ$  are related, then  $E_{\text{cell}}^\circ$  and  $K$  must also be related.

**WATCH NOW!****KEY CONCEPT VIDEO 20.5**

Cell Potential, Free Energy, and the Equilibrium Constant

Before we look at the nature of each of these relationships in detail, let's consider the following generalizations.

For a spontaneous redox reaction (one that proceeds in the forward direction when all reactants and products are in their standard states):

- $\Delta G^\circ$  is negative ( $<0$ )
- $E_{\text{cell}}^\circ$  is positive ( $>0$ )
- $K > 1$

For a nonspontaneous reaction (one that proceeds in the reverse direction when all reactants and products are in their standard states):

- $\Delta G^\circ$  is positive ( $>0$ )
- $E_{\text{cell}}^\circ$  is negative ( $<0$ )
- $K < 1$

## The Relationship between $\Delta G^\circ$ and $E_{\text{cell}}^\circ$

We can derive a relationship between  $\Delta G^\circ$  and  $E_{\text{cell}}^\circ$  by briefly returning to the definition of potential difference from Section 20.3—a potential difference is a measure of the difference of potential energy per unit charge ( $q$ ):

$$E = \frac{\text{potential energy difference (in J)}}{\text{charge (in C)}}$$

Since the potential energy difference represents the maximum amount of work that can be done by the system on the surroundings, we can write:

$$w_{\text{max}} = -qE_{\text{cell}}^\circ \quad [20.1]$$

The negative sign follows the convention used throughout this book that work done by the system on the surroundings is negative.

We can quantify the charge ( $q$ ) that flows in an electrochemical reaction by using **Faraday's constant ( $F$ )**, which represents the charge in coulombs of 1 mol of electrons:

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

The total charge is  $q = nF$ , where  $n$  is the number of moles of electrons from the balanced chemical equation and  $F$  is Faraday's constant. Substituting  $q = nF$  into Equation 20.1:

$$\begin{aligned} w_{\text{max}} &= -qE_{\text{cell}}^\circ \\ &= -nFE_{\text{cell}}^\circ \end{aligned} \quad [20.2]$$

Finally, recall from Chapter 19 that the standard change in free energy for a chemical reaction ( $\Delta G^\circ$ ) represents the maximum amount of work that can be done by the reaction. Therefore,  $w_{\text{max}} = \Delta G^\circ$ . Making this substitution into Equation 20.2, we arrive at the following important result:

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ \quad [20.3]$$

where  $\Delta G^\circ$  is the standard change in free energy for an electrochemical reaction,  $n$  is the number of moles of electrons transferred in the balanced equation,  $F$  is Faraday's constant, and  $E_{\text{cell}}^\circ$  is the standard cell potential. Example 20.6 shows how to apply this equation to calculate the standard free energy change for an electrochemical cell.

WATCH NOW!

## INTERACTIVE WORKED EXAMPLE 20.6

**EXAMPLE 20.6** Relating  $\Delta G^\circ$  and  $E_{\text{cell}}^\circ$ Use the tabulated electrode potentials to calculate  $\Delta G^\circ$  for the reaction:

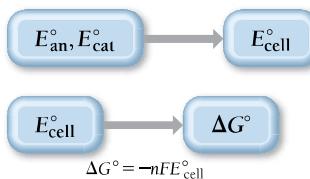
Is the reaction spontaneous?

**SORT** You are given a redox reaction and asked to find  $\Delta G^\circ$ .

**GIVEN:**  $\text{I}_2(\text{s}) + 2 \text{Br}^-(\text{aq}) \longrightarrow 2 \text{I}^-(\text{aq}) + \text{Br}_2(\text{l})$

**FIND:**  $\Delta G^\circ$

**STRATEGIZE** Refer to the values of electrode potentials in Table 20.1 to calculate  $E_{\text{cell}}^\circ$ . Then use Equation 20.3 to calculate  $\Delta G^\circ$  from  $E_{\text{cell}}^\circ$ .

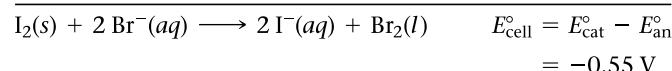
**CONCEPTUAL PLAN**

**SOLVE** Separate the reaction into oxidation and reduction half-reactions and find the standard electrode potentials for each. Determine  $E_{\text{cell}}^\circ$  by subtracting  $E_{\text{an}}$  from  $E_{\text{cat}}$ .

**SOLUTION**

**Oxidation (Anode):**  $2 \text{Br}^-(\text{aq}) \longrightarrow \text{Br}_2(\text{l}) + 2\text{e}^-$   $E^\circ = 1.09 \text{ V}$

**Reduction (Cathode):**  $\text{I}_2(\text{s}) + 2\text{e}^- \longrightarrow 2 \text{I}^-(\text{aq})$   $E^\circ = 0.54 \text{ V}$



Calculate  $\Delta G^\circ$  from  $E_{\text{cell}}^\circ$ . The value of  $n$  (the number of moles of electrons) corresponds to the number of electrons that are canceled in the half-reactions. Remember that  $1 \text{ V} = 1 \text{ J/C}$ .

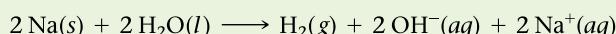
$$\Delta G^\circ = -nFE_{\text{cell}}^\circ$$

$$\begin{aligned} &= -2 \text{ mol e}^- \left( \frac{96,485 \text{ C}}{\text{mol e}^-} \right) \left( -0.55 \frac{\text{J}}{\text{C}} \right) \\ &= +1.1 \times 10^5 \text{ J} \end{aligned}$$

Since  $\Delta G^\circ$  is positive, the reaction is not spontaneous under standard conditions.

**CHECK** The answer is in the correct units (joules) and seems reasonable in magnitude ( $\approx 110 \text{ kJ}$ ). You have seen (in Chapter 19) that values of  $\Delta G^\circ$  typically range from plus or minus tens to hundreds of kilojoules. The sign is positive, as expected for a reaction in which  $E_{\text{cell}}^\circ$  is negative.

**FOR PRACTICE 20.6** Use tabulated electrode potentials to calculate  $\Delta G^\circ$  for the reaction.



Is the reaction spontaneous?

**PERIODIC TRENDS AND THE DIRECTION OF SPONTANEITY FOR REDOX REACTIONS**

Consider the result of Example 20.6. The calculation revealed that the reaction is not spontaneous. Based on conceptual reasoning, which of the following best explains why  $\text{I}_2$  does not oxidize  $\text{Br}^-$ ?

- (a) Br is more electronegative than I; therefore, you do not expect  $\text{Br}^-$  to give up an electron to  $\text{I}_2$ .
- (b) I is more electronegative than Br; therefore, you do not expect  $\text{I}_2$  to give up an electron to  $\text{Br}^-$ .
- (c)  $\text{Br}^-$  is in solution and  $\text{I}_2$  is a solid. Solids do not gain electrons from substances in solution.

**20.6**  
**Cc**  
Conceptual Connection

ANSWER NOW!



## The Relationship between $E_{\text{cell}}^{\circ}$ and $K$

We can derive a relationship between the standard cell potential ( $E_{\text{cell}}^{\circ}$ ) and the equilibrium constant for the redox reaction occurring in the cell ( $K$ ) by returning to the relationship between  $\Delta G^{\circ}$  and  $K$  that we learned in Chapter 19. Recall from Section 19.10 that:

$$\Delta G^{\circ} = -RT \ln K \quad [20.4]$$

By setting Equations 20.3 and 20.4 equal to each other, we get:

$$\begin{aligned} -nFE_{\text{cell}}^{\circ} &= -RT \ln K \\ E_{\text{cell}}^{\circ} &= \frac{RT}{nF} \ln K \end{aligned} \quad [20.5]$$

Equation 20.5 is usually simplified for use at 25 °C by making the following substitutions:

$$R = 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}; T = 298.15 \text{ K}; F = \left( \frac{96,485 \text{ C}}{\text{mole}^{-}} \right); \text{and } \ln K = 2.303 \log K$$

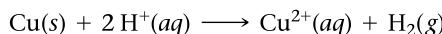
Substituting into Equation 20.5, we get the following important result:

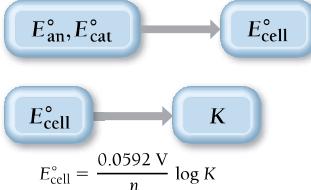
$$E_{\text{cell}}^{\circ} = \frac{0.0592 \text{ V}}{n} \log K \quad [20.6]$$

where  $E_{\text{cell}}^{\circ}$  is the standard cell potential,  $n$  is the number of moles of electrons transferred in the redox reaction, and  $K$  is the equilibrium constant for the balanced redox reaction at 25 °C. Example 20.7 demonstrates how to use Equation 20.6.

### EXAMPLE 20.7 Relating $E_{\text{cell}}^{\circ}$ and $K$

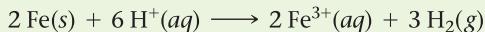
Use the tabulated electrode potentials to calculate  $K$  for the oxidation of copper by H<sup>+</sup> (at 25 °C):



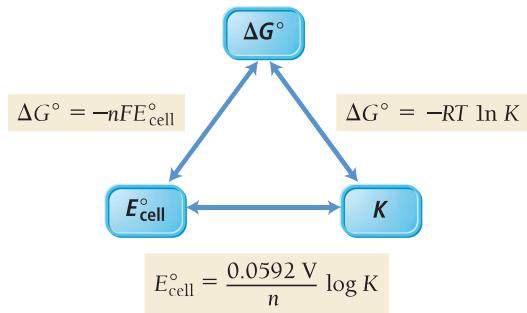
<b>SORT</b> You are given a redox reaction and asked to find $K$ .	<b>GIVEN:</b> Cu(s) + 2 H <sup>+</sup> (aq) → Cu <sup>2+</sup> (aq) + H <sub>2</sub> (g) <b>FIND:</b> $K$
<b>STRATEGIZE</b> Refer to the values of electrode potentials in Table 20.1 to calculate $E_{\text{cell}}^{\circ}$ . Then use Equation 20.6 to calculate $K$ from $E_{\text{cell}}^{\circ}$ .	<b>CONCEPTUAL PLAN</b>  $E_{\text{cell}}^{\circ} = \frac{0.0592 \text{ V}}{n} \log K$
<b>SOLVE</b> Separate the reaction into oxidation and reduction half-reactions and find the standard electrode potentials for each. Find $E_{\text{cell}}^{\circ}$ by subtracting $E_{\text{an}}$ from $E_{\text{cat}}$ .	<b>SOLUTION</b> <b>Oxidation</b> <b>(Anode):</b> Cu(s) → Cu <sup>2+</sup> (aq) + 2e <sup>-</sup> $E^{\circ} = 0.34 \text{ V}$ <b>Reduction</b> <b>(Cathode):</b> 2 H <sup>+</sup> (aq) + 2e <sup>-</sup> → H <sub>2</sub> (g) $E^{\circ} = 0.00 \text{ V}$ $\begin{array}{ll} \text{Cu(s)} + 2 \text{H}^{+}(\text{aq}) \longrightarrow \text{Cu}^{2+}(\text{aq}) + \text{H}_2(\text{g}) & E_{\text{cell}}^{\circ} = E_{\text{cat}}^{\circ} - E_{\text{an}}^{\circ} \\ & = -0.34 \text{ V} \end{array}$
Calculate $K$ from $E_{\text{cell}}^{\circ}$ . The value of $n$ (the number of moles of electrons) corresponds to the number of electrons that are canceled in the half-reactions.	$E_{\text{cell}}^{\circ} = \frac{0.0592 \text{ V}}{n} \log K$ $\log K = E_{\text{cell}}^{\circ} \frac{n}{0.0592 \text{ V}}$ $\log K = -0.34 \frac{2}{0.0592} = -11.486$ $K = 10^{-11.486} = 3.3 \times 10^{-12}$

**CHECK** The answer has no units, as expected for an equilibrium constant. The magnitude of the answer is small, indicating that the reaction lies far to the left at equilibrium, as expected for a reaction in which  $E_{\text{cell}}^{\circ}$  is negative.

**FOR PRACTICE 20.7** Use the tabulated electrode potentials to calculate  $K$  for the oxidation of iron by  $\text{H}^{+}$  (at 25 °C):



Notice that the fundamental quantity in the given relationships is the standard change in free energy ( $\Delta G^{\circ}$ ). From that quantity, we can calculate both  $E_{\text{cell}}^{\circ}$  and  $K$ . The relationship between these three quantities is summarized with the following diagram:



**RELATING  $K$ ,  $\Delta G_{\text{rxn}}^{\circ}$ , AND  $E_{\text{cell}}^{\circ}$**  A redox reaction has an equilibrium constant of  $K = 1.2 \times 10^3$ . Which statement is true regarding  $\Delta G_{\text{rxn}}^{\circ}$  and  $E_{\text{cell}}^{\circ}$  for this reaction?

- (a)  $E_{\text{cell}}^{\circ}$  is positive and  $\Delta G_{\text{rxn}}^{\circ}$  is positive.
- (b)  $E_{\text{cell}}^{\circ}$  is negative and  $\Delta G_{\text{rxn}}^{\circ}$  is negative.
- (c)  $E_{\text{cell}}^{\circ}$  is positive and  $\Delta G_{\text{rxn}}^{\circ}$  is negative.
- (d)  $E_{\text{cell}}^{\circ}$  is negative and  $\Delta G_{\text{rxn}}^{\circ}$  is positive.

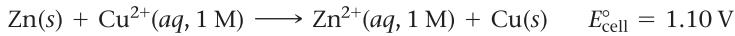


ANSWER NOW!

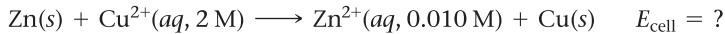


## 20.6 Cell Potential and Concentration

We have learned how to find  $E_{\text{cell}}^{\circ}$  under standard conditions. For example, we know that when  $[\text{Cu}^{2+}] = 1 \text{ M}$  and  $[\text{Zn}^{2+}] = 1 \text{ M}$ , the following reaction produces a potential of 1.10 V:



However, what if  $[\text{Cu}^{2+}] > 1 \text{ M}$  and  $[\text{Zn}^{2+}] < 1 \text{ M}$ ? For example, how would the cell potential for the following conditions be different from the potential under standard conditions?



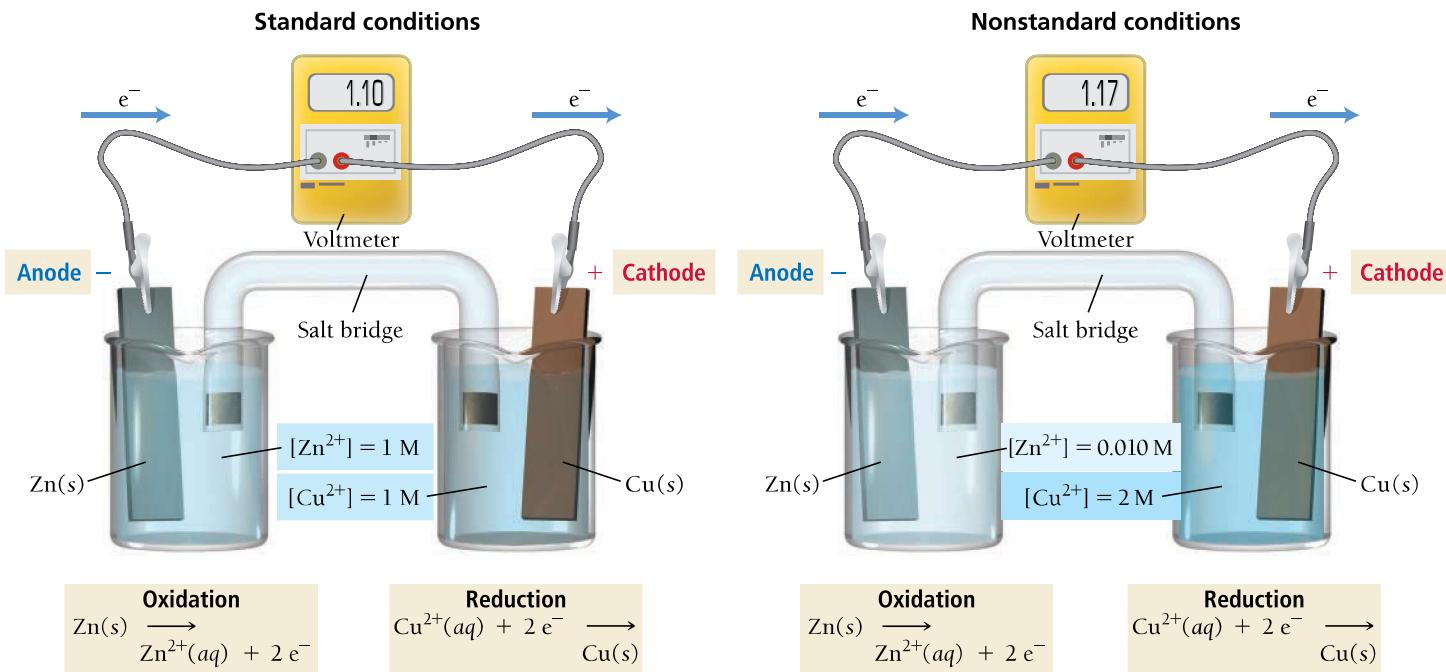
Since the concentration of a reactant is greater than standard conditions and since the concentration of product is less than standard conditions, we can use Le Châtelier's principle to predict that the reaction has an even stronger tendency to occur in the forward direction and that  $E_{\text{cell}}$  is therefore greater than +1.10 V (Figure 20.11►).

### Cell Potential under Nonstandard Conditions: The Nernst Equation

We can derive an exact relationship between  $E_{\text{cell}}$  (under nonstandard conditions) and  $E_{\text{cell}}^{\circ}$  by considering the relationship between the change in free energy ( $\Delta G$ ) and the *standard* change in free energy ( $\Delta G^{\circ}$ ) from Section 19.9:

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

[20.7]



**▲ FIGURE 20.11 Cell Potential and Concentration** This figure compares the  $Zn/Cu^{2+}$  electrochemical cell under standard and nonstandard conditions. In this case, the nonstandard conditions consist of a higher  $Cu^{2+}$  concentration ( $[Cu^{2+}] > 1 \text{ M}$ ) at the cathode and a lower  $Zn^{2+}$  concentration at the anode ( $[Zn^{2+}] < 1 \text{ M}$ ). According to Le Châtelier's principle, the forward reaction has a greater tendency to occur, resulting in a greater overall cell potential than the cell potential under standard conditions.

where  $R$  is the gas constant ( $8.314 \text{ J/mol} \cdot \text{K}$ ),  $T$  is the temperature in kelvins, and  $Q$  is the reaction quotient corresponding to the nonstandard conditions. Since we know the relationship between  $\Delta G$  and  $E_{\text{cell}}$  (Equation 20.3), we can substitute into Equation 20.7:

$$\begin{aligned}\Delta G &= \Delta G^\circ + RT \ln Q \\ -nFE_{\text{cell}} &= -nFE_{\text{cell}}^\circ + RT \ln Q\end{aligned}$$

We then divide each side by  $-nF$  to arrive at:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{nF} \ln Q \quad [20.8]$$

As we have seen,  $R$  and  $F$  are constants; at  $T = 25^\circ \text{C}$ ,  $\frac{RT}{nF} \ln Q = \frac{0.0592 \text{ V}}{n} \log Q$ .

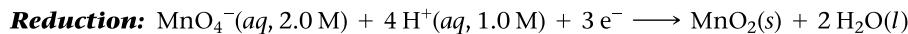
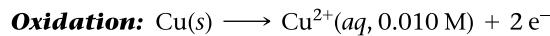
Substituting into Equation 20.8, we arrive at the **Nernst equation**:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592 \text{ V}}{n} \log Q \quad [20.9]$$

where  $E_{\text{cell}}$  is the cell potential in volts,  $E_{\text{cell}}^\circ$  is the *standard* cell potential in volts,  $n$  is the number of moles of electrons transferred in the redox reaction, and  $Q$  is the reaction quotient. Notice that, under standard conditions,  $Q = 1$ , and (since  $\log 1 = 0$ )  $E_{\text{cell}} = E_{\text{cell}}^\circ$ , as expected. Example 20.8 shows how to calculate the cell potential under nonstandard conditions.

## EXAMPLE 20.8 Calculating $E_{\text{cell}}$ under Nonstandard Conditions

Determine the cell potential for an electrochemical cell based on the following two half-reactions:



<p><b>SORT</b> You are given the half-reactions for a redox reaction and the concentrations of the aqueous reactants and products. You are asked to find the cell potential.</p>	<p><b>GIVEN:</b> <math>[\text{MnO}_4^-] = 2.0 \text{ M}</math>; <math>[\text{H}^+] = 1.0 \text{ M}</math>; <math>[\text{Cu}^{2+}] = 0.010 \text{ M}</math></p> <p><b>FIND:</b> <math>E_{\text{cell}}</math></p>
<p><b>STRATEGIZE</b> Use the tabulated values of electrode potentials to calculate <math>E_{\text{cell}}^\circ</math>. Then use Equation 20.9 to calculate <math>E_{\text{cell}}</math>.</p>	<p><b>CONCEPTUAL PLAN</b></p> <pre> graph LR     A["E_an^°, E_cat^°"] --&gt; B["E_cell^°"]     B --&gt; C["E_cell"]     D["E_cell^°, [MnO4^-], [H^+], [Cu2+]"] --&gt; E["E_cell"]     E --&gt; F["E_cell = E_cell^° - 0.0592 V / n log Q"]   </pre>
<p><b>SOLVE</b> Write the oxidation and reduction half-reactions, multiplying by the appropriate coefficients to cancel the electrons. Find the standard electrode potentials for each half-reaction. Find <math>E_{\text{cell}}^\circ</math>.</p>	<p><b>SOLUTION</b></p> <p><b>Oxidation</b></p> <p>(Anode): <math>3[\text{Cu}(s) \longrightarrow \text{Cu}^{2+}(aq) + 2 \text{e}^-]</math> <math>E^\circ = 0.34 \text{ V}</math></p> <p><b>Reduction</b></p> <p>(Cathode): <math>2[\text{MnO}_4^-(aq) + 4 \text{H}^+(aq) + 3 \text{e}^- \longrightarrow \text{MnO}_2(s) + 2 \text{H}_2\text{O}(l)]</math> <math>E^\circ = 1.68 \text{ V}</math></p> $3 \text{Cu}(s) + 2 \text{MnO}_4^-(aq) + 8 \text{H}^+(aq) \longrightarrow 3 \text{Cu}^{2+}(aq) + 2 \text{MnO}_2(s) + 4 \text{H}_2\text{O}(l)$ $E_{\text{cell}}^\circ = E_{\text{cat}}^° - E_{\text{an}}^° = 1.34 \text{ V}$
<p>Calculate <math>E_{\text{cell}}</math> from <math>E_{\text{cell}}^\circ</math>. The value of <math>n</math> (the number of moles of electrons) corresponds to the number of electrons (six in this case) canceled in the half-reactions. Determine <math>Q</math> based on the overall balanced equation and the given concentrations of the reactants and products. (Note that pure liquid water, solid <math>\text{MnO}_2</math>, and solid copper are omitted from the expression for <math>Q</math>.)</p>	$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^\circ - \frac{0.0592 \text{ V}}{n} \log Q \\ &= E_{\text{cell}}^\circ - \frac{0.0592 \text{ V}}{n} \log \frac{[\text{Cu}^{2+}]^3}{[\text{MnO}_4^-]^2 [\text{H}^+]^8} \\ &= 1.34 \text{ V} - \frac{0.0592 \text{ V}}{6} \log \frac{(0.010)^3}{(2.0)^2 (1.0)^8} \\ &= 1.34 \text{ V} - (-0.065 \text{ V}) \\ &= 1.41 \text{ V} \end{aligned}$
<p><b>CHECK</b> The answer has the correct units (V). The value of <math>E_{\text{cell}}</math> is larger than <math>E_{\text{cell}}^\circ</math>, as expected based on Le Châtelier's principle because one of the aqueous reactants has a concentration greater than standard conditions and the one aqueous product has a concentration less than standard conditions. Therefore, the reaction has a greater tendency to proceed toward products and a greater cell potential.</p>	<p><b>FOR PRACTICE 20.8</b> Determine the cell potential of an electrochemical cell based on the following two half-reactions:</p>
<p><b>Oxidation:</b> <math>\text{Ni}(s) \longrightarrow \text{Ni}^{2+}(aq, 2.0 \text{ M}) + 2 \text{e}^-</math></p> <p><b>Reduction:</b> <math>\text{VO}_2^+(aq, 0.010 \text{ M}) + 2 \text{H}^+(aq, 1.0 \text{ M}) + \text{e}^- \longrightarrow \text{VO}^{2+}(aq, 2.0 \text{ M}) + \text{H}_2\text{O}(l)</math></p>	

From Equation 20.9, we can conclude the following:

- When a redox reaction within a voltaic cell occurs under standard conditions,  $Q = 1$ ; therefore,  $E_{\text{cell}} = E_{\text{cell}}^{\circ}$ .

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q \\ &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log 1 \quad \text{log } 1 = 0 \\ &= E_{\text{cell}}^{\circ} \end{aligned}$$

- When a redox reaction within a voltaic cell occurs under conditions in which  $Q < 1$ , the greater concentration of reactants relative to products drives the reaction to the right, resulting in  $E_{\text{cell}} > E_{\text{cell}}^{\circ}$ .
- When a redox reaction within an electrochemical cell occurs under conditions in which  $Q > 1$ , the greater concentration of products relative to reactants drives the reaction to the left, resulting in  $E_{\text{cell}} < E_{\text{cell}}^{\circ}$ .
- When a redox reaction reaches equilibrium,  $Q = K$ . The redox reaction has no tendency to occur in either direction and  $E_{\text{cell}} = 0$ :

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q \quad E_{\text{cell}}^{\circ} \text{ (see Equation 20.6)} \\ &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log K \\ &= E_{\text{cell}}^{\circ} - E_{\text{cell}}^{\circ} \\ &= 0 \end{aligned}$$

This last point explains why batteries do not last forever—as the reactants are depleted, the reaction proceeds toward equilibrium and the potential tends toward zero.

**ANSWER NOW!**



## 20.8 Cc Conceptual Connection

**RELATING  $Q$ ,  $K$ ,  $E_{\text{cell}}$ , AND  $E_{\text{cell}}^{\circ}$**  In an electrochemical cell,  $Q = 0.0010$  and  $K = 0.10$ . What can you conclude about  $E_{\text{cell}}$  and  $E_{\text{cell}}^{\circ}$ ?

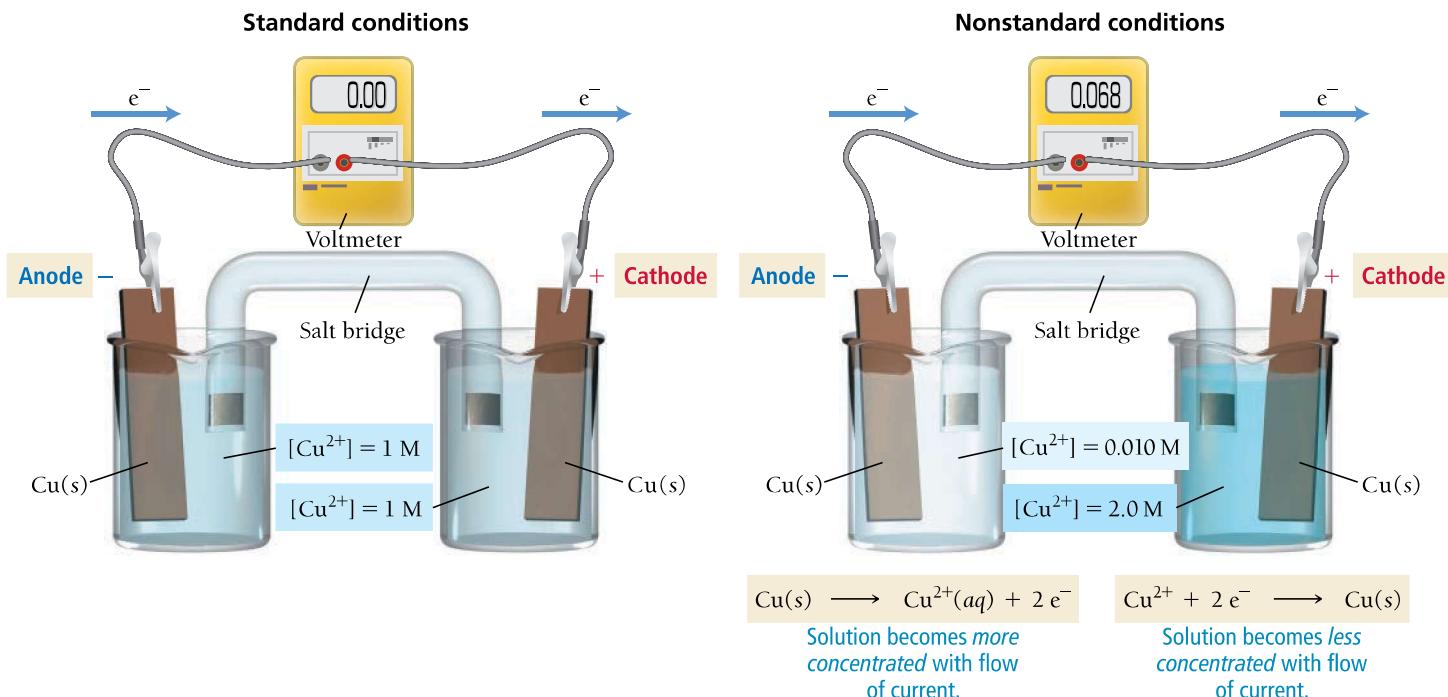
- $E_{\text{cell}}$  is positive and  $E_{\text{cell}}^{\circ}$  is negative.
- $E_{\text{cell}}$  is negative and  $E_{\text{cell}}^{\circ}$  is positive.
- Both  $E_{\text{cell}}$  and  $E_{\text{cell}}^{\circ}$  are positive.
- Both  $E_{\text{cell}}$  and  $E_{\text{cell}}^{\circ}$  are negative.

## Concentration Cells

Since cell potential depends not only on the half-reactions occurring in the cell, but also on the *concentrations* of the reactants and products in those half-reactions, we can construct a voltaic cell in which both half-reactions are the same, but in which *a difference in concentration drives the current flow*. For example, consider the electrochemical cell shown in Figure 20.12►, in which copper is oxidized at the anode and copper ions are reduced at the cathode. The second part of Figure 20.12 depicts this cell under nonstandard conditions, with  $[\text{Cu}^{2+}] = 2.0 \text{ M}$  in one half-cell and  $[\text{Cu}^{2+}] = 0.010 \text{ M}$  in the other:

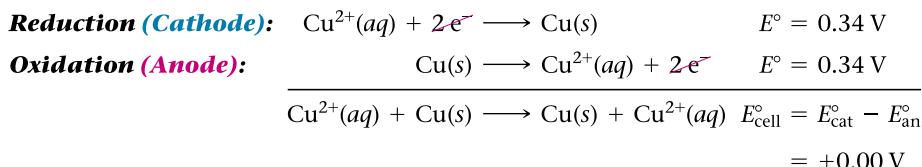


## A Concentration Cell



▲ **FIGURE 20.12 Cu/Cu<sup>2+</sup> Concentration Cell** If two half-cells have the same Cu<sup>2+</sup> concentration, the cell potential is zero. If one half-cell has a greater Cu<sup>2+</sup> concentration than the other, a spontaneous reaction occurs. In the reaction, Cu<sup>2+</sup> ions in the more concentrated cell are reduced (to solid copper), while Cu<sup>2+</sup> ions in the more dilute cell are formed (from solid copper). The concentration of copper ions in the two half-cells tends toward equality.

The half-reactions are identical, and the *standard* cell potential is therefore zero:



Because of the different concentrations in the two half-cells, the cell potential must be calculated using the Nernst equation:

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^\circ - \frac{0.0592 \text{ V}}{2} \log \frac{0.010}{2.0} \\ &= 0.000 \text{ V} + 0.068 \text{ V} \\ &= 0.068 \text{ V} \end{aligned}$$

The cell produces a potential of 0.068 V. *Electrons spontaneously flow from the half-cell with the lower copper ion concentration to the half-cell with the higher copper ion concentration.* We can imagine a concentration cell in the same way we think about any concentration gradient. If we mix a concentrated solution of Cu<sup>2+</sup> with a dilute solution, the Cu<sup>2+</sup> ions flow from the concentrated solution to the dilute one. Similarly, in a concentration cell, the transfer of electrons *from* the dilute half-cell results in the formation of Cu<sup>2+</sup> ions in the dilute half-cell. The electrons flow to the concentrated cell, where they react with Cu<sup>2+</sup> ions and reduce them to Cu(s). Therefore, *the flow of electrons has the effect of increasing the concentration of Cu<sup>2+</sup> in the dilute cell and decreasing the concentration of Cu<sup>2+</sup> in the concentrated half-cell.*

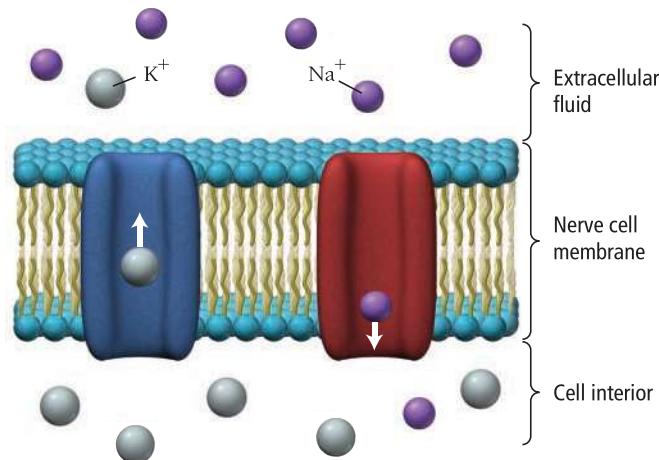


# CHEMISTRY AND MEDICINE

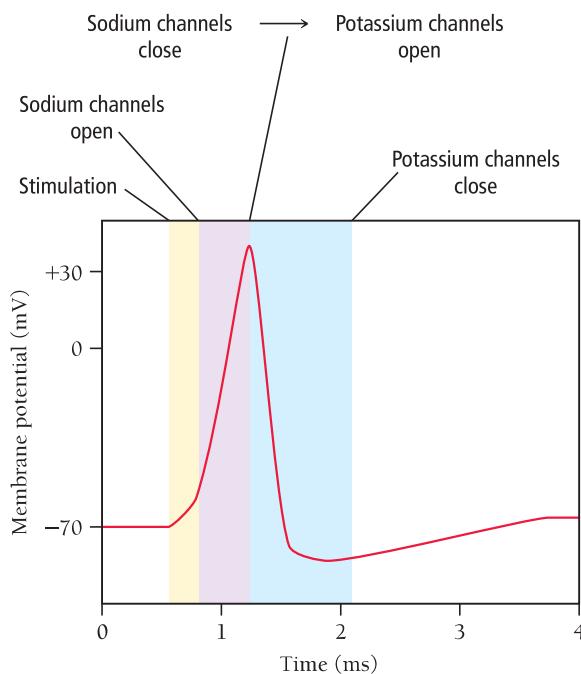
## Concentration Cells in Human Nerve Cells

**R**ecall from Section 9.1 that tiny pumps in the membranes of human nerve cells pump ions—especially sodium ( $\text{Na}^+$ ) and potassium ( $\text{K}^+$ )—through those membranes, establishing a concentration gradient for each type of ion. The concentration of sodium ions is higher outside the cell than within, while exactly the opposite is true for potassium ions. These concentration gradients result in an electrical potential across the cell membrane, called the resting potential, of about  $-70\text{ mV}$ . (The interior of the cell is negative with respect to the exterior.)

When the nerve cell is stimulated, certain channels in the membrane open, allowing  $\text{Na}^+$  ions to rush into the cell and causing the potential to temporarily rise to about  $+30\text{ mV}$  (Figure 20.13▼). Other channels that allow  $\text{K}^+$  ions to rush out of the cell open in turn, bringing the potential back down to near its resting potential. The result is a spike in the electrochemical potential across the membrane, which provides the stimulus for a similar spike in the neighboring segment of the membrane.



▲ FIGURE 20.13 Concentration Changes in Nerve Cells



▲ FIGURE 20.14 Potential Changes across the Nerve Cell Membrane The changes in ion concentrations that take place when a nerve cell is stimulated result in a spike in the electrochemical potential across the membrane.

(Figure 20.14▲). In this way, an electrical signal moves down the length of a nerve cell.

When the electrical signal reaches the end of the nerve cell, it triggers the release of a chemical neurotransmitter, which travels to the neighboring nerve cell and stimulates the same kind of electrochemical spike. In this way, neural signals travel throughout the brain and nervous system.



## 20.7 Batteries: Using Chemistry to Generate Electricity

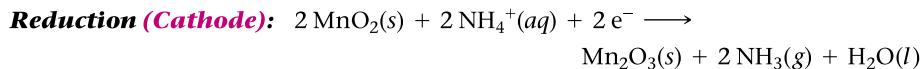
We have seen that we can combine the electron-losing tendency of one substance with the electron-gaining tendency of another to create electrical current in a voltaic cell. Batteries are voltaic cells conveniently packaged to act as portable sources of electricity. The actual oxidation and reduction reactions vary depending on the particular type of battery. In this section, we examine several different types.

### Dry-Cell Batteries

Common batteries, such as the kind in a flashlight, are called **dry-cell batteries** because they do not contain large amounts of liquid water. There are several familiar types of dry-cell batteries. The most inexpensive are composed of a zinc case that acts as the anode (Figure 20.15(a)►). The zinc is oxidized according to the reaction:

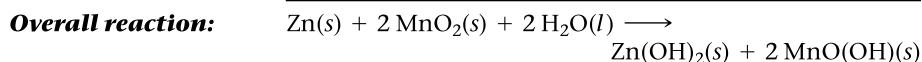
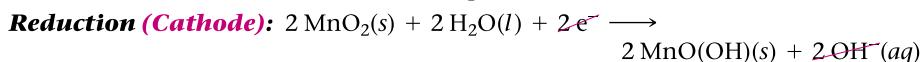
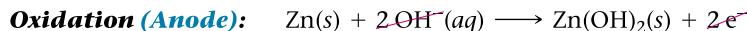


The cathode is a carbon rod immersed in a moist paste of  $\text{MnO}_2$  that also contains  $\text{NH}_4\text{Cl}$ . The  $\text{MnO}_2$  is reduced to  $\text{Mn}_2\text{O}_3$  according to the reaction:



These two half-reactions produce a voltage of about 1.5 V. Two or more of these batteries can be connected in series (cathode-to-anode connection) to produce higher voltages.

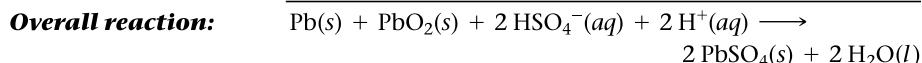
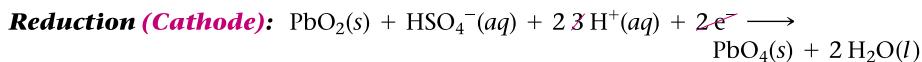
The more common **alkaline batteries** (Figure 20.15(b)►) employ slightly different half-reactions in a basic medium (therefore the name alkaline). In an alkaline battery, the zinc is oxidized in a basic environment:



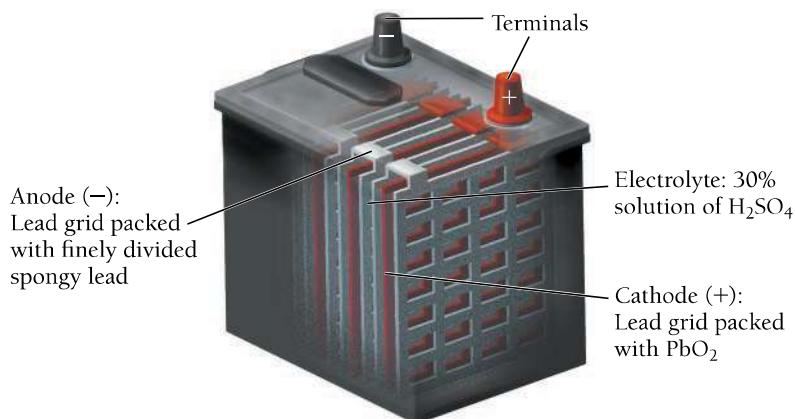
Alkaline batteries have a longer working life and a longer shelf life than their nonalkaline counterparts.

## Lead–Acid Storage Batteries

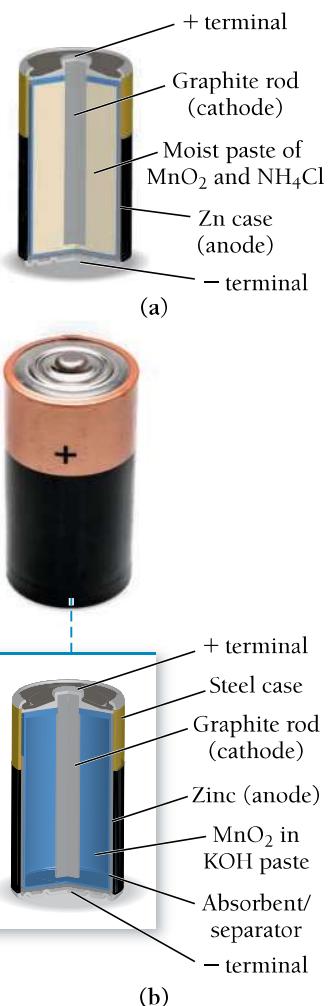
The batteries in most automobiles are **lead–acid storage batteries**. These batteries consist of six electrochemical cells wired in series (Figure 20.16▼). Each cell produces 2 V for a total of 12 V. Each cell contains a porous lead anode where oxidation occurs and a lead(IV) oxide cathode where reduction occurs according to the reactions:



Both the anode and the cathode are immersed in sulfuric acid ( $\text{H}_2\text{SO}_4$ ). As electrical current is drawn from the battery, both electrodes become coated with  $\text{PbSO}_4$ . If the battery is run for a long time without recharging, too much  $\text{PbSO}_4$  develops on the surface of the electrodes and the battery goes dead. The lead–acid storage battery can be recharged by an electrical current (which must come from an external source such as an alternator in a car). The current causes the preceding reaction to occur in reverse, converting the  $\text{PbSO}_4$  back to  $\text{Pb}$  and  $\text{PbSO}_4$ .



**▲ FIGURE 20.16 Lead–Acid Storage Battery** A lead–acid storage battery consists of six cells wired in series. Each cell contains a porous lead anode and a lead oxide cathode, both immersed in sulfuric acid.



**▲ FIGURE 20.15 Dry-Cell Battery**

(a) In a common dry-cell battery, the zinc case acts as the anode and a graphite rod immersed in a moist, slightly acidic paste of  $\text{MnO}_2$  and  $\text{NH}_4\text{Cl}$  acts as the cathode. (b) Longer-lived alkaline batteries employ a graphite cathode immersed in a paste of  $\text{MnO}_2$  and a base.

## Other Rechargeable Batteries

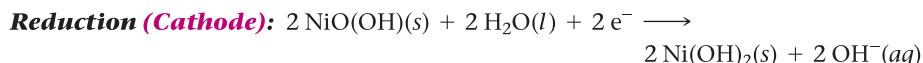
The ubiquity of power electronic products such as laptops and smartphones, as well as the growth in popularity of hybrid electric vehicles, drives the need for efficient, long-lasting, rechargeable batteries. The most common types include the **nickel–cadmium (NiCad) battery**, the **nickel–metal hydride (NiMH) battery**, and the **lithium ion battery**.



▲ Several types of batteries, including NiCad, NiMH, and lithium ion batteries, are recharged by chargers that use household current.

### The Nickel–Cadmium (NiCad) Battery

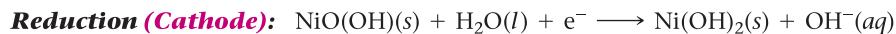
Nickel–cadmium batteries consist of a solid cadmium anode and a  $\text{NiO(OH)}(s)$  cathode. The electrolyte is usually  $\text{KOH}(aq)$ . During operation, the cadmium is oxidized and the  $\text{NiO(OH)}$  is reduced according to the equations:



The overall reaction produces about 1.30 V. As current is drawn from the NiCad battery, solid cadmium hydroxide accumulates on the anode and solid nickel(II) hydroxide accumulates on the cathode. But if current is run in the opposite direction, the reactants can be regenerated from the products. A common problem in recharging NiCad and other rechargeable batteries is knowing when to stop. Once all of the products of the reaction are converted back to reactants, the charging process should ideally terminate. If charging does not stop, the electrical current drives other, usually unwanted, reactions such as the electrolysis of water to form hydrogen and oxygen gas. These reactions typically damage the battery and may sometimes even cause an explosion. Consequently, most commercial battery chargers have sensors that measure when the charging is complete. These sensors rely on the small changes in voltage or increases in temperature that occur once the products have all been converted back to reactants.

### The Nickel–Metal Hydride (NiMH) Battery

Although NiCad batteries were the standard rechargeable battery for many years, they are being replaced by other types of rechargeable batteries, in part because of the toxicity of cadmium and the resulting disposal problems. One of these replacements is the nickel–metal hydride or NiMH battery. The NiMH battery employs the same cathode reaction as the NiCad battery, but it uses a different anode reaction. In the anode of a NiMH battery, hydrogen atoms held in a metal alloy are oxidized. If we let M represent the metal alloy, we can write the half-reactions as follows:



In addition to being more environmentally friendly than NiCad batteries, NiMH batteries also have a greater energy density (energy content per unit battery mass), as we can see in Table 20.2. In some cases, an NiMH battery can carry twice the energy of a NiCad battery of the same mass, making NiMH batteries the most common choice for hybrid electric vehicles.

### The Lithium Ion Battery

The newest and most expensive common type of rechargeable battery is the lithium ion battery. Since lithium is the least dense metal ( $0.53 \text{ g/cm}^3$ ), lithium batteries have high-energy densities (see Table 20.2). The lithium battery works differently than the other batteries we have examined so far, and the details of its operation are beyond the scope of our current

**TABLE 20.2 ■ Energy Density and Overcharge Tolerance of Several Rechargeable Batteries**

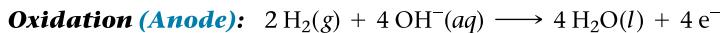
Battery Type	Energy Density (W · h/kg)	Overcharge Tolerance
NiCad	45–80	Moderate
NiMH	60–120	Low
Li ion	110–160	Low
Pb storage	30–50	High

discussion. Briefly, we can describe operation of the lithium battery as being due primarily to the motion of lithium ions from the anode to the cathode. The anode is composed of graphite into which lithium ions are incorporated between layers of carbon atoms. Upon discharge, the lithium ions spontaneously migrate to the cathode, which consists of a lithium transition metal oxide such as  $\text{LiCoO}_2$  or  $\text{LiMn}_2\text{O}_4$ . The transition metal is reduced during this process. Upon recharging, the transition metal is oxidized, forcing the lithium to migrate back into the graphite (Figure 20.17►). The flow of lithium ions from the anode to the cathode causes a corresponding flow of electrons in the external circuit. Lithium ion batteries are commonly used in applications where light weight and high-energy density are important. These include smartphones, laptop computers, and digital cameras.

## Fuel Cells

Fuel cells may one day replace—or at least work in combination with—centralized power grid electricity. In addition, vehicles powered by fuel cells may one day usurp vehicles powered by internal combustion engines. Fuel cells are like batteries; the key difference is that a battery is self-contained, while in a fuel cell the reactants need to be constantly replenished from an external source. With use, normal batteries lose their ability to generate voltage because the reactants become depleted as electrical current is drawn from the battery. In a **fuel cell**, the reactants—the fuel provided from an external source—constantly flow through the battery, generating electrical current as they undergo a redox reaction.

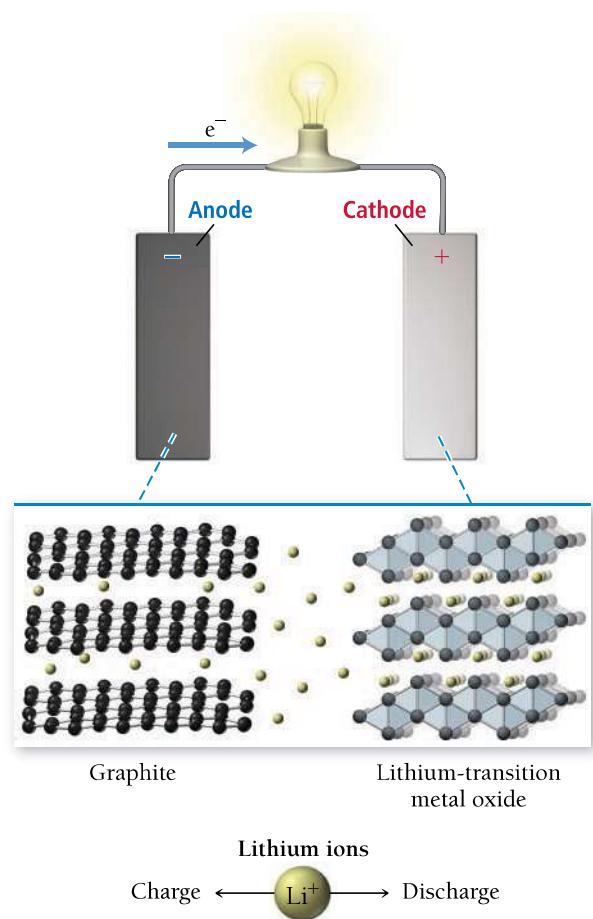
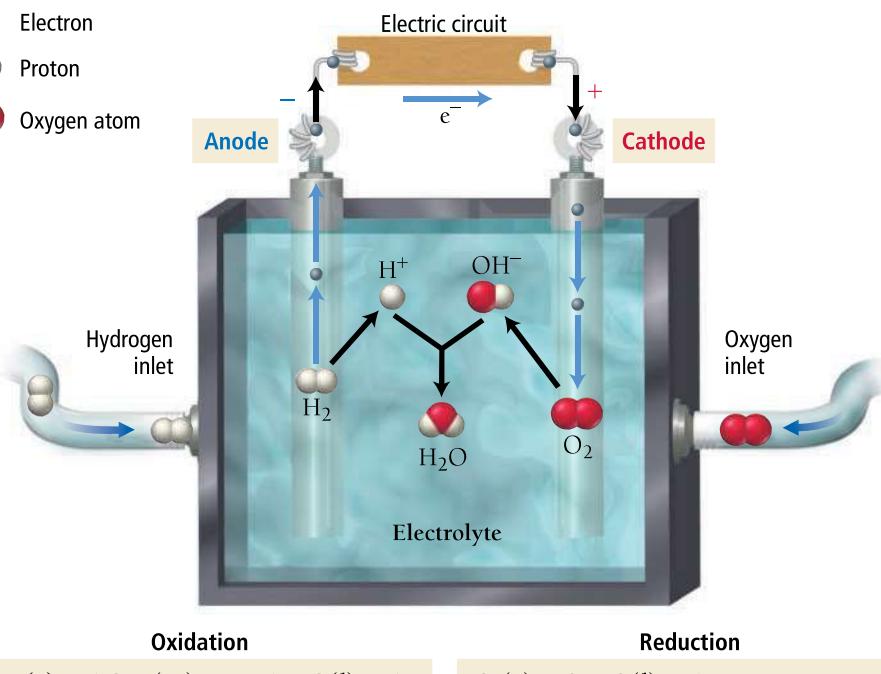
The most common fuel cell is the hydrogen–oxygen fuel cell (Figure 20.18▼). In this cell, hydrogen gas flows past the anode (a screen coated with platinum catalyst) and undergoes oxidation:



## Hydrogen–Oxygen Fuel Cell

In this fuel cell, hydrogen and oxygen combine to form water.

- Electron
- Proton
- Oxygen atom



▲ FIGURE 20.17 Lithium Ion Battery In the lithium ion battery, the spontaneous flow of lithium ions from the graphite anode to the lithium transition metal oxide cathode causes a corresponding flow of electrons in the external circuit.

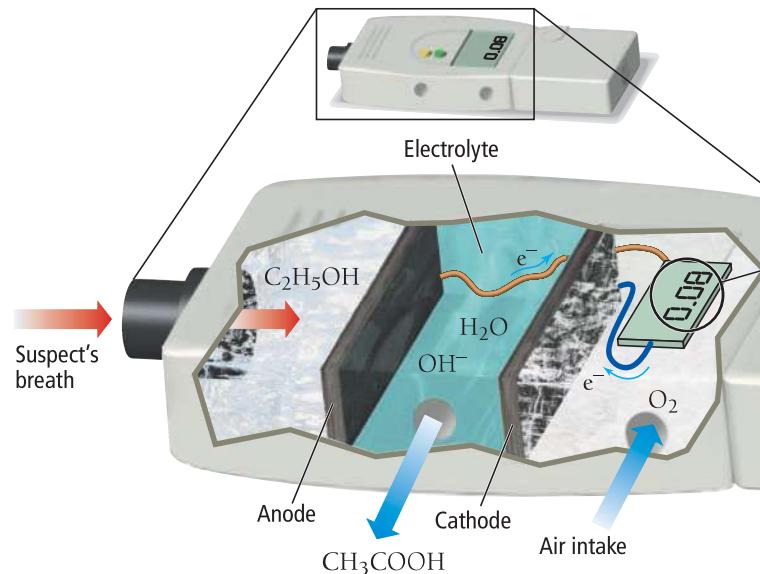
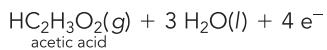
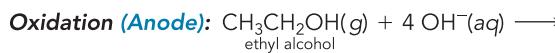
◀ FIGURE 20.18 Hydrogen–Oxygen Fuel Cell



## CHEMISTRY IN YOUR DAY

### The Fuel-Cell Breathalyzer

**P**olice use a device called a breathalyzer to measure the amount of ethyl alcohol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) in the bloodstream of a person suspected of driving under the influence of alcohol (Figure 20.19▼). Breathalyzers work because the quantity of ethyl alcohol in the breath is proportional to the quantity of ethyl alcohol in the bloodstream. One type of breathalyzer employs a fuel cell to measure the quantity of alcohol in the breath. When a suspect blows into the breathalyzer, ethyl alcohol is oxidized to acetic acid at the anode:



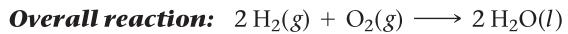
▲ **FIGURE 20.19** Fuel-Cell Breathalyzer The fuel-cell breathalyzer works by oxidizing ethyl alcohol in the breath to acetic acid. The electrical current that is produced is proportional to the concentration of ethyl alcohol in the breath.



Oxygen gas flows past the cathode (a similar screen) and undergoes reduction:



The half-reactions sum to the following overall reaction:



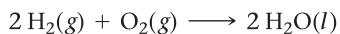
Notice that the only product is water. In the space shuttle program, hydrogen–oxygen fuel cells consume hydrogen to provide electricity and astronauts drink the water that is produced by the reaction. In order for hydrogen-powered fuel cells to become more widely used, a more readily available source of hydrogen must be developed.

### 20.8

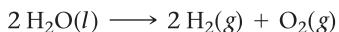
## Electrolysis: Driving Nonspontaneous Chemical Reactions with Electricity

In a voltaic cell, a spontaneous redox reaction produces electrical current. In an *electrolytic cell*, electrical current drives an otherwise nonspontaneous redox reaction through a process called **electrolysis**. We have seen that the reaction of hydrogen

with oxygen to form water is spontaneous and can be used to produce an electrical current in a fuel cell. Conversely, by *supplying* electrical current, we can cause the reverse reaction to occur, separating water into hydrogen and oxygen (Figure 20.20▼):



(spontaneous—produces electrical current; occurs in a voltaic cell)



(nonspontaneous—consumes electrical current; occurs in an electrolytic cell)

Recall from Section 20.7 that one of the problems associated with the widespread adoption of hydrogen fuel cells is the scarcity of hydrogen. Where will the hydrogen to power these fuel cells come from? One possible solution is to obtain hydrogen from water through solar-powered electrolysis. A solar-powered electrolytic cell can produce hydrogen from water when the sun is shining. The hydrogen made in this way could be converted back to water to generate electricity and could also be used to power fuel-cell vehicles.

Electrolysis also has numerous other applications. For example, most metals are found in Earth's crust as metal oxides. Converting an oxide to a pure metal requires that the metal be reduced, a nonspontaneous process. Electrolysis can be used to produce these metals. Thus, sodium is produced by the electrolysis of molten sodium chloride (discussed in the following subsection).

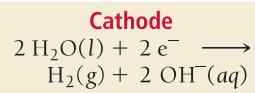
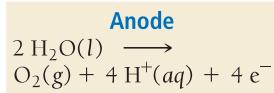
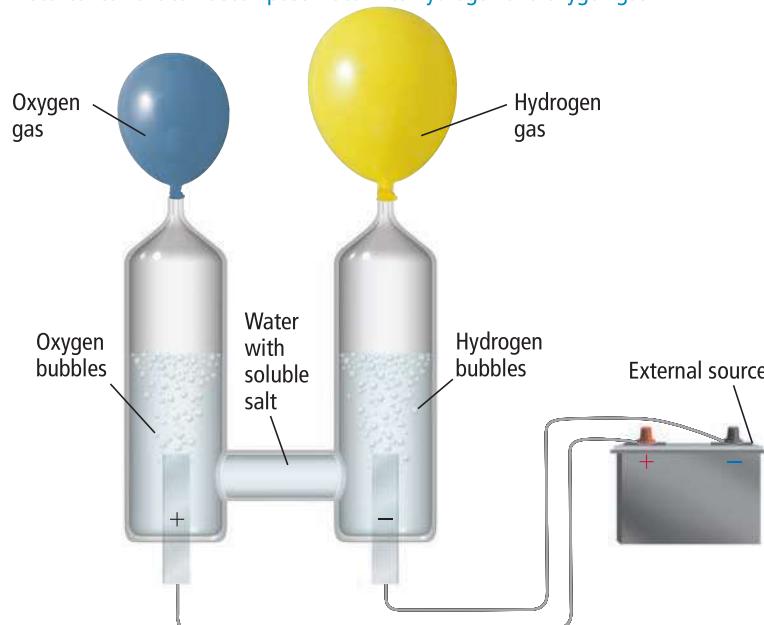
Electrolysis is also used to plate metals onto other metals. For example, silver can be plated onto a less expensive metal using the electrolytic cell shown in Figure 20.21▼. In this cell, a silver electrode is placed in a solution containing silver ions. An electrical current causes the oxidation of silver at the anode (replenishing the silver ions in solution) and the reduction of silver ions at the cathode (coating the less expensive metal with solid silver):



Since the standard cell potential of the reaction is zero, the reaction is not spontaneous under standard conditions. An external power source can be used to drive current flow and cause the reaction to occur.

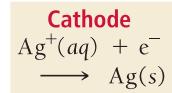
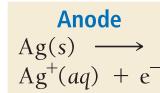
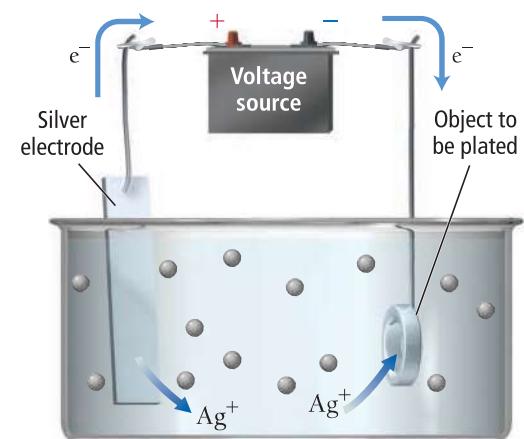
## Electrolysis of Water

Electrical current can decompose water into hydrogen and oxygen gas.



## Electrolytic Cell for Silver Plating

Silver can be plated from a solution of silver ions onto metallic objects in an electrolytic cell.

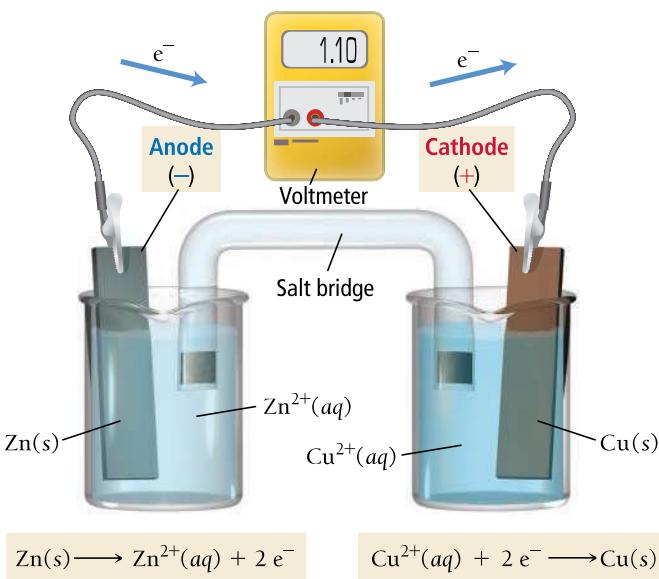


▲ FIGURE 20.20 Electrolysis of Water

▲ FIGURE 20.21 Silver Plating

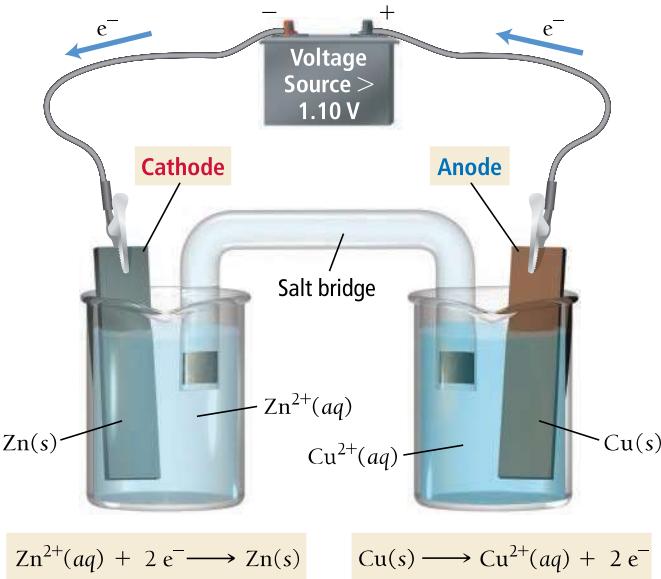
### Voltaic Cell

In a Zn/Cu<sup>2+</sup> voltaic cell, the reaction proceeds in the spontaneous direction.



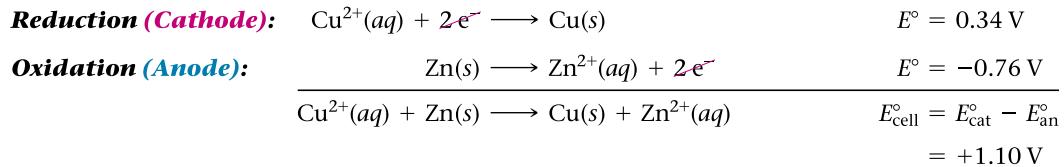
### Electrolytic Cell

In a Zn<sup>2+</sup>/Cu electrolytic cell, electrical current drives the reaction in the nonspontaneous direction.



▲ FIGURE 20.22 Voltaic versus Electrolytic Cells

The voltage required to cause electrolysis depends on the specific half-reactions. For example, we have seen that the oxidation of zinc and the reduction of Cu<sup>2+</sup> produce a voltage of 1.10 V under standard conditions:



If a power source producing *more than* 1.10 V is inserted into the Zn/Cu<sup>2+</sup> voltaic cell, electrons can be forced to flow in the opposite direction, causing the reduction of Zn<sup>2+</sup> and the oxidation of Cu, as shown in Figure 20.22▲. Notice that in the electrolytic cell, the anode has become the cathode (oxidation always occurs at the anode) and the cathode has become the anode.

In a *voltaic cell*, the anode is the source of electrons and is therefore labeled with a negative charge. The cathode draws electrons and is therefore labeled with a positive charge. In an *electrolytic cell*, however, the source of the electrons is the external power source. The external power source must *draw electrons away* from the anode; thus, the anode must be connected to the positive terminal of the battery (as shown in Figure 20.22). Similarly, the power source drives electrons toward the cathode (where they are used in reduction), so the cathode must be connected to the *negative* terminal of the battery. The charge labels (+ and -) on an electrolytic cell are opposite of what they are in a voltaic cell.

#### Summarizing Characteristics of Electrochemical Cell Types:

##### In all electrochemical cells:

- Oxidation occurs at the anode.
- Reduction occurs at the cathode.

##### In voltaic cells:

- The anode is the source of electrons and has a negative charge (anode -).
- The cathode draws electrons and has a positive charge (cathode +).

**In electrolytic cells:**

- Electrons are drawn away from the anode, which must be connected to the positive terminal of the external power source (anode +).
- Electrons are forced to the cathode, which must be connected to the negative terminal of the power source (cathode -).

**VOLTAIC AND ELECTROLYTIC CELLS** Which statement is true for both electrolytic and voltaic cells?

- The cell spontaneously produces a positive voltage.
- Electrons flow from the anode to the cathode.
- Oxidation occurs at the cathode.

20.9

Conceptual  
Connection

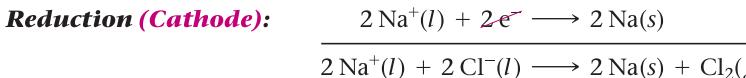
ANSWER NOW!

**Predicting the Products of Electrolysis**

Predicting the products of an electrolysis reaction is in some cases relatively straightforward and in other cases more complex. We cover the simpler cases first and follow with the more complex ones.

**Pure Molten Salts**

Consider the electrolysis of a molten salt such as sodium chloride, shown in Figure 20.23►.  $\text{Na}^+$  and  $\text{Cl}^-$  are the only species present in the cell. The chloride ion cannot be further reduced ( $-1$  is its lowest oxidation state), so it must be oxidized. The sodium ion cannot be further oxidized ( $+1$  is its highest oxidation state), so it must be reduced. Thus, we can write the half-reactions:



Although the reaction as written is not spontaneous, it can be driven to occur in an electrolytic cell by an external power source.

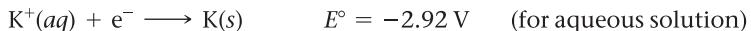
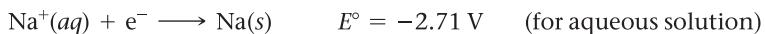
We can generalize as follows:

- In the electrolysis of a pure molten salt, the anion is oxidized and the cation is reduced.

**Mixtures of Cations or Anions**

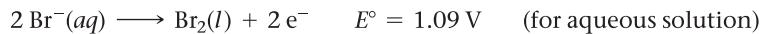
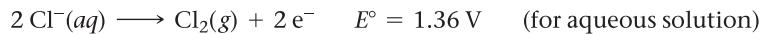
What if a molten salt contains more than one anion or cation? For example, suppose our electrolysis cell contains both  $\text{NaCl}$  and  $\text{KCl}$ . Which of the two cations is reduced at the cathode? In order to answer this question, we must determine which of the two cations is more easily reduced.

Although the values of electrode potentials for aqueous solutions given in Table 20.1 do not apply to molten salts, the relative ordering of the electrode potentials does reflect the relative ease with which the metal cations are reduced. We can see from the table that the reduction of  $\text{Na}^+$  is listed *above* the reduction of  $\text{K}^+$ ; that is,  $\text{Na}^+$  has a more positive electrode potential:



Therefore,  $\text{Na}^+$  is easier to reduce than  $\text{K}^+$ . Consequently, in a mixture of  $\text{NaCl}$  and  $\text{KCl}$ ,  $\text{Na}^+$  has a greater tendency to be reduced at the cathode.

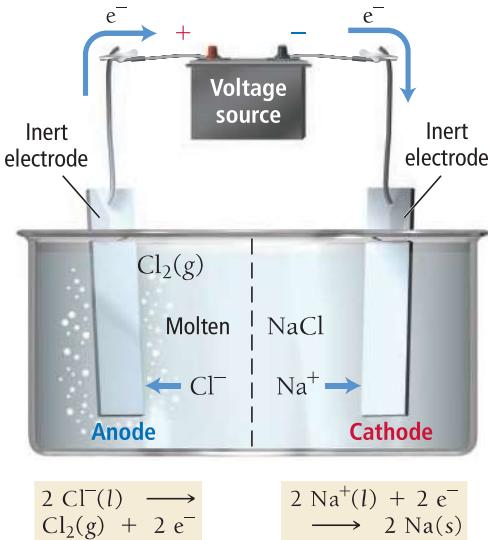
Similarly, what if a mixture of molten salts contained more than one anion? For example, in a mixture of  $\text{NaBr}$  and  $\text{NaCl}$ , which of the two anions is oxidized at the cathode? The answer is similar: the anion that is more easily oxidized (the one with the more negative electrode potential):



20.9

Conceptual  
Connection**Electrolysis of a Molten Salt**

In the electrolysis of a pure molten salt, the anion (in this case) is oxidized and the cation (in this case) is reduced.



**▲ FIGURE 20.23** Electrolysis of Molten  $\text{NaCl}$

Throughout this discussion, "more positive" means the same thing as "less negative."

Throughout this discussion, "more negative" means the same thing as "less positive."

Remember NIO and PIR:  
**N.I.O.**—More Negative Is Oxidation  
**P.I.R.**—More Positive Is Reduction

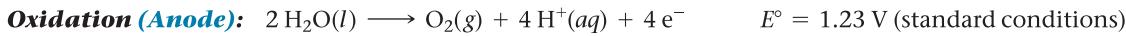
Since the electrode potential for the bromine half-reaction is more negative, electrons are more easily extracted from it. The bromide ion is therefore oxidized at the anode.

We can generalize as follows:

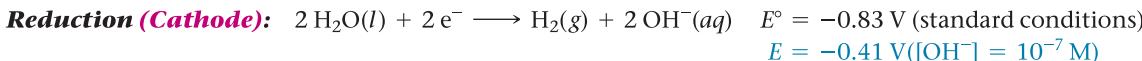
- The cation that is most easily reduced (the one with the more positive electrode potential) is reduced first.
- The anion that is most easily oxidized (the one with the more negative electrode potential) is oxidized first.

### Aqueous Solutions

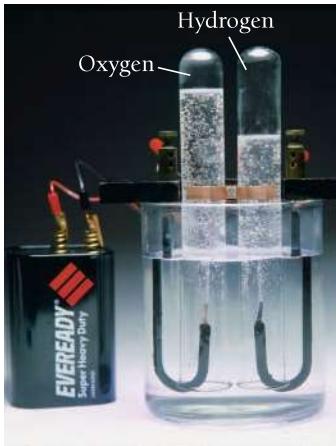
Electrolysis in an aqueous solution is complicated by the possibility of the electrolysis of water itself. Recall that water can be either oxidized or reduced according to the following half-reactions:



$$E = 0.82 \text{ V} ([\text{H}^+] = 10^{-7} \text{ M})$$



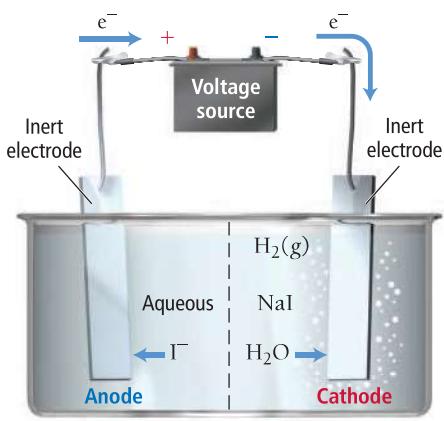
$$E = -0.41 \text{ V} ([\text{OH}^-] = 10^{-7} \text{ M})$$



▲ Pure water is a poor conductor of electrical current, but the addition of an electrolyte allows electrolysis to take place, producing hydrogen and oxygen gas in a stoichiometric ratio.

### Electrolysis of an Aqueous Salt Solution

$\text{I}^-$  is oxidized to  $\text{I}_2$  at the anode and  $\text{H}_2\text{O}$  is reduced to  $\text{H}_2$  at the cathode.



▲ **FIGURE 20.24** Electrolysis of Aqueous NaI

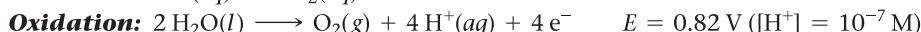
In this cell, the sodium ions are not reduced because their electrode potential is more negative than the electrode potential of water.

The electrode potentials under standard conditions are shown to the right of each half-reaction. However, in pure water at room temperature, the concentrations of  $\text{H}^+$  and  $\text{OH}^-$  are not standard. The electrode potentials for  $[\text{H}^+] = 10^{-7} \text{ M}$  and  $[\text{OH}^-] = 10^{-7} \text{ M}$  are shown in blue. Using those electrode potentials, we can calculate  $E_{\text{cell}}$  for the electrolysis of water as follows:

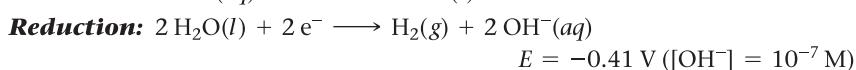
$$E_{\text{cell}} = E_{\text{cat}} - E_{\text{an}} = -0.41 \text{ V} - 0.82 \text{ V} = -1.23 \text{ V}$$

When a battery with a potential of several volts is connected to an electrolysis cell containing pure water, no reaction occurs because the concentration of ions in pure water is too low to conduct any significant electrical current. When an electrolyte such as  $\text{Na}_2\text{SO}_4$  is added to the water, however, electrolysis occurs readily.

In any aqueous solution in which electrolysis is to take place, the electrolysis of water is also possible. For example, consider the electrolysis of a sodium iodide solution, as shown in Figure 20.24▼. For the electrolysis of molten  $\text{NaI}$ , we can readily predict that  $\text{I}^-$  is oxidized at the anode and that  $\text{Na}^+$  is reduced at the cathode. In an aqueous solution, however, two different oxidation half-reactions are possible at the anode, the oxidation of  $\text{I}^-$  and the oxidation of water:



Similarly, two different reduction half-reactions are possible at the cathode, the reduction of  $\text{Na}^+$  and the reduction of water:



How do we know which reactions actually occur? In both cases, the answer is the same: *the half-reaction that occurs more easily*. For oxidation, the half-reaction with the more negative electrode potential is the easier one from which to extract electrons. In this case, therefore, the iodide ion is oxidized at the anode. For reduction, the half-reaction with the more positive electrode potential is the one that accepts electrons more easily. In this case, therefore, water is reduced at the cathode. Notice that  $\text{Na}^+$  cannot be reduced in an aqueous solution—water is reduced before  $\text{Na}^+$ .

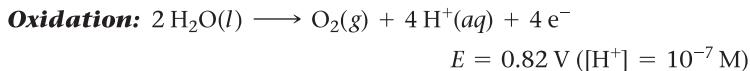
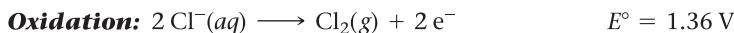
We can make the following generalization:

- The cations of active metals—those that are not easily reduced, such as  $\text{Li}^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Al}^{3+}$ —cannot be reduced from aqueous solutions by electrolysis because water is reduced at a lower voltage.

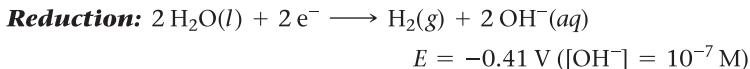
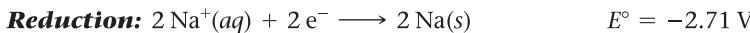
### The Electrolysis of Aqueous Sodium Chloride and Overvoltage

An additional complication that we must consider when predicting the products of electrolysis is *overvoltage*—an additional voltage that must be applied in order to make some nonspontaneous reactions occur.

We can demonstrate this concept by considering the electrolysis of a sodium chloride solution, shown in Figure 20.25►. In order to predict the product of the electrolysis, we consider the two possible oxidation half-reactions:



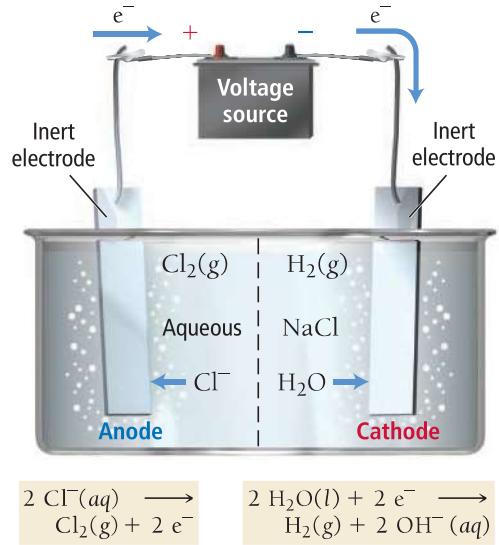
and the two possible reduction half-reactions:



Since the oxidation of water has a more negative electrode potential than the oxidation of  $\text{Cl}^-$ , we would initially predict that it would be easier to remove electrons from water, and thus water should be oxidized at the anode. Similarly, since the reduction of water has a more positive electrode potential than the reduction of  $\text{Na}^+$ , we would expect that it would be easier to get water to accept electrons, so water should be reduced at the cathode. In other words, we initially predict that a sodium chloride solution would simply result in the electrolysis of water, producing oxygen gas at the anode and hydrogen gas at the cathode. If we construct such a cell, however, we find that, although hydrogen gas is indeed formed at the cathode (as predicted), oxygen gas is *not* formed at the anode—chlorine gas is formed instead. Why? The answer is that even though the electrode potential for the oxidation of water is 0.82 V, the reaction actually requires a voltage greater than 0.82 V in order to occur. (The reasons for this behavior are related to kinetic factors that are beyond the scope of our current discussion.) This additional voltage, the *overvoltage*, increases the voltage required for the oxidation of water to about 1.4 V. The result is that the chloride ion oxidizes more easily than water and  $\text{Cl}_2(g)$  is observed at the anode.

### The Effect of Overvoltage on the Electrolysis of Aqueous NaCl

Because of overvoltage, the anode reaction of this cell is the oxidation of  $\text{Cl}^-$  to  $\text{Cl}_2$  gas (rather than the oxidation of water to  $\text{H}^+$  and  $\text{O}_2$  gas).



▲ FIGURE 20.25 Electrolysis of Aqueous NaCl: The Effect of Overvoltage

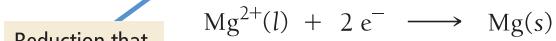
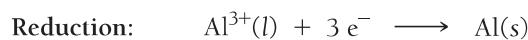
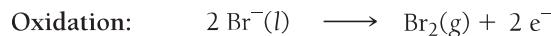
### EXAMPLE 20.9 Predicting the Products of Electrolysis Reactions

Predict the half-reaction occurring at the anode and the half-reaction occurring at the cathode for electrolysis for each reaction.

- (a) a mixture of molten  $\text{AlBr}_3$  and  $\text{MgBr}_2$
- (b) an aqueous solution of LiI

#### SOLUTION

(a) In the electrolysis of a molten salt, the anion is oxidized and the cation is reduced. However, this mixture contains two cations. Start by writing the possible oxidation and reduction half-reactions that might occur. Because  $\text{Br}^-$  is the only anion, write the equation for its oxidation, which occurs at the anode. At the cathode, both the reduction of  $\text{Al}^{3+}$  and the reduction of  $\text{Mg}^{2+}$  are possible. The one that actually occurs is the one that occurs more easily. Since the reduction of  $\text{Al}^{3+}$  has a more positive electrode potential in aqueous solution, this ion is more easily reduced. Therefore, the reduction of  $\text{Al}^{3+}$  occurs at the cathode.



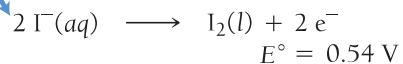
Reduction that actually occurs (more positive potential)

Continued—

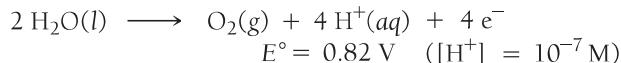
- (b) Since LiI is in an aqueous solution, two different oxidation half-reactions are possible at the anode, the oxidation of  $\text{I}^-$  and the oxidation of water. Write half-reactions for each including the electrode potential. Remember to use the electrode potential of water under conditions in which  $[\text{H}^+] = 10^{-7}$  M. Since the oxidation of  $\text{I}^-$  has the more negative electrode potential, it is the half-reaction to occur at the anode. Similarly, write half-reactions for the two possible reduction half-reactions that might occur at the cathode, the reduction of  $\text{Li}^+$  and the reduction of water. Since the reduction of water has the more positive electrode potential (even when considering overvoltage, which would raise the necessary voltage by about 0.4–0.6 V), it is the half-reaction to occur at the cathode.

Oxidation that actually occurs  
(more negative potential)

**Oxidation:**



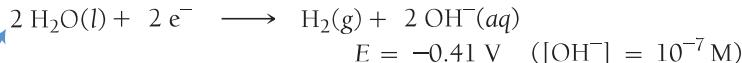
**Oxidation:**



**Reduction:**



**Reduction:**

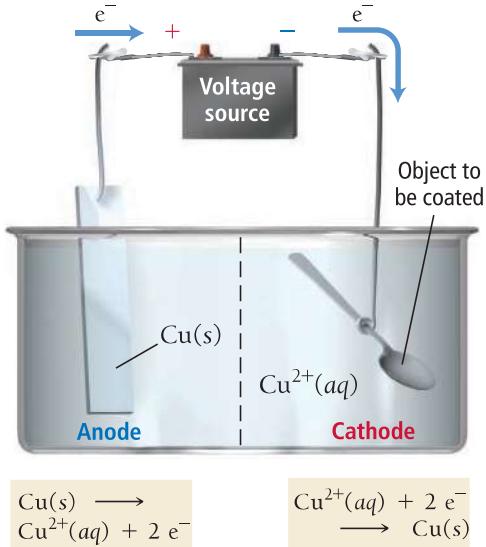


Reduction that actually occurs  
(more positive potential)

**FOR PRACTICE 20.9** Predict the half-reactions occurring at the anode and the cathode for the electrolysis of aqueous  $\text{Na}_2\text{SO}_4$ .

### Electrolytic Cell for Copper Plating

In this cell, copper ions are plated onto other metals.

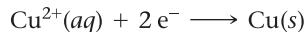


**▲ FIGURE 20.26** Electrolytic Cell for Copper Plating In this cell, it takes two moles of electrons to plate one mole of copper atoms.

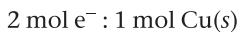
### Stoichiometry of Electrolysis

In an electrolytic cell, electrical current is used to drive a particular chemical reaction. In a sense, the electrons act as a reactant and therefore have a stoichiometric relationship with the other reactants and products. Unlike ordinary reactants, for which we usually measure quantity as mass, for electrons we measure quantity as charge.

For example, consider an electrolytic cell used to coat copper onto metals, as shown in Figure 20.26◀. The half-reaction by which copper is deposited onto the metal is:



For every 2 mol of electrons that flow through the cell, 1 mol of solid copper is plated. We can write the stoichiometric relationship:



We can determine the number of moles of electrons that have flowed in a given electrolysis cell by measuring the total charge that has flowed through the cell, which in turn depends on the *magnitude* of the current and on the *time* that the current runs. Recall from Section 20.3 that the unit of current is the ampere:

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

If we multiply the amount of current (in A) flowing through the cell by the time (in s) that the current flowed, we find the total charge that passed through the cell in that time:

$$\text{Current} \left( \frac{\text{C}}{\text{s}} \right) \times \text{time (s)} = \text{charge (C)}$$

The relationship between charge and the number of moles of electrons is given by Faraday's constant, which, as we saw previously, corresponds to the charge in coulombs of 1 mol of electrons:

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

These relationships can be used to solve problems involving the stoichiometry of electrolytic cells, as demonstrated in Example 20.10.

**ELECTROLYSIS** Silver plating uses the reaction  $\text{Ag}^+(aq) + \text{e}^- \rightarrow \text{Ag}(s)$ . How many moles of electrons must pass through an electrolytic cell for silver plating in order to plate 3 moles of Ag?

- (a) 1 mole  $\text{e}^-$       (b) 2 mole  $\text{e}^-$       (c) 3 mole  $\text{e}^-$       (d) 4 mole  $\text{e}^-$

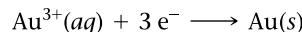


ANSWER NOW!



### EXAMPLE 20.10 Stoichiometry of Electrolysis

Gold can be plated out of a solution containing  $\text{Au}^{3+}$  according to the half-reaction:



What mass of gold (in grams) is plated by a 25-minute flow of 5.5 A current?

**SORT** You are given the half-reaction for the plating of gold, which shows the stoichiometric relationship between moles of electrons and moles of gold. You are also given the current and duration. You must find the mass of gold that will be deposited in that time.

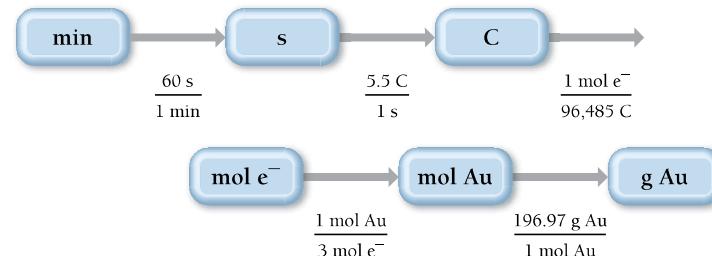
**STRATEGIZE** You need to find the amount of gold, which is related stoichiometrically to the number of electrons that have flowed through the cell. Begin with time in minutes and convert to seconds. Then, because current is a measure of charge per unit time, use the given current and the time to find the number of coulombs. Use Faraday's constant to calculate the number of moles of electrons and the stoichiometry of the reaction to find the number of moles of gold. Finally, use the molar mass of gold to convert to mass of gold.

**SOLVE** Follow the conceptual plan to solve the problem, canceling units to arrive at the mass of gold.

**GIVEN:** 3 mol  $\text{e}^-$  : 1 mol Au  
5.5 amps  
25 min

**FIND:** g Au

#### CONCEPTUAL PLAN

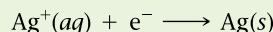


#### SOLUTION

$$25 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{5.5 \text{ C}}{1 \text{ s}} \times \frac{1 \text{ mol e}^-}{96,485 \text{ C}} \times \frac{1 \text{ mol Au}}{3 \text{ mol e}^-} \times \frac{196.97 \text{ g Au}}{1 \text{ mol Au}} = 5.6 \text{ g Au}$$

**CHECK** The answer has the correct units (g Au). The magnitude of the answer is reasonable if you consider that 10 amps of current for 1 hour is the equivalent of about 1/3 mol of electrons (check for yourself), which would produce 1/9 mol (or about 20 g) of gold.

**FOR PRACTICE 20.10** Silver can be plated out of a solution containing  $\text{Ag}^+$  according to the half-reaction:

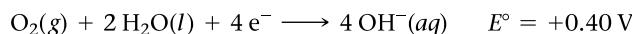


How much time (in minutes) does it take to plate 12 g of silver using a current of 3.0 A?

### 20.9

### Corrosion: Undesirable Redox Reactions

**Corrosion** is the (usually) gradual, nearly always undesired, oxidation of metals that are exposed to oxidizing agents in the environment. From Table 20.1, we can see that the reduction of oxygen in the presence of water has an electrode potential of +0.40 V:





▲ A metal must usually be reduced to extract it from its ore. In corrosion, the metal is oxidized back to its more natural state.



▲ Aluminum is stable because its oxide forms a protective film over the underlying metal, preventing further oxidation.

In the presence of acid, the reduction of oxygen has an even more positive electrode potential of +1.23 V:

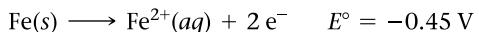


The reduction of oxygen, therefore, has a strong tendency to occur and can bring about the oxidation of other substances, especially metals. Notice that the half-reactions for the reduction of most metal ions are listed *below* the half-reactions for the reduction of oxygen in Table 20.1. Consequently, the oxidation (or corrosion) of those metals is spontaneous when paired with the reduction of oxygen. Corrosion is the opposite of the process by which metals are extracted from their ores. In extraction, the free metal is reduced out from its ore. In corrosion, the metal is oxidized.

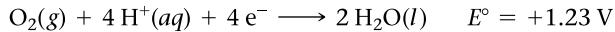
## Corrosion of Iron

Given the ease with which metals oxidize in the presence of oxygen, acid, and water, why are metals used so frequently as building materials in the first place? Many metals form oxides that coat the surface of the metal and prevent further corrosion. For example, bare aluminum metal, with an electrode potential of  $-1.66 \text{ V}$ , is quickly oxidized in the presence of oxygen. However, the oxide that forms at the surface of aluminum is  $\text{Al}_2\text{O}_3$ . In its crystalline form,  $\text{Al}_2\text{O}_3$  is sapphire, a highly inert and structurally solid substance. The  $\text{Al}_2\text{O}_3$  coating acts to protect the underlying aluminum metal, preventing further corrosion.

The oxides of iron, in contrast, are not structurally stable, and they tend to flake away from the underlying metal, exposing it to further corrosion. A significant part of the iron produced each year is used to replace rusted iron. Rusting is a redox reaction in which iron is oxidized according to the following half-reaction:

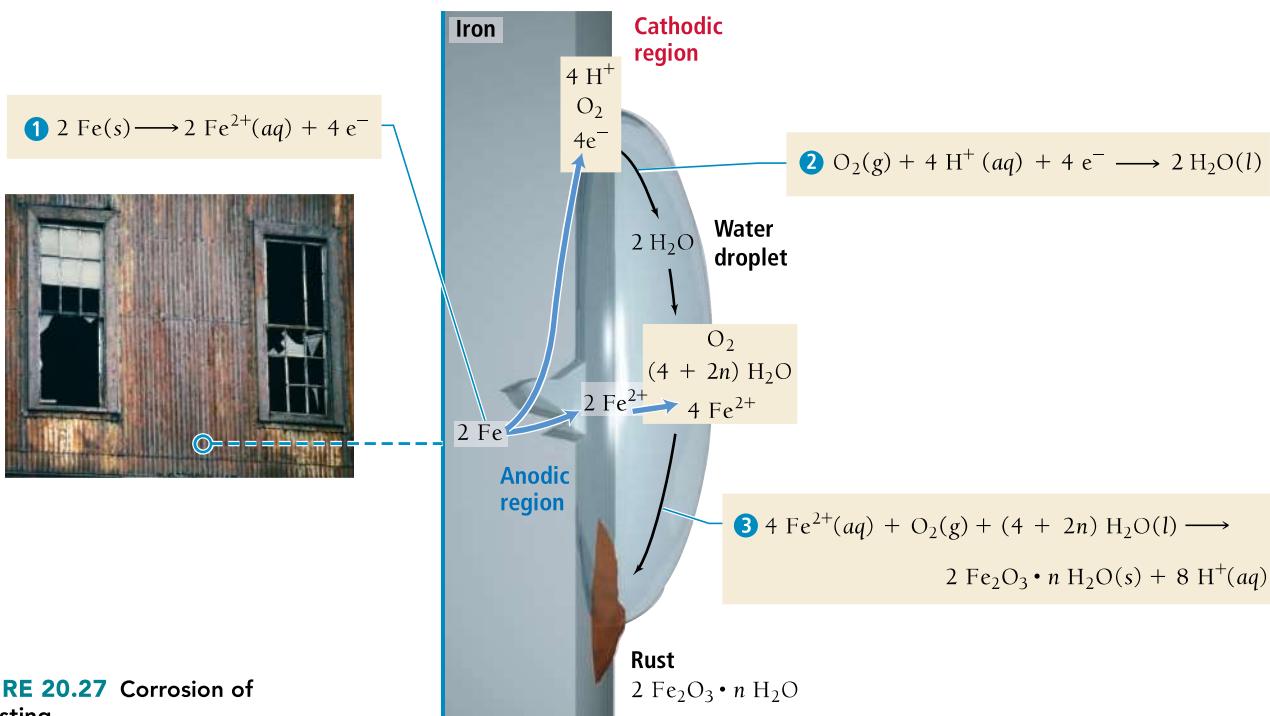


This oxidation reaction tends to occur at defects on the surface of the iron—known as *anodic regions* because oxidation is occurring at these locations—as shown in Figure 20.27▼. The electrons produced at the anodic region travel through the metal to areas called *cathodic regions* where they react with oxygen and  $\text{H}^+$  ions dissolved in moisture:

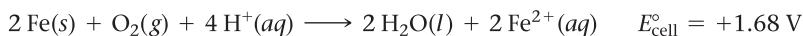


### The Rusting of Iron

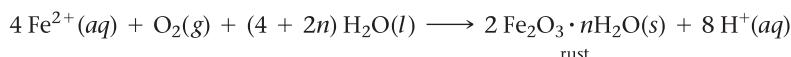
The oxidation of iron occurs at anodic regions on the metal surface. The iron ions migrate to cathodic regions, where they react with oxygen and water to form rust.



(The  $\text{H}^+$  ions come from carbonic acid, which naturally forms in water from carbon dioxide in air.) The overall reaction has a cell potential of +1.68 V and is highly spontaneous:



The  $\text{Fe}^{2+}$  ions formed in the anodic regions can migrate through moisture on the surface of the iron to cathodic regions, where they are further oxidized by reaction with more oxygen:



Rust is a hydrated form of iron(III) oxide whose exact composition depends on the conditions under which it forms.

Consider each of the following important aspects of the formation of rust:

- *Moisture must be present for rusting to occur.* The presence of water is necessary because water is a reactant in the last reaction and because charge (either electrons or ions) must be free to flow between the anodic and cathodic regions.
- *Additional electrolytes promote rusting.* The presence of an electrolyte (such as sodium chloride) on the surface of iron promotes rusting because it enhances current flow. This is why cars rust so quickly in cold climates where roads are salted, or in coastal areas where seawater mist is present.
- *The presence of acids promotes rusting.* Because  $\text{H}^+$  ions are involved in the reduction of oxygen, lower pH enhances the cathodic reaction and leads to faster rusting.

## Preventing the Corrosion of Iron

Preventing the rusting of iron is a major industry. The most obvious way to prevent rust is to keep iron dry. Without water, the redox reaction cannot occur. Another way to prevent rust is to coat iron with a substance that is impervious to water. Cars, for example, are painted and sealed to prevent rust. A scratch in the paint can lead to rusting of the underlying iron.

Rust can also be prevented by placing a *sacrificial electrode* in electrical contact with the iron. The sacrificial electrode must be composed of a metal that oxidizes more easily than iron (that is, it must be below iron in Table 20.1).

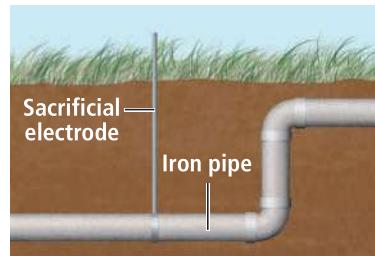
The sacrificial electrode oxidizes in place of the iron (just as the more easily oxidizable species in a mixture is the one to oxidize), protecting the iron from oxidation. A related way to protect iron from rusting is to coat it with a metal that oxidizes more easily than iron. Galvanized nails, for example, are coated with a thin layer of zinc. Since zinc has a more negative electrode potential than iron, it will oxidize in place of the underlying iron (just as a sacrificial electrode does). The oxide of zinc is not crumbly and remains on the nails as a protective coating.



▲ In galvanized nails, a layer of zinc prevents the underlying iron from rusting. The zinc oxidizes in place of the iron, forming a protective layer of zinc oxide.



▲ A scratch in paint often allows the underlying iron to rust.



▲ If a metal more active than iron, such as magnesium or aluminum, is in electrical contact with iron, the metal rather than the iron will be oxidized. This principle underlies the use of sacrificial electrodes to prevent the corrosion of iron.

**SACRIFICIAL ELECTRODES** Which of these metals does not act as a sacrificial electrode for iron?

(a) Cu

(b) Mg

(c) Zn

(d) Mn

## 20.11

Cc  
Conceptual Connection

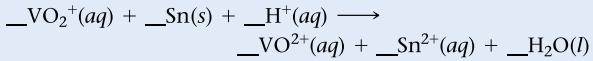
ANSWER NOW!



## Self-Assessment Quiz

- Q1.** Balance the redox reaction equation (occurring in acidic solution) and choose the correct coefficients for each reactant and product.

**MISSED THIS?** Read Section 20.2; Watch KCV 20.2, IWE 20.2



- a) 2,1,4  $\longrightarrow$  2,1,2      b) 1,1,2  $\longrightarrow$  1,1,1  
 c) 2,1,2  $\longrightarrow$  2,1,1      d) 2,1,2  $\longrightarrow$  2,1,2

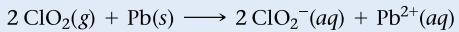
- Q2.** Which statement is true for voltaic cells?

**MISSED THIS?** Read Section 20.3

- a) Electrons flow from the anode to the cathode.  
 b) Electrons flow from the more negatively charged electrode to the more positively charged electrode.  
 c) Electrons flow from higher potential energy to lower potential energy.  
 d) All of the above are true.

- Q3.** Use Table 20.1 to calculate  $E_{\text{cell}}^\circ$  for the reaction.

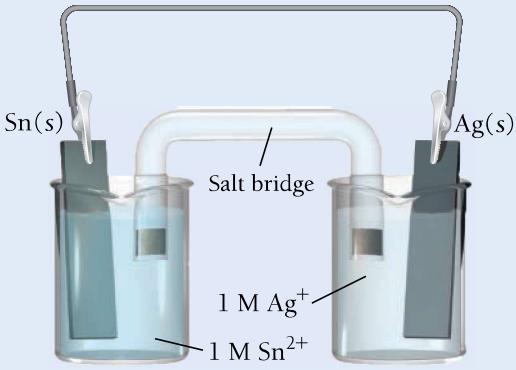
**MISSED THIS?** Read Section 20.4; Watch KCV 20.4, IWE 20.4



- a) 1.77 V      b) 2.03 V  
 c) 0.82 V      d) 1.08 V

- Q4.** Use Table 20.1 to determine which statement is true of the voltaic cell pictured here.

**MISSED THIS?** Read Section 20.4; Watch KCV 20.4



- a) Sn is the anode; Ag is the cathode; electrons flow from left to right.  
 b) Sn is the cathode; Ag is the anode; electrons flow from left to right.  
 c) Sn is the anode; Ag is the cathode; electrons flow from right to left.  
 d) Sn is the cathode; Ag is the anode; electrons flow from right to left.

- Q5.** Use Table 20.1 to determine which metal *does not* dissolve in hydrochloric acid (HCl). **MISSED THIS?** Read Section 20.4

- a) Zn      b) Cd      c) Cu      d) Fe

- Q6.** The Zn/Zn<sup>2+</sup> electrode has a standard electrode potential of  $E^\circ = -0.76$  V. How does the relative potential energy of an electron at the Zn/Zn<sup>2+</sup> electrode compare to the potential energy of an electron at the standard hydrogen electrode?

**MISSED THIS?** Read Section 20.4; Watch KCV 20.4

- a) An electron at the Zn/Zn<sup>2+</sup> electrode has a higher potential energy than an electron at the standard hydrogen electrode.

- b) An electron at the Zn/Zn<sup>2+</sup> electrode has a lower potential energy than an electron at the standard hydrogen electrode.

- c) An electron at the Zn/Zn<sup>2+</sup> electrode has the same potential energy as an electron at the standard hydrogen electrode.

- d) Nothing can be concluded about the relative potential energy of an electron at the standard electrode potential.

- Q7.** Use Table 20.1 to calculate  $\Delta G^\circ$  for the reaction.

**MISSED THIS?** Read Section 20.5; Watch KCV 20.5, IWE 20.6



- a) +30.9 kJ      b) -30.9 kJ      c) -185 kJ      d) +185 kJ

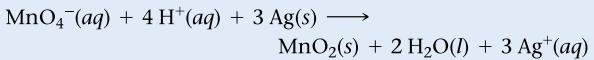
- Q8.** A redox reaction has an  $E_{\text{cell}}^\circ = -0.56$  V. What can you conclude about the equilibrium constant ( $K$ ) for the reaction?

**MISSED THIS?** Read Section 20.5; Watch KCV 20.5

- a)  $K < 1$       b)  $K > 1$       c)  $K = 0$   
 d) Nothing can be concluded about  $K$  from  $E_{\text{cell}}^\circ$ .

- Q9.** Find  $E_{\text{cell}}$  for an electrochemical cell based on the following reaction with  $[\text{MnO}_4^-] = 2.0$  M,  $[\text{H}^+] = 1.0$  M, and  $[\text{Ag}^+] = 0.010$  M.  $E_{\text{cell}}^\circ$  for the reaction is +0.88 V.

**MISSED THIS?** Read Section 20.6



- a) 0.83 V      b) 1.00 V      c) 0.76 V      d) 0.93 V

- Q10.** In an electrochemical cell,  $Q = 0.010$  and  $K = 855$ . What can you conclude about  $E_{\text{cell}}$  and  $E_{\text{cell}}^\circ$ ?

**MISSED THIS?** Read Section 20.6

- a)  $E_{\text{cell}}$  is positive and  $E_{\text{cell}}^\circ$  is negative.  
 b)  $E_{\text{cell}}$  is negative and  $E_{\text{cell}}^\circ$  is positive.  
 c)  $E_{\text{cell}}$  and  $E_{\text{cell}}^\circ$  are both negative.  
 d)  $E_{\text{cell}}$  and  $E_{\text{cell}}^\circ$  are both positive.

- Q11.** Which reaction occurs at the *anode* of a lead storage battery?

**MISSED THIS?** Read Section 20.7

- a)  $\text{Zn}(s) + 2 \text{OH}^-(aq) \longrightarrow \text{Zn}(\text{OH})_2(s) + 2 \text{e}^-$   
 b)  $\text{PbO}_2(s) + \text{HSO}_4^-(aq) + 3 \text{H}^+(aq) + 2 \text{e}^- \longrightarrow \text{PbSO}_4(s) + 2 \text{H}_2\text{O}(l)$   
 c)  $\text{Pb}(s) + \text{HSO}_4^-(aq) \longrightarrow \text{PbSO}_4(s) + \text{H}^+(aq) + 2 \text{e}^-$   
 d)  $\text{O}_2(g) + 2 \text{H}_2\text{O}(l) + 4 \text{e}^- \longrightarrow 4 \text{OH}^-(aq)$

- Q12.** Which reaction could be used to generate electricity in a voltaic electrochemical cell?

**MISSED THIS?** Read Section 20.4; Watch KCV 20.4

- a)  $\text{Pb}^{2+}(aq) + \text{Mg}(s) \longrightarrow \text{Mg}^{2+}(aq) + \text{Pb}(s)$   
 b)  $\text{Zn}^{2+}(aq) + \text{Sn}(s) \longrightarrow \text{Sn}^{2+}(aq) + \text{Zn}(s)$   
 c)  $\text{NaCl}(aq) + \text{AgNO}_3(aq) \longrightarrow \text{AgCl}(s) + \text{NaNO}_3(aq)$   
 d) None of the above

- Q13.** Which reaction occurs at the cathode of an electrolytic cell containing a mixture of molten KCl and ZnCl<sub>2</sub>?

**MISSED THIS?** Read Section 20.8

- a)  $\text{K}(s) \longrightarrow \text{K}^+(l) + \text{e}^-$   
 b)  $\text{K}^+(l) + \text{e}^- \longrightarrow \text{K}(s)$   
 c)  $\text{Zn}^{2+}(l) + 2 \text{e}^- \longrightarrow \text{Zn}(s)$   
 d)  $2 \text{Cl}^-(l) \longrightarrow \text{Cl}_2(g) + 2 \text{e}^-$



- Q14.** Copper is plated onto the cathode of an electrolytic cell containing  $\text{CuCl}_2(aq)$ . How long does it take to plate 111 mg of copper with a current of 3.8 A?
- MISSED THIS? Read Section 20.8**

a)  $1.3 \times 10^3$  s      b) 44 s      c) 89 s      d) 22 s

**Answers:** 1. (a) 2. (d) 3. (d) 4. (a) 5. (c) 6. (a) 7. (c) 8. (a) 9. (b) 10. (d) 11. (c) 12. (a) 13. (c) 14. (c) 15. (d)

- Q15.** Which metal can be used as a sacrificial electrode to prevent the rusting of an iron pipe?
- MISSED THIS? Read Section 20.9**

a) Au      b) Ag      c) Cu      d) Mn

## CHAPTER 20 IN REVIEW

### TERMS

#### Section 20.3

electrical current (901)  
electrochemical cell (902)  
voltaic (galvanic) cell (902)  
electrolytic cell (902)  
half-cell (902)  
electrode (902)  
ampere (A) (903)  
potential difference (903)  
volt (V) (903)  
electromotive force (emf) (903)  
cell potential (cell emf) ( $E_{\text{cell}}$ ) (904)

standard cell potential  
(standard emf) ( $E_{\text{cell}}^{\circ}$ ) (904)  
anode (904)  
cathode (904)  
salt bridge (904)

#### Section 20.4

standard electrode potential  
( $E^{\circ}$ )  
standard hydrogen electrode  
(SHE) (906)

#### Section 20.5

Faraday's constant ( $F$ ) (914)

#### Section 20.6

Nernst equation (918)

#### Section 20.7

dry-cell battery (922)  
alkaline battery (923)  
lead-acid storage battery  
(923)

nickel–cadmium (NiCad)  
battery (924)  
nickel–metal hydride (NiMH)  
battery (924)  
lithium ion battery (924)  
fuel cell (925)

#### Section 20.8

electrolysis (926)

#### Section 20.9

corrosion (933)

### CONCEPTS

#### Pulling the Plug on the Power Grid (20.1)

- Oxidation–reduction reactions are reactions in which electrons are transferred from one reactant to another.
- In the most common form of fuel cell, an electrical current is created as hydrogen is oxidized and oxygen is reduced; water is the only product.

#### Balancing Oxidation–Reduction Equations (20.2)

- Oxidation is the loss of electrons and corresponds to an increase in oxidation state; reduction is the gain of electrons and corresponds to a decrease in oxidation state.
- We can balance redox reactions using the half-reaction method, in which the oxidation and reduction reactions are balanced separately and then added. This method differs slightly for redox reactions in acidic and in basic solutions.

#### Voltaic (or Galvanic) Cells: Generating Electricity from Spontaneous Chemical Reactions (20.3)

- A voltaic electrochemical cell separates the reactants of a spontaneous redox reaction into two half-cells that are connected by a wire and a means to exchange ions so that electricity is generated.
- In an electrochemical cell, the electrode where oxidation occurs is the anode and the electrode where reduction occurs is the cathode; electrons flow from the anode to the cathode.
- The rate of electrons flowing through a wire is measured in amperes (A), and the cell potential is measured in volts (V).
- A salt bridge allows ions to flow between the half-cell solutions and prevent the buildup of charge.
- The cell diagram or line notation symbolizes electrochemical cells concisely by separating the components of the reaction using lines or commas.

#### Standard Electrode Potentials (20.4)

- The electrode potentials of half-cells are measured in relation to that of a standard hydrogen electrode, which is assigned an electrode potential of zero under standard conditions (solution concentrations of 1 M, gas pressures of 1 atm, and a temperature of 25 °C).
- A species with a highly positive  $E^{\circ}$  has a strong tendency to attract electrons and undergo reduction (and is therefore an excellent oxidizing agent).
- A species with a highly negative  $E^{\circ}$  has a strong tendency to repel electrons and undergo oxidation (and is therefore an excellent reducing agent).

#### Cell Potential, Free Energy, and the Equilibrium Constant (20.5)

- In a spontaneous reaction,  $E_{\text{cell}}^{\circ}$  is positive, the change in free energy ( $\Delta G^{\circ}$ ) is negative, and the equilibrium constant ( $K$ ) is greater than 1.
- In a nonspontaneous reaction,  $E_{\text{cell}}^{\circ}$  is negative,  $\Delta G^{\circ}$  is positive, and  $K$  is less than 1.
- Because  $E_{\text{cell}}^{\circ}$ ,  $\Delta G^{\circ}$ , and  $K$  all relate to spontaneity, we can derive equations relating all three quantities.

#### Cell Potential and Concentration (20.6)

- The standard cell potential ( $E_{\text{cell}}^{\circ}$ ) is related to the cell potential ( $E_{\text{cell}}$ ) by the Nernst equation,  $E_{\text{cell}} = E_{\text{cell}}^{\circ} - (0.0592 \text{ V}/n) \log Q$ .
- As shown by the Nernst equation,  $E_{\text{cell}}$  is related to the reaction quotient ( $Q$ );  $E_{\text{cell}}$  equals zero when  $Q$  equals  $K$ .
- In a concentration cell, the reactions at both electrodes are identical and electrons flow because of a difference in concentration. Nerve cells are a biological example of concentration cells.

## Batteries: Using Chemistry to Generate Electricity (20.7)

- Batteries are packaged voltaic cells.
- Dry-cell batteries, including alkaline batteries, do not contain large amounts of water.
- The reactions in rechargeable batteries, such as lead–acid storage, nickel–cadmium, nickel–metal hydride, and lithium ion batteries, can be reversed.
- Fuel cells are similar to batteries except that fuel-cell reactants must be continually replenished from an external source.

## Electrolysis: Driving Nonspontaneous Chemical Reactions with Electricity (20.8)

- An electrolytic electrochemical cell differs from a voltaic cell in that (1) an electrical charge is used to drive the reaction, and (2) although the anode is still the site of oxidation and the cathode

the site of reduction, they are represented with signs opposite those of a voltaic cell (anode +, cathode –).

- In electrolysis reactions, the anion is oxidized; if there is more than one anion, the anion with the more negative  $E^\circ$  is oxidized.
- We can use stoichiometry to calculate the quantity of reactants consumed or products produced in an electrolytic cell.

## Corrosion: Undesirable Redox Reactions (20.9)

- Corrosion is the undesired oxidation of metal by environmental oxidizing agents.
- When some metals, such as aluminum, oxidize, they form a stable compound that prevents further oxidation. Iron, in contrast, does not form a structurally stable compound when oxidized, and therefore, rust flakes off and exposes more iron to corrosion.
- Iron corrosion can be prevented by protecting iron from water, minimizing the presence of electrolytes and acids, or using a sacrificial electrode.

## EQUATIONS AND RELATIONSHIPS

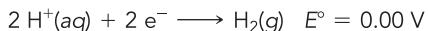
### Definition of an Ampere (20.3)

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

### Definition of a Volt (20.3)

$$1 \text{ V} = 1 \text{ J/s}$$

### Standard Hydrogen Electrode (20.4)



### Equation for Cell Potential (20.4)

$$E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ$$

### Relating $\Delta G^\circ$ and $E_{\text{cell}}^\circ$ (20.5)

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ \quad F = \frac{96,485 \text{ C}}{\text{mol e}^-}$$

### Relating $E_{\text{cell}}^\circ$ and $K$ (20.5)

$$E_{\text{cell}}^\circ = \frac{0.0592 \text{ V}}{n} \log K \quad (\text{at } 25^\circ \text{ C})$$

### The Nernst Equation (20.6)

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592 \text{ V}}{n} \log Q \quad (\text{at } 25^\circ \text{ C})$$

## LEARNING OUTCOMES

Chapter Objectives	Assessment
Balance acidic solution redox equations using the half-reaction method (20.2)	Examples 20.1, 20.2 For Practice 20.1, 20.2 Exercises 37–40
Balance basic solution redox equations using the half-reaction method (20.2)	Example 20.3 For Practice 20.3 Exercises 41–42
Identify the parts of a voltaic cell (20.3)	Exercises 43–44
Represent electrochemical cells using cell diagram notation (20.3)	Exercises 49–52
Calculate standard cell potentials ( $E_{\text{cell}}^\circ$ ) for electrochemical cells (20.4)	Example 20.4 For Practice 20.4 Exercises 45–48, 61–62
Predict the spontaneity of redox reactions (20.4)	Example 20.5 For Practice 20.5 Exercises 53–54, 61–62
Identify solutions that can selectively oxidize metals and metal ions (20.4)	Exercises 55–60, 63–64
Calculate standard free energy changes ( $\Delta G^\circ$ ) for electrochemical reactions from standard cell potentials ( $E_{\text{cell}}^\circ$ ) (20.5)	Example 20.6 For Practice 20.6 Exercises 65–66
Perform calculations involving $\Delta G^\circ$ , $E_{\text{cell}}^\circ$ , and $K$ for electrochemical reactions (20.5)	Example 20.7 For Practice 20.7 Exercises 67–72, 103–104
Analyze cell potentials under nonstandard conditions (20.6)	Example 20.8 For Practice 20.8 Exercises 73–82
Analyze batteries in terms of mass components, redox reactions, and standard cell potentials (20.7)	Exercises 83–86
Analyze electrolytic cells in terms of component parts, reactions, voltages, and direction of electron flow (20.8)	Exercises 89–90, 97–98
Analyze molten-salt electrolysis reactions in terms of products and half-reactions (20.8)	Exercises 91–94
Analyze aqueous-solution electrolysis reactions in terms of products and half-reactions (20.8)	Example 20.9 For Practice 20.9 Exercises 95–96
Perform stoichiometric calculations for electrolysis reactions (20.8)	Example 20.10 For Practice 20.10 Exercises 99–102
Predict metals that act as sacrificial electrodes for iron (20.9)	Exercises 87–88

# EXERCISES

## REVIEW QUESTIONS

**Mastering Chemistry** provides end-of-chapter exercises, feedback-enriched tutorial problems, animations, and interactive activities to encourage problem-solving practice and deeper understanding of key concepts and topics.

1. In electrochemistry, spontaneous redox reactions are used for what purpose?
2. In electrochemistry, what kind of reaction can be driven by electricity?
3. Give the basic definitions of oxidation and reduction and explain the basic procedure for balancing redox reactions.
4. Explain the difference between a voltaic (or galvanic) electrochemical cell and an electrolytic cell.
5. What reaction (oxidation or reduction) occurs at the anode of a voltaic cell? What is the sign of the anode? Do electrons flow toward or away from the anode?
6. What reaction (oxidation or reduction) occurs at the cathode of a voltaic cell? What is the sign of the cathode? Do electrons flow toward or away from the cathode?
7. Explain the purpose of a salt bridge in an electrochemical cell.
8. What unit is used to measure the magnitude of electrical current? What unit is used to measure the magnitude of a potential difference? Explain how electrical current and potential difference differ.
9. What is the definition of the standard cell potential ( $E_{\text{cell}}^{\circ}$ )? What does a large positive standard cell potential imply about the spontaneity of the redox reaction occurring in the cell? What does a negative standard cell potential imply about the reaction?
10. Describe the basic features of a cell diagram (or line notation) for an electrochemical cell.
11. Why do some electrochemical cells employ inert electrodes such as platinum?
12. Describe the standard hydrogen electrode (SHE) and explain its use in determining standard electrode potentials.
13. How is the cell potential of an electrochemical cell ( $E_{\text{cell}}^{\circ}$ ) related to the potentials of the half-cells?
14. Does a large positive electrode potential indicate a strong oxidizing agent or a strong reducing agent? What about a large negative electrode potential?
15. Is a spontaneous redox reaction obtained by pairing any reduction half-reaction with one listed above it or with one listed below it in Table 20.1?
16. How can Table 20.1 be used to predict whether or not a metal will dissolve in HCl? In  $\text{HNO}_3$ ?
17. Explain why  $E_{\text{cell}}^{\circ}$ ,  $\Delta G_{\text{rxn}}^{\circ}$ , and  $K$  are all interrelated.
18. Does a redox reaction with a small equilibrium constant ( $K < 1$ ) have a positive or a negative  $E_{\text{cell}}^{\circ}$ ? Does it have a positive or a negative  $\Delta G_{\text{rxn}}^{\circ}$ ?
19. How does  $E_{\text{cell}}$  depend on the concentrations of the reactants and products in the redox reaction occurring in the cell? What effect does increasing the concentration of a reactant have on  $E_{\text{cell}}$ ? Increasing the concentration of a product?
20. Use the Nernst equation to show that  $E_{\text{cell}} = E_{\text{cell}}^{\circ}$  under standard conditions.
21. What is a concentration electrochemical cell?
22. What are the anode and cathode reactions in a common dry-cell battery? In an alkaline battery?
23. What are the anode and cathode reactions in a lead-acid storage battery? What happens when the battery is recharged?
24. What are the three common types of portable rechargeable batteries, and how does each one work?
25. What is a fuel cell? What is the most common type of fuel cell, and what reactions occur at its anode and cathode?
26. Explain how a fuel-cell breathalyzer works.
27. List some applications of electrolysis.
28. The anode of an electrolytic cell must be connected to which terminal—positive or negative—of the power source?
29. What species is oxidized, and what species is reduced in the electrolysis of a pure molten salt?
30. If an electrolytic cell contains a mixture of species that can be oxidized, how do you determine which species will actually be oxidized? If it contains a mixture of species that can be reduced, how do you determine which one will actually be reduced?
31. Why does the electrolysis of an aqueous sodium chloride solution produce hydrogen gas at the cathode?
32. What is overvoltage in an electrochemical cell? Why is it important?
33. How is the amount of current flowing through an electrolytic cell related to the amount of product produced in the redox reaction?
34. What is corrosion? Why is corrosion only a problem for some metals (such as iron)?
35. Explain the role of each of the following in promoting corrosion: moisture, electrolytes, and acids.
36. How can the corrosion of iron be prevented?

## PROBLEMS BY TOPIC

### Balancing Redox Reactions

37. Balance each redox reaction occurring in acidic aqueous solution.  
**MISSED THIS? Read Section 20.2; Watch KCV 20.2, IWE 20.2**
  - a.  $\text{K}(s) + \text{Cr}^{3+}(aq) \longrightarrow \text{Cr}(s) + \text{K}^{+}(aq)$
  - b.  $\text{Al}(s) + \text{Fe}^{2+}(aq) \longrightarrow \text{Al}^{3+}(aq) + \text{Fe}(s)$
  - c.  $\text{BrO}_3^-(aq) + \text{N}_2\text{H}_4(g) \longrightarrow \text{Br}^-(aq) + \text{N}_2(g)$
38. Balance each redox reaction occurring in acidic aqueous solution.
  - a.  $\text{Zn}(s) + \text{Sn}^{2+}(aq) \longrightarrow \text{Zn}^{2+}(aq) + \text{Sn}(s)$
  - b.  $\text{Mg}(s) + \text{Cr}^{3+}(aq) \longrightarrow \text{Mg}^{2+}(aq) + \text{Cr}(s)$
  - c.  $\text{MnO}_4^-(aq) + \text{Al}(s) \longrightarrow \text{Mn}^{2+}(aq) + \text{Al}^{3+}(aq)$

39. Balance each redox reaction occurring in acidic aqueous solution.  
**MISSED THIS? Read Section 20.2; Watch KCV 20.2, IWE 20.2**
  - a.  $\text{PbO}_2(s) + \text{I}^-(aq) \longrightarrow \text{Pb}^{2+}(aq) + \text{I}_2(s)$
  - b.  $\text{SO}_3^{2-}(aq) + \text{MnO}_4^-(aq) \longrightarrow \text{SO}_4^{2-}(aq) + \text{Mn}^{2+}(aq)$
  - c.  $\text{S}_2\text{O}_3^{2-}(aq) + \text{Cl}_2(g) \longrightarrow \text{SO}_4^{2-}(aq) + \text{Cl}^-(aq)$
40. Balance each redox reaction occurring in acidic aqueous solution.
  - a.  $\text{I}^-(aq) + \text{NO}_2^-(aq) \longrightarrow \text{I}_2(s) + \text{NO}(g)$
  - b.  $\text{ClO}_4^-(aq) + \text{Cl}^-(aq) \longrightarrow \text{ClO}_3^-(aq) + \text{Cl}_2(g)$
  - c.  $\text{NO}_3^-(aq) + \text{Sn}^{2+}(aq) \longrightarrow \text{Sn}^{4+}(aq) + \text{NO}(g)$

41. Balance each redox reaction occurring in basic aqueous solution.

**MISSED THIS?** Read Section 20.2; Watch KCV 20.2, IWE 20.3

- $\text{H}_2\text{O}_2(aq) + \text{ClO}_2(aq) \longrightarrow \text{ClO}_2^-(aq) + \text{O}_2(g)$
- $\text{Al}(s) + \text{MnO}_4^-(aq) \longrightarrow \text{MnO}_2(s) + \text{Al}(\text{OH})_4^-(aq)$
- $\text{Cl}_2(g) \longrightarrow \text{Cl}^-(aq) + \text{ClO}^-(aq)$

42. Balance each redox reaction occurring in basic aqueous solution.

- $\text{MnO}_4^-(aq) + \text{Br}^-(aq) \longrightarrow \text{MnO}_2(s) + \text{BrO}_3^-(aq)$
- $\text{Ag}(s) + \text{CN}^-(aq) + \text{O}_2(g) \longrightarrow \text{Ag}(\text{CN})_2^-(aq)$
- $\text{NO}_2^-(aq) + \text{Al}(s) \longrightarrow \text{NH}_3(g) + \text{AlO}_2^-(aq)$

### Voltaic Cells, Standard Cell Potentials, and Direction of Spontaneity

43. Sketch a voltaic cell for each redox reaction. Label the anode and cathode and indicate the half-reaction that occurs at each electrode and the species present in each solution. Also indicate the direction of electron flow. **MISSED THIS?** Read Section 20.3

- $2 \text{Ag}^+(aq) + \text{Pb}(s) \longrightarrow 2 \text{Ag}(s) + \text{Pb}^{2+}(aq)$
- $2 \text{ClO}_2(g) + 2 \text{I}^-(aq) \longrightarrow 2 \text{ClO}_2^-(aq) + \text{I}_2(s)$
- $\text{O}_2(g) + 4 \text{H}^+(aq) + 2 \text{Zn}(s) \longrightarrow 2 \text{H}_2\text{O}(l) + 2 \text{Zn}^{2+}(aq)$

44. Sketch a voltaic cell for each redox reaction. Label the anode and cathode and indicate the half-reaction that occurs at each electrode and the species present in each solution. Also indicate the direction of electron flow.

- $\text{Ni}^{2+}(aq) + \text{Mg}(s) \longrightarrow \text{Ni}(s) + \text{Mg}^{2+}(aq)$
- $2 \text{H}^+(aq) + \text{Fe}(s) \longrightarrow \text{H}_2(g) + \text{Fe}^{2+}(aq)$
- $2 \text{NO}_3^-(aq) + 8 \text{H}^+(aq) + 3 \text{Cu}(s) \longrightarrow 2 \text{NO}(g) + 4 \text{H}_2\text{O}(l) + 3 \text{Cu}^{2+}(aq)$

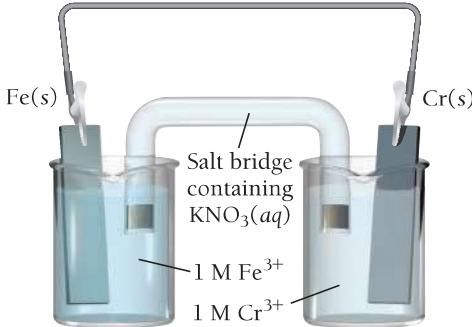
45. Calculate the standard cell potential for each of the electrochemical cells in Problem 43.

**MISSED THIS?** Read Section 20.4; Watch KCV 20.4, IWE 20.4

46. Calculate the standard cell potential for each of the electrochemical cells in Problem 44.

47. Consider the voltaic cell:

**MISSED THIS?** Read Sections 20.3, 20.4; Watch KCV 20.4, IWE 20.4

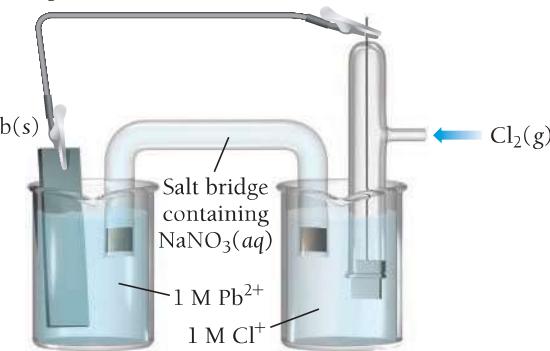


- Determine the direction of electron flow and label the anode and the cathode.
- Write a balanced equation for the overall reaction and calculate  $E_{\text{cell}}^\circ$ .
- Label each electrode as negative or positive.
- Indicate the direction of anion and cation flow in the salt bridge.

48. Consider the voltaic cell:

- Determine the direction of electron flow and label the anode and the cathode.
- Write a balanced equation for the overall reaction and calculate  $E_{\text{cell}}^\circ$ .

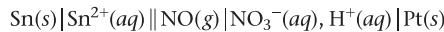
- Label each electrode as negative or positive.
- Indicate the direction of anion and cation flow in the salt bridge.



49. Use line notation to represent each electrochemical cell in Problem 43. **MISSED THIS?** Read Section 20.3

50. Use line notation to represent each electrochemical cell in Problem 44.

51. Make a sketch of the voltaic cell represented by the line notation. Write the overall balanced equation for the reaction and calculate  $E_{\text{cell}}^\circ$ . **MISSED THIS?** Read Section 20.3



52. Make a sketch of the voltaic cell represented by the line notation. Write the overall balanced equation for the reaction and calculate  $E_{\text{cell}}^\circ$ .



53. Determine whether or not each redox reaction occurs spontaneously in the forward direction.

**MISSED THIS?** Read Section 20.4; Watch KCV 20.4

- $\text{Ni}(s) + \text{Zn}^{2+}(aq) \longrightarrow \text{Ni}^{2+}(aq) + \text{Zn}(s)$
- $\text{Ni}(s) + \text{Pb}^{2+}(aq) \longrightarrow \text{Ni}^{2+}(aq) + \text{Pb}(s)$
- $\text{Al}(s) + 3 \text{Ag}^+(aq) \longrightarrow \text{Al}^{3+}(aq) + 3 \text{Ag}(s)$
- $\text{Pb}(s) + \text{Mn}^{2+}(aq) \longrightarrow \text{Pb}^{2+}(aq) + \text{Mn}(s)$

54. Determine whether or not each redox reaction occurs spontaneously in the forward direction.

- $\text{Ca}^{2+}(aq) + \text{Zn}(s) \longrightarrow \text{Ca}(s) + \text{Zn}^{2+}(aq)$
- $2 \text{Ag}^+(aq) + \text{Ni}(s) \longrightarrow 2 \text{Ag}(s) + \text{Ni}^{2+}(aq)$
- $\text{Fe}(s) + \text{Mn}^{2+}(aq) \longrightarrow \text{Fe}^{2+}(aq) + \text{Mn}(s)$
- $2 \text{Al}(s) + 3 \text{Pb}^{2+}(aq) \longrightarrow 2 \text{Al}^{3+}(aq) + 3 \text{Pb}(s)$

55. Which metal could you use to reduce  $\text{Mn}^{2+}$  ions but not  $\text{Mg}^{2+}$  ions? **MISSED THIS?** Read Section 20.4; Watch KCV 20.4

56. Which metal can be oxidized with an  $\text{Sn}^{2+}$  solution but not with an  $\text{Fe}^{2+}$  solution?

57. Determine whether or not each metal dissolves in 1 M HCl. For those metals that do dissolve, write a balanced redox reaction showing what happens when the metal dissolves.

**MISSED THIS?** Read Section 20.4; Watch KCV 20.4

- $\text{Al}$
- $\text{Ag}$
- $\text{Pb}$

58. Determine whether or not each metal dissolves in 1 M HCl. For those metals that do dissolve, write a balanced redox reaction showing what happens when the metal dissolves.

- $\text{Cu}$
- $\text{Fe}$
- $\text{Au}$

59. Determine whether or not each metal dissolves in 1 M  $\text{HNO}_3$ . For those metals that do dissolve, write a balanced redox reaction showing what happens when the metal dissolves.

**MISSED THIS?** Read Section 20.4; Watch KCV 20.4

- $\text{Cu}$
- $\text{Au}$

60. Determine whether or not each metal dissolves in 1 M  $\text{HIO}_3$ . For those metals that do dissolve, write a balanced redox equation for the reaction that occurs.

- $\text{Au}$
- $\text{Cr}$

61. Calculate  $E_{\text{cell}}^{\circ}$  for each balanced redox reaction and determine if the reaction is spontaneous as written.

**MISSED THIS?** Read Section 20.4; Watch KCV 20.4, IWE 20.4

- $2 \text{Cu}(s) + \text{Mn}^{2+}(aq) \longrightarrow 2 \text{Cu}^{+}(aq) + \text{Mn}(s)$
- $\text{MnO}_2(aq) + 4 \text{H}^{+}(aq) + \text{Zn}(s) \longrightarrow \text{Mn}^{2+}(aq) + 2 \text{H}_2\text{O}(l) + \text{Zn}^{2+}(aq)$
- $\text{Cl}_2(g) + 2 \text{F}^{-}(aq) \longrightarrow \text{F}_2(g) + 2 \text{Cl}^{-}(aq)$
- $\text{PbO}_2(s) + 4 \text{H}^{+}(aq) + \text{Sn}(s) \longrightarrow \text{Pb}^{2+}(aq) + 2 \text{H}_2\text{O}(l) + \text{Sn}^{2+}(aq)$

63. Which metal cation is the best oxidizing agent?

**MISSED THIS?** Read Section 20.4; Watch KCV 20.4

- $\text{Pb}^{2+}$
- $\text{Cr}^{3+}$
- $\text{Fe}^{2+}$
- $\text{Sn}^{2+}$

64. Which metal is the best reducing agent?

- $\text{Mn}$
- $\text{Al}$
- $\text{Ni}$
- $\text{Cr}$

## Cell Potential, Free Energy, and the Equilibrium Constant

65. Use tabulated electrode potentials to calculate  $\Delta G_{\text{rxn}}^{\circ}$  for each reaction at 25 °C.

**MISSED THIS?** Read Section 20.5; Watch KCV 20.5, IWE 20.6

- $\text{Pb}^{2+}(aq) + \text{Mg}(s) \longrightarrow \text{Pb}(s) + \text{Mg}^{2+}(aq)$
- $\text{Br}_2(l) + 2 \text{Cl}^{-}(aq) \longrightarrow 2 \text{Br}^{-}(aq) + \text{Cl}_2(g)$
- $\text{MnO}_2(s) + 4 \text{H}^{+}(aq) + \text{Cu}(s) \longrightarrow \text{Mn}^{2+}(aq) + 2 \text{H}_2\text{O}(l) + \text{Cu}^{2+}(aq)$

66. Use tabulated electrode potentials to calculate  $\Delta G_{\text{rxn}}^{\circ}$  for each reaction at 25 °C.

- $2 \text{Fe}^{3+}(aq) + 3 \text{Sn}(s) \longrightarrow 2 \text{Fe}(s) + 3 \text{Sn}^{2+}(aq)$
- $\text{O}_2(g) + 2 \text{H}_2\text{O}(l) + 2 \text{Cu}(s) \longrightarrow 4 \text{OH}^{-}(aq) + 2 \text{Cu}^{2+}(aq)$
- $\text{Br}_2(l) + 2 \text{I}^{-}(aq) \longrightarrow 2 \text{Br}^{-}(aq) + \text{I}_2(s)$

67. Calculate the equilibrium constant for each of the reactions in Problem 65. **MISSED THIS?** Read Section 20.5; Watch KCV 20.5

68. Calculate the equilibrium constant for each of the reactions in Problem 66.

69. Calculate the equilibrium constant for the reaction between  $\text{Ni}^{2+}(aq)$  and  $\text{Cd}(s)$  (at 25 °C).

**MISSED THIS?** Read Section 20.5; Watch KCV 20.5

70. Calculate the equilibrium constant for the reaction between  $\text{Fe}^{2+}(aq)$  and  $\text{Zn}(s)$  (at 25 °C).

71. Calculate  $\Delta G_{\text{rxn}}^{\circ}$  and  $E_{\text{cell}}^{\circ}$  for a redox reaction with  $n = 2$  that has an equilibrium constant of  $K = 25$  (at 25 °C).

**MISSED THIS?** Read Section 20.5; Watch KCV 20.5

72. Calculate  $\Delta G_{\text{rxn}}^{\circ}$  and  $E_{\text{cell}}^{\circ}$  for a redox reaction with  $n = 3$  that has an equilibrium constant of  $K = 0.050$  (at 25 °C).

## Nonstandard Conditions and the Nernst Equation

73. A voltaic cell employs the following redox reaction:

**MISSED THIS?** Read Section 20.6



Calculate the cell potential at 25 °C under each set of conditions.

- standard conditions

- $[\text{Sn}^{2+}] = 0.0100 \text{ M}; [\text{Mn}^{2+}] = 2.00 \text{ M}$

- $[\text{Sn}^{2+}] = 2.00 \text{ M}; [\text{Mn}^{2+}] = 0.0100 \text{ M}$

74. A voltaic cell employs the redox reaction:



Calculate the cell potential at 25 °C under each set of conditions.

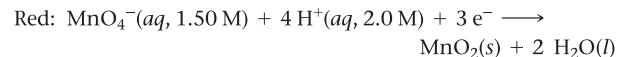
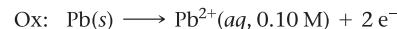
- standard conditions

- $[\text{Fe}^{3+}] = 1.0 \times 10^{-3} \text{ M}; [\text{Mg}^{2+}] = 2.50 \text{ M}$

- $[\text{Fe}^{3+}] = 2.00 \text{ M}; [\text{Mg}^{2+}] = 1.5 \times 10^{-3} \text{ M}$

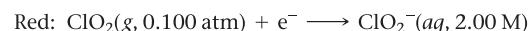
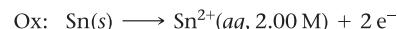
75. An electrochemical cell is based on these two half-reactions:

**MISSED THIS?** Read Section 20.6



Calculate the cell potential at 25 °C.

76. An electrochemical cell is based on these two half-reactions:



Calculate the cell potential at 25 °C.

77. A voltaic cell consists of a  $\text{Zn}/\text{Zn}^{2+}$  half-cell and a  $\text{Ni}/\text{Ni}^{2+}$  half-cell at 25 °C. The initial concentrations of  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  are 1.50 M and 0.100 M, respectively.

**MISSED THIS?** Read Section 20.6

- What is the initial cell potential?

- What is the cell potential when the concentration of  $\text{Ni}^{2+}$  has fallen to 0.500 M?

- What are the concentrations of  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  when the cell potential falls to 0.45 V?

78. A voltaic cell consists of a  $\text{Pb}/\text{Pb}^{2+}$  half-cell and a  $\text{Cu}/\text{Cu}^{2+}$  half-cell at 25 °C. The initial concentrations of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  are 0.0500 M and 1.50 M, respectively.

- What is the initial cell potential?

- What is the cell potential when the concentration of  $\text{Cu}^{2+}$  has fallen to 0.200 M?

- What are the concentrations of  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  when the cell potential falls to 0.35 V?

79. Make a sketch of a concentration cell employing two  $\text{Zn}/\text{Zn}^{2+}$  half-cells. The concentration of  $\text{Zn}^{2+}$  in one of the half-cells is 2.0 M, and the concentration in the other half-cell is  $1.0 \times 10^{-3}$  M. Label the anode and the cathode and indicate the half-reaction occurring at each electrode. Also indicate the direction of electron flow.

**MISSED THIS?** Read Section 20.6

80. Consider the concentration cell:



- Label the anode and cathode.

- Indicate the direction of electron flow.

- Indicate what happens to the concentration of  $\text{Pb}^{2+}$  in each half-cell.

81. A concentration cell consists of two  $\text{Sn}/\text{Sn}^{2+}$  half-cells. The cell has a potential of 0.10 V at 25 °C. What is the ratio of the  $\text{Sn}^{2+}$  concentrations in the two half-cells?

**MISSED THIS?** Read Section 20.6

82. A Cu/Cu<sup>2+</sup> concentration cell has a voltage of 0.22 V at 25 °C. The concentration of Cu<sup>2+</sup> in one of the half-cells is  $1.5 \times 10^{-3}$  M. What is the concentration of Cu<sup>2+</sup> in the other half-cell? (Assume the concentration in the unknown cell is the lower of the two concentrations.)

### Batteries, Fuel Cells, and Corrosion

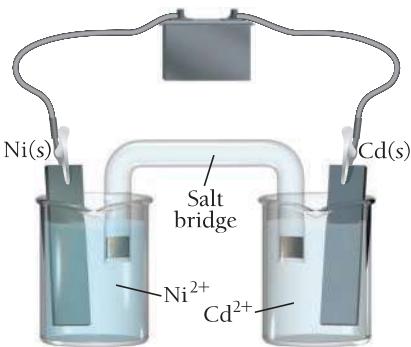
83. Determine the optimum mass ratio of Zn to MnO<sub>2</sub> in an alkaline battery. **MISSED THIS?** Read Section 20.7
84. What mass of lead sulfate is formed in a lead-acid storage battery when 1.00 g of Pb undergoes oxidation?
85. Refer to the tabulated values of  $\Delta G_f^\circ$  in Appendix IIB to calculate  $E_{\text{cell}}^\circ$  for a fuel cell that employs the reaction between methane gas (CH<sub>4</sub>) and oxygen to form carbon dioxide and gaseous water. **MISSED THIS?** Read Sections 20.5, 20.7; Watch IWE 20.6
86. Refer to the tabulated values of  $\Delta G_f^\circ$  in Appendix IIB to calculate  $E_{\text{cell}}^\circ$  for the fuel-cell breathalyzer, which employs the following reaction. ( $\Delta G_f^\circ$  for HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>(g) = -374.2 kJ/mol.)



87. Determine whether or not each metal, if coated onto iron, would prevent the corrosion of iron.  
**MISSED THIS?** Read Section 20.9
- a. Zn      b. Sn      c. Mn
88. Determine whether or not each metal, if coated onto iron, would prevent the corrosion of iron.  
a. Mg      b. Cr      c. Cu

### Electrolytic Cells and Electrolysis

89. Consider the electrolytic cell: **MISSED THIS?** Read Section 20.8



- a. Label the anode and the cathode and indicate the half-reactions occurring at each.
- b. Indicate the direction of electron flow.
- c. Label the terminals on the battery as positive or negative and calculate the minimum voltage necessary to drive the reaction.
90. Draw an electrolytic cell in which Mn<sup>2+</sup> is reduced to Mn and Sn is oxidized to Sn<sup>2+</sup>. Label the anode and cathode, indicate the direction of electron flow, and write an equation for the half-reaction occurring at each electrode. What minimum voltage is necessary to drive the reaction?
91. Write equations for the half-reactions that occur in the electrolysis of molten potassium bromide. **MISSED THIS?** Read Section 20.8
92. What products are obtained in the electrolysis of molten NaI?
93. Write equations for the half-reactions that occur in the electrolysis of a mixture of molten potassium bromide and molten lithium bromide. **MISSED THIS?** Read Section 20.8

94. What products are obtained in the electrolysis of a molten mixture of KI and KBr?
95. Write equations for the half-reactions that occur at the anode and cathode for the electrolysis of each aqueous solution.

**MISSED THIS?** Read Section 20.8

- a. NaBr(aq)      b. PbI<sub>2</sub>(aq)      c. Na<sub>2</sub>SO<sub>4</sub>(aq)

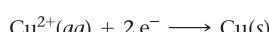
96. Write equations for the half-reactions that occur at the anode and cathode for the electrolysis of each aqueous solution.
- a. Ni(NO<sub>3</sub>)<sub>2</sub>(aq)      b. KCl(aq)      c. CuBr<sub>2</sub>(aq)

97. Make a sketch of an electrolysis cell that electroplates copper onto other metal surfaces. Label the anode and the cathode and indicate the reactions that occur at each.

**MISSED THIS?** Read Section 20.8

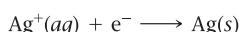
98. Make a sketch of an electrolysis cell that electroplates nickel onto other metal surfaces. Label the anode and the cathode and indicate the reactions that occur at each.

99. Copper can be electroplated at the cathode of an electrolysis cell by the half-reaction: **MISSED THIS?** Read Section 20.8



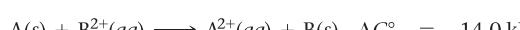
How much time would it take for 325 mg of copper to be plated at a current of 5.6 A?

100. Silver can be electroplated at the cathode of an electrolysis cell by the half-reaction:



What mass of silver would plate onto the cathode if a current of 6.8 A flowed through the cell for 72 min?

101. A major source of sodium metal is the electrolysis of molten sodium chloride. What magnitude of current produces 1.0 kg of sodium metal in 1 hour? **MISSED THIS?** Read Section 20.8
102. What mass of aluminum metal can be produced per hour in the electrolysis of a molten aluminum salt by a current of 25 A?
103. Consider the reaction shown here occurring at 25 °C.  
**MISSED THIS?** Read Section 20.5, Watch KCV 20.5, IWE 20.6



Determine the value of  $E_{\text{cell}}^\circ$  and  $K$  for the reaction and complete the table.

[B <sup>2+</sup> ]	[A <sup>2+</sup> ]	Q	$E_{\text{cell}}$	$\Delta G_{\text{rxn}}$
1.00	1.00			
1.00	$1.00 \times 10^{-4}$			
$1.0 \times 10^{-4}$	1.0			
$3.54 \times 10^{-3}$	1.0			

104. Consider the reaction shown here occurring at 25 °C.

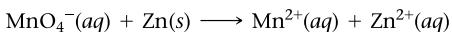


Determine  $E_{\text{cell}}^\circ$ ,  $K$ , and  $\Delta G_{\text{rxn}}^\circ$  for the reaction and complete the table.

[Cd <sup>2+</sup> ]	[Cr <sup>2+</sup> ]	Q	$E_{\text{cell}}$	$\Delta G_{\text{rxn}}$
1.00	1.00			
1.00	$1.00 \times 10^{-5}$			
$1.00 \times 10^{-5}$	1.00			
$4.18 \times 10^{-4}$	1.00			

## CUMULATIVE PROBLEMS

- 105.** Consider the unbalanced redox reaction:



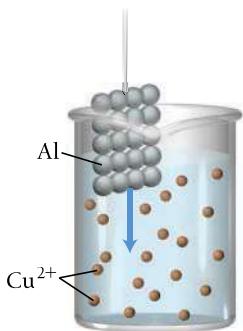
Balance the equation and determine the volume of a 0.500 M  $\text{KMnO}_4$  solution required to completely react with 2.85 g of Zn.

- 106.** Consider the unbalanced redox reaction:

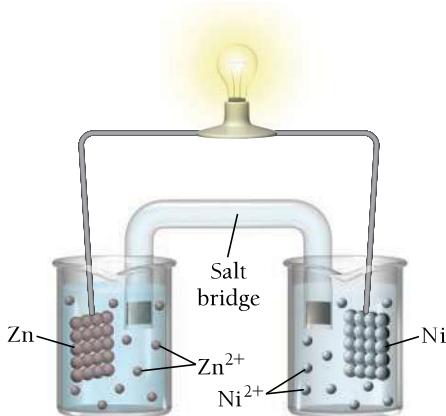


Balance the equation and determine the volume of a 0.850 M  $\text{K}_2\text{Cr}_2\text{O}_7$  solution required to completely react with 5.25 g of Cu.

- 107.** Consider the molecular views of an Al strip and  $\text{Cu}^{2+}$  solution. Draw a similar sketch showing what happens to the atoms and ions after the Al strip is submerged in the solution for a few minutes.



- 108.** Consider the molecular view of an electrochemical cell involving the overall reaction:



Draw a similar sketch of the cell after it has generated a substantial amount of electrical current.

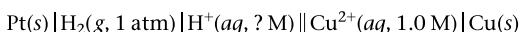
- 109.** Determine whether HI can dissolve each metal sample. If it can, write a balanced chemical reaction showing how the metal dissolves in HI and determine the minimum volume of 3.5 M HI required to completely dissolve the sample.

a. 2.15 g Al      b. 4.85 g Cu      c. 2.42 g Ag

- 110.** Determine if  $\text{HNO}_3$  can dissolve each metal sample. If it can, write a balanced chemical reaction showing how the metal dissolves in  $\text{HNO}_3$  and determine the minimum volume of 6.0 M  $\text{HNO}_3$  required to completely dissolve the sample.

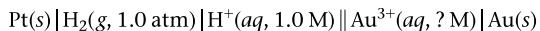
a. 5.90 g Au      b. 2.55 g Cu      c. 4.83 g Sn

- 111.** The cell potential of this electrochemical cell depends on the pH of the solution in the anode half-cell.



What is the pH of the solution if  $E_{\text{cell}}$  is 355 mV?

- 112.** The cell potential of this electrochemical cell depends on the gold concentration in the cathode half-cell.



What is the concentration of  $\text{Au}^{3+}$  in the solution if  $E_{\text{cell}}$  is 1.22 V?

- 113.** A friend wants you to invest in a new battery she has designed that produces 24 V in a single voltaic cell. Why should you be wary of investing in such a battery?

- 114.** What voltage can theoretically be achieved in a battery in which lithium metal is oxidized and fluorine gas is reduced? Why might such a battery be difficult to produce?

- 115.** A battery relies on the oxidation of magnesium and the reduction of  $\text{Cu}^{2+}$ . The initial concentrations of  $\text{Mg}^{2+}$  and  $\text{Cu}^{2+}$  are  $1.0 \times 10^{-4} \text{ M}$  and  $1.5 \text{ M}$ , respectively, in 1.0-liter half-cells.

- What is the initial voltage of the battery?
- What is the voltage of the battery after delivering 5.0 A for 8.0 h?
- How long can the battery deliver 5.0 A before going dead?

- 116.** A rechargeable battery is constructed based on a concentration cell constructed of two  $\text{Ag}/\text{Ag}^+$  half-cells. The volume of each half-cell is 2.0 L, and the concentrations of  $\text{Ag}^+$  in the half-cells are 1.25 M and  $1.0 \times 10^{-3} \text{ M}$ .

- How long can this battery deliver 2.5 A of current before it goes dead?
- What mass of silver is plated onto the cathode by running at 3.5 A for 5.5 h?
- Upon recharging, how long would it take to redissolve  $1.00 \times 10^2 \text{ g}$  of silver at a charging current of 10.0 amps?

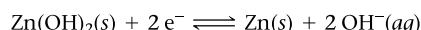
- 117.** If a water electrolysis cell operates at a current of 7.8 A, how long will it take to generate 25.0 L of hydrogen gas at a pressure of 25.0 atm and a temperature of 25 °C?

- 118.** When a suspected drunk driver blows 188 mL of his breath through the fuel-cell breathalyzer described in Section 20.7, the breathalyzer produces an average of 324 mA of current for 10 s. Assuming a pressure of 1.0 atm and a temperature of 25 °C, what percent (by volume) of the driver's breath is ethanol?

- 119.** The  $K_{\text{sp}}$  of  $\text{CuI}$  is  $1.1 \times 10^{-12}$ . Find  $E_{\text{cell}}$  for the cell:



- 120.** The  $K_{\text{sp}}$  of  $\text{Zn}(\text{OH})_2$  is  $1.8 \times 10^{-14}$ . Find  $E_{\text{cell}}$  for the half-reaction:



- 121.** Calculate  $\Delta G_{\text{rxn}}^\circ$  and  $K$  for each reaction.

- The disproportionation of  $\text{Mn}^{2+}(aq)$  to Mn(s) and  $\text{MnO}_2(s)$  in acid solution at 25 °C.
- The disproportionation of  $\text{MnO}_2(s)$  to  $\text{Mn}^{2+}(aq)$  and  $\text{MnO}_4^-(aq)$  in acid solution at 25 °C.

- 122.** Calculate  $\Delta G_{\text{rxn}}^\circ$  and  $K$  for each reaction.

- The reaction of  $\text{Cr}^{2+}(aq)$  with  $\text{Cr}_2\text{O}_7^{2-}(aq)$  in acid solution to form  $\text{Cr}^{3+}(aq)$ .
- The reaction of  $\text{Cr}^{3+}(aq)$  and Cr(s) to form  $\text{Cr}^{2+}(aq)$ . [The electrode potential of  $\text{Cr}^{2+}(aq)$  to Cr(s) is -0.91 V.]

- 123.** The molar mass of a metal (M) is 50.9 g/mol; it forms a chloride of unknown composition. Electrolysis of a sample of the molten chloride with a current of 6.42 A for 23.6 minutes produces 1.20 g of M at the cathode. Determine the empirical formula of the chloride.

- 124.** A metal forms the fluoride  $\text{MF}_3$ . Electrolysis of the molten fluoride by a current of 3.86 A for 16.2 minutes deposits 1.25 g of the metal. Calculate the molar mass of the metal.

- 125.** A sample of impure tin of mass 0.535 g is dissolved in strong acid to give a solution of  $\text{Sn}^{2+}$ . The solution is then titrated with a 0.0448 M solution of  $\text{NO}_3^-$ , which is reduced to  $\text{NO}(g)$ . The equivalence point is reached upon the addition of 0.0344 L of the  $\text{NO}_3^-$  solution. Find the percent by mass of tin in the original sample, assuming that it contains no other reducing agents.
- 126.** A 0.0251-L sample of a solution of  $\text{Cu}^+$  requires 0.0322 L of 0.129 M  $\text{KMnO}_4$  solution to reach the equivalence point. The products of the reaction are  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$ . What is the concentration of the  $\text{Cu}^{2+}$  solution?
- 127.** A current of 11.3 A is applied to 1.25 L of a solution of 0.552 M HBr converting some of the  $\text{H}^+$  to  $\text{H}_2(g)$ , which bubbles out of solution. What is the pH of the solution after 73 minutes?
- 128.** A 215-mL sample of a 0.500 M NaCl solution with an initial pH of 7.00 is subjected to electrolysis. After 15.0 minutes, a 10.0-mL portion (or aliquot) of the solution was removed from the cell and titrated with 0.100 M HCl solution. The endpoint in the titration was reached upon addition of 22.8 mL of HCl. Assuming constant current, what was the current (in A) running through the cell?
- 129.** An  $\text{MnO}_2(s)/\text{Mn}^{2+}(aq)$  electrode in which the pH is 10.24 is prepared. Find the  $[\text{Mn}^{2+}]$  necessary to lower the potential of the half-cell to 0.00 V (at 25 °C).
- 130.** To what pH should you adjust a standard hydrogen electrode to get an electrode potential of -0.122 V? (Assume that the partial pressure of hydrogen gas remains at 1 atm.)

## CHALLENGE PROBLEMS

- 131.** Suppose a hydrogen–oxygen fuel-cell generator produces electricity for a house. Use the balanced redox reactions and the standard cell potential to predict the volume of hydrogen gas (at STP) required each month to generate the electricity. Assume the home uses  $1.2 \times 10^3$  kWh of electricity per month.
- 132.** A voltaic cell designed to measure  $[\text{Cu}^{2+}]$  is constructed of a standard hydrogen electrode and a copper metal electrode in the  $\text{Cu}^{2+}$  solution of interest. If you want to construct a calibration curve for how the cell potential varies with the concentration of copper(II), what do you plot in order to obtain a straight line? What is the slope of the line?
- 133.** The surface area of an object to be gold plated is 49.8 cm<sup>2</sup>, and the density of gold is 19.3 g/cm<sup>3</sup>. A current of 3.25 A is applied to a solution that contains gold in the +3 oxidation state. Calculate the time required to deposit an even layer of gold  $1.00 \times 10^{-3}$  cm thick on the object.
- 134.** To electrodeposit all the Cu and Cd from a solution of  $\text{CuSO}_4$  and  $\text{CdSO}_4$  required 1.20 F of electricity (1 F = 1 mol e<sup>-</sup>). The mixture of Cu and Cd that was deposited had a mass of 50.36 g. What mass of  $\text{CuSO}_4$  was present in the original mixture?
- 135.** Sodium oxalate,  $\text{Na}_2\text{C}_2\text{O}_4$ , in solution is oxidized to  $\text{CO}_2(g)$  by  $\text{MnO}_4^-$ , which is reduced to  $\text{Mn}^{2+}$ . A 50.1-mL volume of a solution of  $\text{MnO}_4^-$  is required to titrate a 0.339-g sample of sodium oxalate. This solution of  $\text{MnO}_4^-$  is used to analyze uranium-containing samples. A 4.62-g sample of a uranium-containing material requires 32.5 mL of the solution for titration. The oxidation of the uranium can be represented by the change  $\text{UO}^{2+} \longrightarrow \text{UO}_2^{2+}$ . Calculate the percentage of uranium in the sample.
- 136.** Three electrolytic cells are connected in a series. The electrolytes in the cells are aqueous copper(II) sulfate, gold(III) sulfate, and silver nitrate. A current of 2.33 A is applied, and after some time 1.74 g Cu is deposited. How long was the current applied? What mass of gold and silver was deposited?
- 137.** The cell  $\text{Pt}(s)|\text{Cu}^+(1\text{ M}), \text{Cu}^{2+}(1\text{ M})||\text{Cu}^+(1\text{ M})|\text{Cu}(s)$  has  $E^\circ = 0.364$  V. The cell  $\text{Cu}(s)|\text{Cu}^{2+}(1\text{ M})||\text{Cu}^+(1\text{ M})|\text{Cu}(s)$  has  $E^\circ = 0.182$  V. Write the cell reaction for each cell and explain the differences in  $E^\circ$ . Calculate  $\Delta G^\circ$  for each cell reaction to help explain these differences.

## CONCEPTUAL PROBLEMS

- 138.** An electrochemical cell has a positive standard cell potential but a negative cell potential. Which statement is true for the cell?  
 a.  $K > 1; Q > K$       b.  $K < 1; Q > K$   
 c.  $K > 1; Q < K$       d.  $K < 1; Q < K$
- 139.** Which oxidizing agent will oxidize  $\text{Br}^-$  but not  $\text{Cl}^-$ ?  
 a.  $\text{K}_2\text{Cr}_2\text{O}_7$  (in acid)    b.  $\text{KMnO}_4$  (in acid)  
 c.  $\text{HNO}_3$
- 140.** A redox reaction employed in an electrochemical cell has a negative  $\Delta G_{\text{rxn}}^\circ$ . Which statement is true?  
 a.  $E_{\text{cell}}^\circ$  is positive;  $K < 1$   
 b.  $E_{\text{cell}}^\circ$  is positive;  $K > 1$   
 c.  $E_{\text{cell}}^\circ$  is negative;  $K > 1$   
 d.  $E_{\text{cell}}^\circ$  is negative;  $K < 1$
- 141.** A redox reaction has an equilibrium constant of  $K = 0.055$ . What is true of  $\Delta G_{\text{rxn}}^\circ$  and  $E_{\text{cell}}^\circ$  for this reaction?

## QUESTIONS FOR GROUP WORK

Discuss these questions with the group and record your consensus answer.

- 142.** Balance the redox reactions by following the steps in the text. Rotate through the group, having each group member do the next step in the process and explain that step to the rest of the group.
- a.  $\text{I}_2(s) \longrightarrow \text{FeI}_2(s)$
  - b.  $\text{Cl}_2(g) + \text{H}_2\text{O}_2(aq) \longrightarrow \text{Cl}^-(aq) + \text{O}_2(g)$  (acidic)
  - c.  $\text{Hg}^{2+}(aq) + \text{H}_2(g) \longrightarrow \text{Hg}(l) + \text{H}_2\text{O}(l)$  (basic)
  - d.  $\text{CH}_3\text{OH}(l) + \text{O}_2(g) \longrightarrow \text{CO}_2(g) + \text{H}_2\text{O}(l)$  (acidic)

Active Classroom Learning

- 143.** Have each group member select a half-reaction from Table 20.1. Each member should calculate the standard cell potential of an electrochemical cell formed between each member's half-reaction and the half-reaction of each of the other group members. For each pair of half-reactions, write the overall balanced chemical reaction that will be spontaneous.
- 144.** Calculate  $\Delta G^\circ$  and  $K$  for each reaction the group created in Question 143. For one of the reactions, explain how the sign or magnitude of each quantity ( $E_{\text{cell}}^\circ$ ,  $\Delta G^\circ$ , and  $K$ ) is consistent with the fact that the reaction is spontaneous in the direction written.

- 145.** Design a device that uses an electrochemical cell to determine the amount of  $\text{Cu}^{2+}$  in a sample of water. Describe, in detail, the construction and the theory of operation of your device. If you are able to measure voltage with one-millivolt accuracy, what will the uncertainty in your measured concentration be?

- 146.** Using a library or the Internet, research a fuel cell that uses methanol for fuel. What is the reaction at the anode? What is the reaction at the cathode? What is the overall reaction? What is the standard cell potential? How many kWh can it generate from 1 L (0.792 kg) of methanol?



## DATA INTERPRETATION AND ANALYSIS

### Measuring Concentration with Voltage

**147.** In this chapter, you have seen that the voltage of an electrochemical cell is sensitive to the concentrations of the reactants and products in the cell. As a result, electrochemical cells can be used to measure the concentrations of certain species in solution. For example, the voltage of an electrochemical cell based on the reaction  $\text{H}_2(g) + \text{Cu}^{2+}(aq) \longrightarrow 2 \text{H}^+(aq) + \text{Cu}(s)$  is sensitive to both the  $\text{Cu}^{2+}$  concentration and the  $\text{H}^+$  concentration in solution. If the  $\text{H}^+$  concentration is held constant, then the voltage only depends on the  $\text{Cu}^{2+}$  concentration, and we can use the cell to measure the  $\text{Cu}^{2+}$  concentration in an unknown solution. The tabulated data shows the measured voltage in the hydrogen/copper electrochemical cell just discussed for several different  $\text{Cu}^{2+}$  concentrations. Examine the data and answer the questions that follow.

[ $\text{Cu}^{2+}$ ]	Voltage (V)	[ $\text{Cu}^{2+}$ ]	Voltage (V)
0.100	0.310	0.500	0.331
0.200	0.319	0.700	0.335
0.300	0.325	1.00	0.340
0.400	0.328		

- Construct a graph of the measured voltage versus the copper concentration. Is the graph linear?
- Determine how you might manipulate the data to produce a linear graph. (*Hint:* See the Nernst equation.)
- Reconstruct a graph of the data using the method to produce a linear graph from part b. Determine the slope and  $y$ -intercept of the best-fitting line to the points in your graph. Could you have predicted the slope and intercept from the Nernst equation?
- The voltage of two unknown solutions are measured and recorded. Use the slope and intercept from part c to determine the  $\text{Cu}^{2+}$  concentrations of the unknown solutions.

Unknown $\text{Cu}^{2+}$ Solution	Voltage (V)
i	0.303
ii	0.338



## ANSWERS TO CONCEPTUAL CONNECTIONS

### Potential Difference and Electrical Current

- 20.1** (a) The volt is a unit of potential difference, the difference in potential energy and the amp is a unit of electrical current, the flow of electrical charge.

### Voltaic Cells

- 20.2** (a) Electrons are negatively charged and therefore flow away from the more negatively charged electrode and toward the more positively charged electrode.

### Standard Electrode Potentials

- 20.3** (b) A negative electrode potential indicates that an electron at that electrode has greater potential energy than it has at a standard hydrogen electrode.

### Selective Oxidation

- 20.4** (d) The reduction of  $\text{HNO}_3$  is below the reduction of  $\text{Br}_2$  and above the reduction of  $\text{I}_2$  in Table 20.1. Since any reduction half-reaction is spontaneous when paired with the reverse of a half-reaction below it in the table, the reduction of  $\text{HNO}_3$  is spontaneous when paired with the oxidation of  $\text{I}^-$  but is not spontaneous when paired with the oxidation of  $\text{Br}^-$ .

### Metals Dissolving in Acids

- 20.5** (c) Ag falls above the half-reaction for the reduction of  $\text{H}^+$  but below the half-reaction for the reduction of  $\text{NO}_3^-$  in Table 20.1.

### Periodic Trends and the Direction of Spontaneity for Redox Reactions

- 20.6** (a) Br is more electronegative than I. If the two atoms were in competition for the electron, the electron would go to the more electronegative atom (Br). Therefore,  $\text{I}_2$  does not spontaneously gain electrons from  $\text{Br}^-$ .

### Relating $K$ , $\Delta G_{rxn}^\circ$ , and $E_{cell}^\circ$

- 20.7** (c) Since  $K > 1$ , the reaction is spontaneous under standard conditions (when  $Q = 1$ , the reaction proceeds toward the products). Therefore,  $E_{cell}^\circ$  is positive and  $\Delta G_{rxn}^\circ$  is negative.

### Relating $Q$ , $K$ , $E_{cell}$ , and $E_{cell}^\circ$

- 20.8** (a) Since  $K > 1$ ,  $E_{cell}^\circ$  is negative (under standard conditions, the reaction is not spontaneous). Since  $Q < K$ ,  $E_{cell}$  is positive (the reaction is spontaneous under the nonstandard conditions of the cell).

### Voltaic and Electrolytic Cells

- 20.9** (b) Since oxidation always occurs at the anode, electrons flow away from the anode and toward the cathode (where reduction occurs).

### Electrolysis

- 20.10** (c) The stoichiometry of the reaction shows that 1 mole of silver plates for every 1 mole of electrons; therefore 3 moles of electrons are required to plate 3 moles of silver.

### Sacrificial Electrodes

- 20.11** (a) Cu. The electrode potential for Fe is more negative than that of Cu. Therefore, Fe oxidizes more easily than Cu.